


 Cite this: *RSC Adv.*, 2026, 16, 28

# Intrinsically microporous polymer (PIM-1) enhanced degradation of heptadecafluoro-1-nonanol at graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>)

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The photochemical transformation of polyfluorinated alkyl substances (PFAS) leads to structural unzipping to give rise to fluoride and further degradation products depending on (i) the type of photocatalyst as well as on (ii) microporous coatings or reaction environments. Here, a substantial increase in photocatalyst performance is observed by coating graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) with an intrinsically microporous polymer (PIM-1) to enhance interaction with heptadecafluoro-1-nonanol (as a PFAS model).

 Received 25th September 2025  
 Accepted 17th December 2025

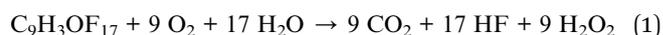
DOI: 10.1039/d5ra07284k

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For several years, polyfluorinated alkyl substances (PFAS) have been desirable as components in consumer products, or technical products such as fire-fighting foams.<sup>1,2</sup> As a result, they are now wide-spread and present as a variety of molecular types that are distributed in our environment with exceptionally slow natural degradation rates<sup>3</sup> and with the potential to harm living organisms.<sup>4</sup> Remediation approaches are currently based on chemical/electrochemical processes,<sup>5</sup> heterogeneous catalysis,<sup>6</sup> adsorption into porous carbons or metal-organic frameworks (MOFs),<sup>7</sup> bio-degradation,<sup>8</sup> or photodegradation with suitable photocatalysts.<sup>9</sup> The photodegradation of PFAS materials has been studied primarily with metal-containing photocatalysts,<sup>10</sup> but recently also with a polymer-modified photocatalyst based on graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>, Fig. 1A).<sup>11</sup> We have prepared and employed g-C<sub>3</sub>N<sub>4</sub> previously for example in photohydrogen production.<sup>12</sup>

For the study of photodegradation processes both the photocatalyst and the mechanism usually take centre stage,<sup>10</sup> however, the surroundings of the photocatalytically active site also play an essential role. For example, intrinsically microporous host materials can beneficially affect the reactivity at the surface of photocatalysts.<sup>13,14</sup> In particular, molecular rigidity in these polymer structures can affect the local concentration and reactivity of reactants without the polymers being degraded themselves.

PFAS molecules degrade *via* fluoride formation/hydrolysis. Processes based on photocatalysis,<sup>15,16</sup> sorption or chemical catalysis,<sup>17</sup> as well as electrocatalysis<sup>18</sup> have been proposed. Here, heptadecafluoro-1-nonanol (HDFN) has been employed as a model PFAS molecule to explore degradation *via* surface-modified photocatalysts. HDFN has been reported previously as a surfactant<sup>19</sup> and as a reagent in polymer surface modification.<sup>20</sup> HDFN degradation in the atmosphere, as a result of attack by ·OH radicals, has been investigated.<sup>21</sup> The hypothetical overall reaction mechanism is given in eqn (1), however, there are many possible intermediates and pathways (as well as follow up reactions with necessarily co-generated H<sub>2</sub>O<sub>2</sub> as has been reported previously<sup>13</sup>) before full degradation occurs.



Each molecule of HDFN ultimately results in 17 equivalents of fluoride and a fluoride selective potentiometric probe

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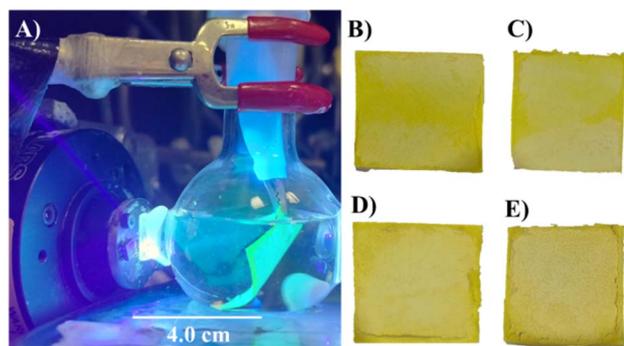



Fig. 2 (A) Blue light turned on with filter paper modified with PIM-1 and  $g\text{-C}_3\text{N}_4$  in 20 mL of 0.10 mol per L phosphate buffer solution at pH 7. (B–D) Photographs of filter paper (area  $2 \times 2 \text{ cm}^2$ ) modified with (B) 5.0 mg  $g\text{-C}_3\text{N}_4$  and 1.0 mg PIM-1, (C) 10.0 mg  $g\text{-C}_3\text{N}_4$  and 1.0 mg PIM-1, (D) 25.0 mg  $g\text{-C}_3\text{N}_4$  and 1.0 mg PIM-1, and (E) 50.0 mg  $g\text{-C}_3\text{N}_4$  and 1.0 mg PIM-1.

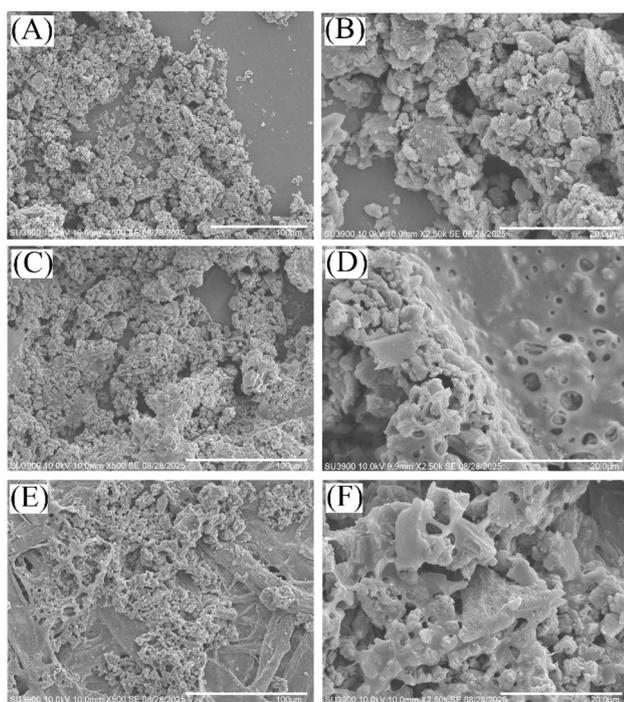


Fig. 3 Scanning electron microscopy (SEM) images in  $500\times$  and  $2500\times$  magnification for (A and B)  $g\text{-C}_3\text{N}_4$  powder on silicon, (C and D)  $g\text{-C}_3\text{N}_4$  co-deposited with PIM-1 (5 : 1 weight ratio) on silicon, and (E and F)  $g\text{-C}_3\text{N}_4$  co-deposited with PIM-1 on filter paper substrate.

## Heptadecafluoro-1-nonanol (HDFN) degradation with $g\text{-C}_3\text{N}_4$

Heptadecafluoro-1-nonanol was chosen as a model for the degradation. Initially, the evaluation of HDFN degradation with  $g\text{-C}_3\text{N}_4$  as a photocatalyst was conducted in a phosphate buffer at pH 12 using various concentrations and compared based on

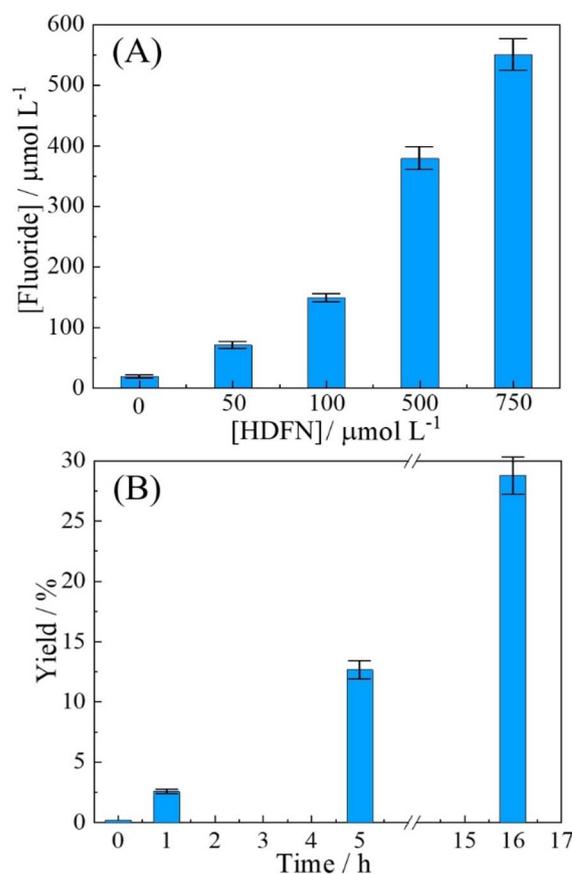


Fig. 4 (A) Plot for photochemical HDFN degradation with 10 mg  $g\text{-C}_3\text{N}_4$  suspended in 10 mL phosphate buffer pH 12 for 0–750  $\mu\text{mol per L}$  HDFN (with magnetic agitation for 1 h). (B) Plot for 500  $\mu\text{mol per L}$  HDFN degradation with time using 10 mg  $g\text{-C}_3\text{N}_4$  suspended/agitated and 10 mL phosphate buffer pH 12 (with magnetic agitation). The determination of fluoride was performed with the pH adjusted to 7. Yield calculated based on 17  $\text{F}^-$  per HDFN molecule (errors estimated  $\pm 5\%$ ).

the analytical signal of the fluoride. It was observed that the degradation of HDFN occurred at different concentrations, with a more rapid increase in fluoride production at higher concentrations (Fig. 4A). Since the fluoride probe could not function at pH 12, the analytical signal for fluoride was always determined at pH 7 after pH adjustment.

With a suspended  $g\text{-C}_3\text{N}_4$  photocatalyst, the 1 h degradation of the concentrations of 50 and 100  $\mu\text{mol per L}$  HDFN can be seen to yield 78 and 156  $\mu\text{M}$  of fluoride, respectively (Fig. 4A). This corresponds to nearly 9.1 and 9.2% of the total fluoride yield, which is promising. Next, the time dependence of fluoride production was investigated for 500  $\mu\text{M}$  HDFN (Fig. 4B). Over time, the conversion/degradation continues and after 16 h of light exposure, close to 30% yield based on total fluoride is observed. Next, the effect of immobilising the photocatalyst with a polymer of intrinsic microporosity is studied.



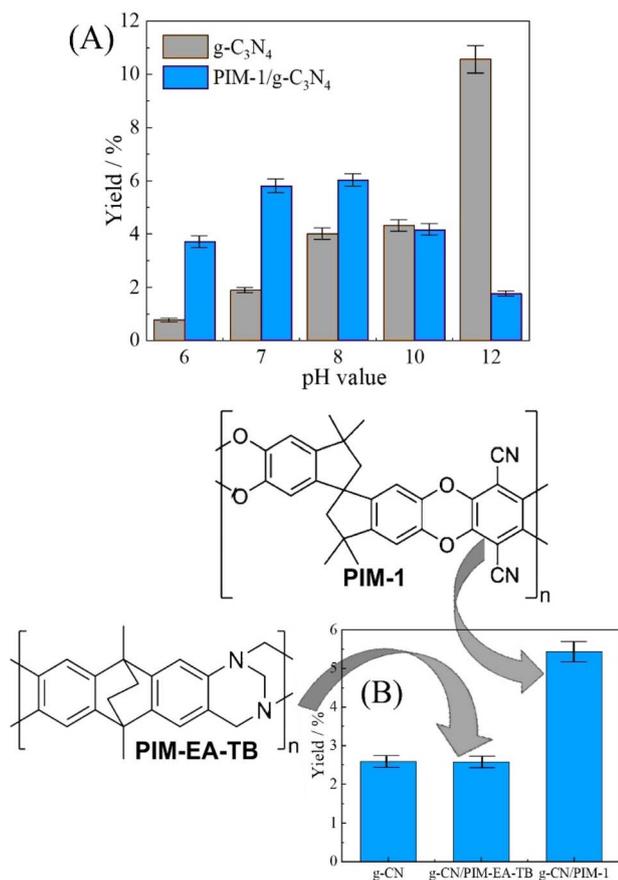


Fig. 5 (A) 100  $\mu\text{mol}$  per L HDFN degradation using 10 mg  $g-C_3N_4$  suspended as powder or 10 mg  $g-C_3N_4$  with 1.0 mg PIM-1 co-immobilised onto  $2 \times 2 \text{ cm}^2$  filter paper and immersed in 10 mL phosphate buffer pH 6, 7, 8, 10, and 12 for 4 h with magnetic agitation, and posterior, determination of fluoride with pH and volume adjusted to 7 and 20 mL, respectively. (B) 100  $\mu\text{mol}$  per L HDFN degradation using 10 mg  $g-C_3N_4$ , 10 mg  $g-C_3N_4$  with 1.0 mg PIM-EA-TB in  $2 \times 2 \text{ cm}^2$  filter paper, and 10 mg  $g-C_3N_4$  with 1.0 mg PIM-1 in  $2 \times 2 \text{ cm}^2$  filter paper and 20 mL phosphate buffer pH 7 with magnetic agitation, and posterior, determination of fluoride (errors estimated  $\pm 5\%$ ).

## Heptadecafluoro-1-nonanol (HDFN) degradation with $g-C_3N_4$ embedded into an intrinsically microporous polymer (PIM-1)

The effect of the pH value on the HDFN degradation rate was examined first using suspended  $g-C_3N_4$  and varying pH in a phosphate buffer solution. Fig. 5A demonstrates that the use of  $g-C_3N_4$  at pH 12 the is most effective, and fluoride yields reach nearly 10% after 4 h of reaction. Alkaline conditions are likely to lead to negatively charged intermediates that are easier to photo-oxidise. In the presence of a buffer solution with a lower pH, degradation occurred at a lower rate.

To evaluate the possibility of immobilizing the photocatalyst into microporous polymer, a cellulose filter paper was employed as a substrate with  $g-C_3N_4$  and with PIM-1 immobilised. Fig. 5A shows data indicating that with a PIM-1 coating, photocatalysis

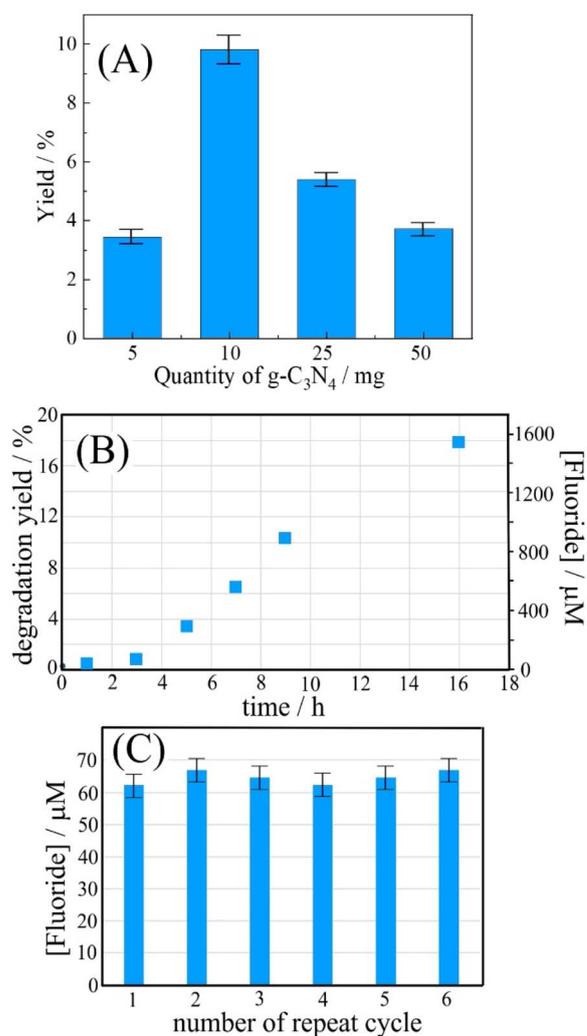


Fig. 6 (A) Fluoride yield for 100  $\mu\text{mol}$  per L HDFN degradation over 4 h time using 5–50 mg  $g-C_3N_4$  (coated with 1.0 mg PIM-1 onto a  $2 \times 2 \text{ cm}^2$  filter paper) immersed in 20 mL phosphate buffer pH 7 with magnetic agitation. (B) Plot of fluoride production and degradation yield versus time for 10 mg  $g-C_3N_4$  (coated with 1.0 mg PIM-1 onto a  $2 \times 2 \text{ cm}^2$  filter paper) immersed in 20 mL phosphate buffer pH 7 with 100 mM HDFN. (C) Bar graph for repeat measurements using the same catalyst impregnated filter paper repeatedly (2 h; 100 mM HDFN; 20 mL phosphate buffer pH 7) (errors estimated  $\pm 5\%$ ).

is enhanced for pH 6, 7, and 8. This enhancement is tentatively attributed here to the accumulation of HDFN molecules within the hydrophobic and porous PIM-1 host. A test with energy-dispersive X-ray spectroscopy (EDS) has been carried out in 0.1 M phosphate buffer at pH 7 and with varying HDFN concentration. PIM-1 films (5 to 10  $\mu\text{m}$  thickness) were immersed for 30 minutes, then rinsed with pure water and dried. Data in Table S1 and Fig. S2 suggest systematic uptake of HDFN into PIM-1, although not with a simple isotherm trend. This is likely due to EDS probing the bulk and the rate of HDFN transport in PIM-1 being limited.

Data in Fig. 5A suggests lower performance for HDFN reacting at  $g-C_3N_4$  in PIM-1. At higher pH the formation of more



hydrophilic anions/complexes might lower the uptake of HDFN into the microporous host. Enhanced HDFN degradation, compared to suspended  $g\text{-C}_3\text{N}_4$ , is particularly interesting at neutral pH conditions. A comparison of two types of intrinsically microporous host materials was attempted for (i) PIM-1 and (ii) PIM-EA-TB; see Fig. 5B. Clearly, the more hydrophobic PIM-1 material is more effective. Repeatability by changing to a fresh solution was tested for the degradation of 500  $\mu\text{mol per L}$  HDFN solution using 10 mg  $g\text{-C}_3\text{N}_4$  at pH values of 7.0 and 12.0, obtaining (for 3 repeats)  $0.9 \pm 0.3\%$  and  $7.8 \pm 0.8\%$ , respectively. More generally, errors in these experiments (typically  $\pm 5\%$  RSD) are associated with  $g\text{-C}_3\text{N}_4$  batch and positioning of the light source.

The distance from the LED light source can directly influence the HDFN degradation rate due to variation in the LED power with distance. Hence, it was evaluated at a 6.0 and 4.0 cm distance using  $g\text{-C}_3\text{N}_4$  without (suspended) and with immobilization employing PIM-1. As expected, decreasing the distance promoted an increase in the degradation of this molecule, yielding 1.90 and 5.82% yields for  $g\text{-C}_3\text{N}_4$  and PIM-1/ $g\text{-C}_3\text{N}_4$ , respectively, at 6.0 cm (power approx.  $14 \text{ mW cm}^{-2}$ ), and 4.16 and 9.45% yields for  $g\text{-C}_3\text{N}_4$  and PIM-1/ $g\text{-C}_3\text{N}_4$ , respectively, at 4.0 cm (power approx.  $27 \text{ mW cm}^{-2}$ ). This distance of 4.0 cm was chosen for the next experiments.

## Heptadecafluoro-1-nonanol (HDFN) degradation with $g\text{-C}_3\text{N}_4$ : light intensity and catalyst recycling

The quantity of  $g\text{-C}_3\text{N}_4$ , ranging from 5 to 50 mg (over  $2 \times 2 \text{ cm}^2$ ), immobilized with PIM-1 onto the filter paper, was evaluated to further increase the rate of HDFN degradation. The results in Fig. 6A demonstrate that an increased  $g\text{-C}_3\text{N}_4$  photocatalyst amount can lead to a decrease in yield. This is likely to be due to thicker catalyst/PIM-1 deposits causing restricted transport of reagents and products. HDFN would have to diffuse *via* micropores into the photoactive film, which will severely limit the rate of photodegradation in thicker deposits. A further problem could be associated with thicker films gradually blocking some of the light. Optimum conditions were obtained using 10 mg  $g\text{-C}_3\text{N}_4$ . Therefore, 10 mg was chosen for further experiments.

The time dependence of HDFN degradation was examined for 100 mM HDFN and the immobilised  $g\text{-C}_3\text{N}_4$  photocatalyst. Similar to the case of suspended  $g\text{-C}_3\text{N}_4$  (Fig. 4B), the production of fluoride continues with time, but with an onset delay in the first 2 h (due to H-atoms on the first carbon, Fig. 1C). The repeat use of the  $g\text{-C}_3\text{N}_4$ /PIM-1 photocatalyst on filter paper was investigated for 2 h exposure and fresh 100  $\mu\text{M}$  HDFN solution in each repeat cycle (Fig. 6C). The catalyst retains photodegradation activity and can therefore be re-used and recovered.

## Conclusion

It has been shown that the photodegradation of heptadecafluoro-1-nonanol (HDFN) with  $g\text{-C}_3\text{N}_4$  is pH-

dependent and more effective in aqueous alkaline environments. Importantly, the use of a PIM-1 microporous polymer as a host environment substantially increases the rate of HDFN degradation even at pH 7 in a phosphate buffer solution. This is tentatively assigned to the accumulation of heptadecafluoro-1-nonanol into the hydrophobic micropores close to the photocatalyst surface. A full study of the adsorption isotherm for HDFN or similar PFAS materials in PFAS will be desirable in the future. The molecularly rigid nature of PIM-1 prevents/suppresses the direct photocatalytic degradation of the host polymer, and it enhances the degradation of the HDFN guest in the microporous environment. The molecularly rigid PIM-1 cannot interact with the photocatalyst surface and therefore maintains catalyst activity.

In the future, the nature of degradation intermediates will have to be assessed and monitored in detail including detection of  $\text{H}_2\text{O}_2$ . More generally, longer term performance testing and catalyst re-use need to be investigated in more detail. New *operando* experimental tool to follow the in/out flow of the fluorine/fluoride will be desirable. The role of composite geometry, *i.e.* the active zone during photocatalysis, needs more attention. The beneficial effect of PIMs and similar microporous materials applied to photocatalysts should be studied and developed more systematically. Initial accumulation of substrates and turnover of reaction intermediates will be affected, and more hydrophobic (potentially also more toxic) intermediates will be potentially retained and destroyed more effectively.

## Author contributions

Fernanda C. O. L. Martins: data curation, formal analysis, investigation, writing – original draft and review & editing; Wanessa R. Melchert: conceptualization, funding acquisition, supervision, writing – review & editing; Akalya Karunakaran: data curation, formal analysis, investigation, methodology, writing – review & editing; Chris R. Bowen: supervision, writing – review & editing; Nicholas Garrod: investigation, data curation; Philip J. Fletcher: investigation, data curation; Mariolino Carta: methodology, supervision, writing – review & editing; Dominic Taylor: methodology, resources, writing – review & editing; Neil B. McKeown: conceptualization, funding acquisition, supervision, writing – review & editing; Frank Marken: conceptualization, formal analysis, methodology, resources, supervision, writing – original draft and review & editing.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

The data supporting this article have been included as part of the main document and the supplementary information (SI). Supplementary information is available. See DOI: <https://doi.org/10.1039/d5ra07284k>.



## Acknowledgements

F. C. O. L. Martins and W. R. Melchert acknowledge the financial support from Brazilian Government Agencies, including the Brazilian National Council for Scientific and Technological Development (CNPq, grants 305538/2022-5) and, in part by the Coordination of Superior Level Staff Improvement (CAPES) – Finance Code 001. A. Karunakaran thanks the National Overseas Scholarship-India. F. Marken acknowledges initial funding from EPSRC (EP/K004956/1). C. R. Bowen acknowledges support of UKRI Frontier Research Guarantee, EP/X023265/1.

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