

Ion-amplified photochemical filtering drives plastic carbon transformation into redox-active dissolved organic matter

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Abstract

Microplastics represent a rapidly expanding global anthropogenic carbon reservoir, yet the mechanisms governing the transformation of plastic carbon into environmentally reactive dissolved organic matter (DOM) under ionic environments remain poorly understood. Here, this study investigate the photochemical transformation of DOM from non-biodegradable polyethylene (PE) and biodegradable poly(butylene adipate-co-terephthalate) (PBAT) microplastics in ultrapure and ionic water matrices. Ultrahigh-resolution molecular evidence reveals a novel “ion-amplified photochemical filtering” effect framework, that profoundly reorganizes plastic-derived DOM molecular pools. Ionic exposure sharply reduces molecular formula richness from 320 and 422 to 145 and 262 for PE and PBAT, respectively. The ion-filtered DOM pools retain polymer-specific molecular signatures, with PE-derived DOM dominated by high H/C aliphatic moieties, while PBAT-derived DOM exhibits higher oxygenation levels. This ionic filtering drives consistent molecular focusing, concentrating DOM toward lipid-, protein-, and amino sugar-like domains with a constrained carbon oxidation state near -1.25 . Photochemical aging simplifies DOM structures, lowers aromatic density, and enhances ROS generation. PBAT-derived DOM exhibits higher redox reactivity than PE-derived DOM, further verified by Cr(VI) probing. This work establishes a formula-level ionic filtering framework that reshapes plastic carbon into redox-active DOM, advancing mechanistic understanding of microplastic biogeochemical cycling in natural aquatic environments.

Introduction

Aquatic dissolved organic matter (DOM) is a pivotal component governing global carbon biogeochemical cycling, microbial metabolism and contaminant transformation, with its environmental biogeochemical functions inherently dependent on molecular composition, oxidation state and reactive functional characteristics rather than merely total carbon abundance^{1–4}. Despite extensive efforts to characterize natural DOM sources and transformation processes, how anthropogenic carbon reservoirs derived from emerging organic pollutants are converted into reactive DOM remains poorly understood^{5,6}.

Microplastics (MPs), as a representative new type of emerging organic pollutants, have created a large, persistent anthropogenic carbon reservoir in aquatic ecosystems^{5,7}. Unlike natural organic matter, which is generally biodegradable, most microplastics consist of high-molecular-weight polymers that are initially chemically inert and poorly integrated into biogeochemical carbon cycles^{7,8}. Environmental forcing (such as sunlight-relevant UV-A/UV-B exposure, redox-active ions, and other physicochemical aging processes) can fundamentally alter polymer structures, triggering bond cleavage, introducing new functional groups, and releasing dissolved organic compounds into solution^{8,9}. Recent studies have shown that microplastics can indeed modify aquatic DOM pools via physical fragmentation, surface oxidation, and leaching of organic constituents^{6,9–13}. However, most existing studies have examined only bulk carbon release or broad compositional changes, offering limited insight into the molecular transformation pathways and redox evolution of microplastic-derived DOM^{5,10–13}. In particular, the

degree to which environmental forcing induces specific molecular-level reactions (e.g., oxidation, reduction, demethylation, dehydration, radical-mediated transformations) remains poorly constrained^{12,13}.

Furthermore, the transformation profiles and final environmental reactivity of MP-DOM are associated with polymer intrinsic properties and freshwater ionic background conditions^{12–16}. Variations in polymer chemical backbone and structural composition determine the inherent photolytic susceptibility of different microplastics, driving divergent DOM molecular diversification and oxygenation trajectories during photoaging^{8,11–13}. Meanwhile, ubiquitous inorganic ions in freshwater environments actively participate in photochemical radical generation and quenching, reshaping polymer degradation efficiency, modulating the stability of photogenerated DOM intermediates, and further mediating the selective molecular evolution of microplastic-released organic fractions^{14,15}. Such dual control by polymer intrinsic properties and aquatic ionic conditions potentially reshapes both molecular structural rearrangement and redox-associated functional performance of microplastic-derived DOM, yet systematic molecular-scale understanding of their combined regulatory effects remains largely undocumented^{12–16}.

To fill this knowledge gap, the present study investigates the molecular transformation and redox functional evolution of DOM released from PE and PBAT microplastics under controlled photo-oxidative conditions. Accelerated 254 nm short-wavelength UV irradiation is adopted to explore mechanistic photochemical processes, with experiments conducted in both ultrapure water and freshwater ionic matrix. Multiple advanced characterization techniques, including optical spectroscopy, ultrahigh-resolution FT-ICR mass spectrometry and electron paramagnetic resonance, are integrated to systematically characterize molecular formula composition, structural evolution and reactive oxygen species generation performance. This work aims to clarify the existence of photochemical molecular filtering effects, and further reveal how polymer chemistry and freshwater ionic environments co-regulate the molecular signatures and redox-active functionality of plastic-derived DOM.

Results

Optical signatures and molecular diversity of MP-DOM

The molecular and optical signatures of PE- and PBAT-derived DOM under UV-only and UV/Ion forcing were investigated via optical spectroscopy and FT-ICR-MS. Results show that photochemical ageing induced optical responses strongly dependent on both polymer type and aqueous matrix condition. For PE-derived DOM, UV-only irradiation caused an obvious early increase in SUVA₂₅₄ value, peaking at $10.4 \pm 0.3 \text{ L mg}^{-1} \text{ m}^{-1}$ on day 7 and then decreased gradually thereafter. In contrast, UV/Ion treatment significantly lowered SUVA₂₅₄ levels, with values dropping to $1.9 \pm 0.2 \text{ L mg}^{-1} \text{ m}^{-1}$ on day 7 and remaining stable at low values until day 28 ($1.4 \pm 0.2 \text{ L mg}^{-1} \text{ m}^{-1}$). PBAT-derived DOM showed completely different optical trends. Under UV-only conditions, SUVA₂₅₄ remained relatively low ($3.2 \pm 0.3 \text{ L mg}^{-1} \text{ m}^{-1}$ on day 7),

whereas UV/Ion treatment induced a distinct recovery in the late incubation stage, reaching $3.1 \pm 0.3 \text{ L mg}^{-1} \text{ m}^{-1}$ on day 28 (Fig. 1a). E_2/E_3 ratios further indicated inconsistent trends between chromophore abundance and molecular size redistribution^{17,18}. For PE-derived DOM, E_2/E_3 decreased from 1.962 ± 0.010 and 0.487 ± 0.011 to 1.000 ± 0.012 and 0.212 ± 0.009 under UV-only and UV/Ion conditions, respectively. For PBAT-derived DOM, UV-only exposure led to minor changes, with E_2/E_3 decreasing from 0.762 ± 0.050 to 0.543 ± 0.030 , while UV/Ion treatment caused a much stronger reduction from 1.727 ± 0.060 to 0.861 ± 0.020 (Fig. 1b). These inconsistent optical trends suggested that the ionic matrix modulates chromophore formation and redistribution through polymer-specific pathways, rather than simply accelerating general photobleaching processes^{14,15}.

FT-ICR-MS analysis further revealed matrix- and polymer-induced differences at the molecular formula level. Compared with UV-only treatment, UV/Ion exposure caused obvious contraction of the overall molecular formula range. The number of molecular formulae decreased from 320 to 145 for PE-derived DOM (a 54.7% reduction) and from 422 to 262 for PBAT-derived DOM (a 37.9% reduction) (Fig. 2a–d). This formula contraction reflected selective molecular screening rather than random molecular loss. The residual formulae from PE-MP were mainly distributed in high-H/C aliphatic regions and slightly shifted toward higher O/C ratios, corresponding to chemical spaces dominated by lipid, protein and amino sugar-like components. In contrast, PBAT-derived DOM retained a wider compositional distribution and extended to higher-O/C regions, consistent with higher degrees of molecular oxygenation during phototransformation. Variations in the relative proportion of CHO, CHNO and CHOS molecular formula groups further reflected ionic regulation on heteroatom-containing molecular components, although these formula-level classifications do not provide direct structural evidence for covalent heteroatom bonding (Fig. 1c–e). Thus, the freshwater ionic environment enhances UV-induced molecular screening, restructuring complex polymer-derived DOM into structurally simple but polymer-specific molecular assemblages.

Optical spectroscopy and FT-ICR-MS reveal polymer- and matrix-dependent restructuring of microplastic-derived dissolved organic matter (DOM) under photo-oxidative forcing. **(a)** Specific ultraviolet absorbance at 254 nm (SUVA_{254}), used as an operational proxy for chromophoric/aromatic character, and **(b)** E_2/E_3 ratios (A_{254}/A_{365}), used as a treatment-consistent optical indicator of chromophore redistribution, were measured for polyethylene (PE)- and poly(butylene adipate-co-terephthalate) (PBAT)-derived DOM under UV-only and UV/Ion conditions over 7–28 days. **(c)** Relative signal contributions of CHO, CHNO and CHOS assigned molecular formula classes resolved by FT-ICR-MS. **(d)** Intensity-weighted elemental ratios (H/C, O/C, N/C and S/C) summarizing bulk formula-level stoichiometry. **(e)** Van Krevelen-based functional-class distributions, including lignin-like, lipid-like, protein/amino sugar-like and other assigned formula groups. **(f)** UV–Vis absorption spectra showing wavelength-dependent chromophoric responses across treatments. Together, these measurements show that the freshwater ionic matrix alters UV-driven DOM evolution by modulating optical chromophore expression and shifting the assigned molecular formula space toward polymer-dependent compositional states. Error bars

denote standard deviation ($n = 3$). Asterisks indicate statistical significance ($*P < 0.05$, $**P < 0.01$, $***P < 0.001$).

Figure 2 | Van Krevelen maps reveal ion-amplified molecular filtering and polymer-specific routing.

Van Krevelen distributions of FT-ICR-MS assigned formulae resolve selective restructuring of microplastic-derived dissolved organic matter (DOM) under UV-only and UV/Ion conditions. **(a, b)** Polyethylene (PE)-derived DOM and **(c, d)** poly(butylene adipate-co-terephthalate) (PBAT)-derived DOM. Each point represents a unique assigned molecular formula plotted by H/C and O/C ratios and color-coded by formula class (CHO, CHNO or CHOS). Relative to UV-only exposure, UV/Ion forcing markedly contracted the assigned formula space, reducing formula richness from 320 to 145 in PE-derived DOM and from 422 to 262 in PBAT-derived DOM. The surviving PE-derived formulae remained largely within high-H/C aliphatic domains while shifting toward heteroatom-bearing assigned formula space, consistent with selective retention of aliphatic products. In contrast, PBAT-derived formulae retained a broader compositional footprint and extended toward higher-O/C domains, indicating oxygenation-biased molecular routing. These patterns show that the freshwater ionic matrix amplifies UV-driven molecular filtering while preserving polymer-specific chemical constraints.

Ion-amplified mass–intensity focusing

Mass–intensity density mapping was conducted to clarify whether the contraction of formula space was caused by non-specific molecular loss or selective signal concentration within key residual molecular domains. UV/Ion treatment induced obvious redistribution of molecular signals toward low-to-intermediate molecular mass ranges. PE- and PBAT-derived DOM showed scattered mass–intensity distributions under UV-only conditions, while UV/Ion treatment produced sharply focused, high-intensity molecular regions for both polymers (Fig. 3a–d). This signal concentration was strongly dependent on polymer type and molecular functional class. For PE-derived DOM, lipid-like formulae exhibited the most obvious response, with the total relative signal intensity increasing by 36% under UV/Ion treatment. For PBAT-derived DOM, the greatest intensity enhancement occurred in protein- and amino sugar-like formulae, with a 33% signal increase. Lignin-like formulae showed moderate contraction without obvious signal enhancement (Fig. 3e–h), while lipid-like and protein/amino sugar-like fractions exhibited clear signal concentration (Fig. 3i–p), indicating selective reduction of aromatic-related molecular components rather than accumulation of aromatic photodegradation products.

Intensity-weighted mass trends further confirmed obvious molecular simplification under UV/Ion conditions. The mass centroid of PE-derived DOM shifted from 328 to 312 Da under UV/Ion treatment, while that of PBAT-derived DOM shifted from 354 to 336 Da, whereas UV-only exposure only caused slight shifts (328 to 323 Da for PE and 354 to 349 Da for PBAT, respectively). These mass shifts indicated that ion-enhanced photochemical screening not only reduced the total number of molecular formulae but also concentrated residual molecular signals in low-to-intermediate mass ranges, with PE preferentially retaining lipid-like components and PBAT retaining protein/amino sugar-like components.

Two-dimensional density maps of FT-ICR-MS assigned formulae show how photo-oxidative forcing redistributes microplastic-derived dissolved organic matter (DOM) across molecular mass and relative signal intensity. **(a–d)** Total assigned DOM formulae from PBAT and PE under UV-only and UV/Ion conditions. **(e–h)** Lignin-like, **(i–l)** lipid-like and **(m–p)** protein/amino sugar-like fractions. Heatmaps represent the joint distribution of molecular mass (m/z) and relative intensity for assigned formulae within each treatment and functional class. Compared with UV-only exposure, UV/Ion forcing concentrated surviving formulae into lower-to-intermediate mass regions and produced more focused high-intensity domains. This signal focusing was class- and polymer-dependent: the relative cumulative signal contribution increased most strongly in PE-derived lipid-like formulae (36%) and PBAT-derived protein/amino sugar-like formulae (33%). These patterns indicate that UV/Ion-driven molecular filtering is accompanied by non-random redistribution of relative signal intensity into polymer-specific survivor domains, rather than uniform loss or non-selective accumulation of photoproducts.

Formula-level structural streamlining and class-conserved refining

Molecular structural parameters and inferred transformation networks were analysed to verify whether concentrated residual molecular domains originated from orderly structural modification rather than random formula removal. Principal component analysis clearly separated PE- and PBAT-derived DOM into distinct compositional clusters, and photochemical treatment induced regular shifts along axes related to H/C ratio, O/C ratio, nominal oxidation state of carbon (NOSC), modified aromaticity index (AI_{mod}), double bond equivalents (DBE) and carbon number^{19–23} (Fig. 4a, b). PE-derived DOM showed limited compositional variation, consistent with the dominant retention of high-H/C aliphatic photoproducts. PBAT-derived DOM covered a wider multivariate range and shifted toward higher O/C regions^{24–27}, consistent with increased oxygenation shown in Van Krevelen diagrams (Fig. 2). Density distributions of C-1-DBE, AI_{mod} and DBE further confirmed that UV/Ion treatment did not uniformly remove all unsaturated or condensed molecular formulae. Instead, structural parameters were redistributed in a class-dependent manner, forming final molecular features with higher oxygenation, lower aromaticity and narrower molecular mass distribution (Fig. 4c–h).

Formula-based transformation networks further demonstrated that structural simplification was dominated by intra-class molecular modification rather than large-scale cross-class molecular redistribution. For PE-derived DOM, approximately 80.1% of the intensity-weighted transformation flux followed intra-class pathways, and lipid-like modification accounted for more than 55% of the total flux under both UV-only and UV/Ion conditions. PBAT-derived DOM exhibited different network characteristics. For instance, protein/amino sugar-like modification became dominant with a flux of 1.54×10^9 intensity units under UV/Ion forcing, exceeding that of lipid-related transformation pathways (Fig. 5). Although these transformation networks reflect formula-level variation trends rather than direct structural identification of specific reaction products^{21–23}, the structural parameters and network analysis confirmed that UV/Ion induced DOM simplification is achieved through polymer-specific and

intra-class molecular modification, instead of random formula loss or large-scale functional group transformation.

Multivariate and structural descriptors of FT-ICR-MS assigned formulae were used to evaluate how photo-oxidative forcing constrains the molecular endpoints of microplastic-derived dissolved organic matter (DOM). **(a, b)** Formula-level principal component analysis (PCA) of PBAT- and PE-derived DOM, with loadings showing contributions from elemental ratios (H/C, O/C, N/C and S/C), carbon number, double bond equivalents (DBE), modified aromaticity index (AI_{mod}) and nominal oxidation state of carbon (NOSC). **(c, d)** Density distributions of C-1-DBE for major functional formula classes, reflecting shifts in carbon-chain and unsaturation-related structural descriptors. **(e–g)** AI_{mod} distributions for lignin-like and protein/amino sugar-like assigned formulae, showing treatment-dependent redistribution of aromaticity-associated formula space. **(h)** Molecular mass frequency distributions showing a shift toward lower-to-intermediate m/z ranges under UV/Ion forcing. Together, these formula-level descriptors indicate that UV/Ion-driven molecular filtering is accompanied by structural streamlining, in which surviving formulae are constrained toward lower-aromatic, oxidation-associated and mass-focused molecular domains rather than being retained as a random subset of the original DOM pool.

Sankey diagrams showing putative transformation networks of microplastic-derived dissolved organic matter (DOM) inferred from FT-ICR-MS assigned molecular formulae. Links were constructed by formula-pair matching across sequential formula-difference categories, including chain scission, oxidation, dehydrogenation and unsaturation-related changes. Flow widths represent relative intensity-weighted formula-pair links and should be interpreted as formula-level network evidence rather than direct structural identification of individual reaction products. Networks are shown for PE- and PBAT-derived DOM under UV-only and UV/Ion conditions. The inferred topology is dominated by class-conserved refining, with major flows retained within lipid-like and protein/amino sugar-like formula spaces, while cross-class redistribution remains comparatively limited. Under UV/Ion conditions, this channelization becomes more pronounced, indicating stronger within-class refinement of the surviving DOM formula pool.

Molecular survivor cores and redox-state convergence

To assess whether UV/Ion screening reshapes existing photochemical molecular pool or forms completely new DOM assemblages, pool-overlap analysis was performed to distinguish common core molecular formulae from treatment-specific components. Functional-class distributions, NOSC profiles and carbon-normalized structural indices were then compared to identify molecular and redox convergence despite different parent polymer properties.

Pool-overlap analysis showed that UV/Ion-screened DOM was dominated by common-core residual molecular formulae rather than treatment-specific unique formulae. For PE-derived DOM, 51.4% of assigned formulae were shared between UV-only and UV/Ion conditions, whereas 44.3% were unique to UV-only treatment, and only 4.3% were unique to UV/Ion treatment. PBAT-derived DOM had a larger

shared core, accounting for 64.9% of total formulae, with 30.0% unique to UV-only and 5.1% unique to UV/Ion treatment (Fig. 6a–d). The low proportion of UV/Ion-specific formulae confirmed that the freshwater ionic matrix primarily reshaped DOM through selective molecular retention and elimination, rather than generating a large number of ion-specific molecular formulae.

Despite divergent Van Krevelen evolutionary trends, the UV/Ion-filtered molecular endpoints showed partial convergence in functional class composition. PE-derived DOM under UV/Ion forcing was dominated by lipid-like formulae (45.3%) and protein/amino sugar-like formulae (40.6%), while lignin-like components decreased to 1.1%. PBAT-derived DOM also maintained high proportions of lipid-like (47.2%) and protein/amino sugar-like fractions (23.4%) under UV/Ion conditions (Fig. 7). NOSC distributions further revealed clear convergence in redox state²⁰, with both PE- and PBAT-derived UV/Ion-filtered DOM concentrated near -1.25 , despite differences in formula quantity, mass–intensity distribution and polymer-specific molecular evolution (Fig. 7). These results indicated that ion-amplified photochemical filtering preserved polymer-specific compositional characteristics while constraining residual DOM within consistent redox state ranges.

Carbon-normalized structural indices further elucidated the structural basis underlying this convergent feature. For lignin-like formulae under UV/Ion treatment, Al_{mod}/C decreased from 0.013692 and 0.016901 to 0.011849 and 0.014055 in PE- and PBAT-derived DOM, respectively, indicating decreased aromaticity-associated formula density¹⁹ (Fig. 8c, d). Condensation-related parameters were redistributed rather than uniformly reduced, with a slight increase in mean C-1-DBE/C for lignin-like formulae in both polymer groups (increased from 0.6162 and 0.4547 to 0.6273 and 0.4686 in PE and PBAT lignin-like formulae, respectively) (Fig. 8a, b). DBE/C decreased obviously in dominant low-aromatic molecular groups, including lipid-like and protein/amino sugar-like formulae for both PE and PBAT (Fig. 8e, f). These structural trends confirm that UV/Ion filtering maintains a large shared molecular core, reduces aromaticity-associated formula density and rebalances molecular unsaturation in a class-dependent manner.

Pool-overlap analysis was used to distinguish shared and treatment-specific assigned formulae in microplastic-derived dissolved organic matter (DOM) under UV-only and UV/Ion conditions. **(a, b)** Van Krevelen diagrams of PE- and PBAT-derived DOM, with assigned formulae classified as Core formulae detected under both UV-only and UV/Ion conditions, UV-only formulae detected only under UV-only exposure, or UV/Ion-only formulae detected only under UV/Ion forcing. **(c, d)** Proportional contributions of each pool to total assigned formula richness. In PE-derived DOM, 51.4% of formulae were shared between UV-only and UV/Ion conditions, whereas 44.3% were UV-only and 4.3% were UV/Ion-only. In PBAT-derived DOM, the shared core was larger, accounting for 64.9% of formulae, with 30.0% UV-only and 5.1% UV/Ion-only formulae. The small UV/Ion-only fractions, together with the large shared cores, indicate that the freshwater ionic matrix primarily reshapes DOM through selective molecular retention and loss rather than by generating a large set of unique UV/Ion-specific products. The partially distinct Van Krevelen distributions of the three pools further show that UV/Ion-driven filtering reorganizes the assigned formula space in a polymer-dependent manner.

Functional-class mapping and NOSC distributions were used to evaluate whether UV/Ion-filtered microplastic-derived dissolved organic matter (DOM) converges toward common molecular endpoints despite distinct polymer origins. Alluvial diagrams show the relative mapping between Van Krevelen-based functional formula classes, including lipid-like, protein/amino sugar-like, lignin-like, carbohydrate-like and other assigned formula groups, and elemental formula classes, including CHO, CHNO and CHOS. The central density plots summarize nominal oxidation state of carbon (NOSC) distributions for PE- and PBAT-derived DOM under UV/Ion forcing. Although PE and PBAT follow different molecular routing patterns in Van Krevelen space, their UV/Ion-filtered DOM pools converge toward lipid-like and protein/amino sugar-like formula spaces and display overlapping NOSC-defined redox-state distributions centred near -1.25 . These patterns indicate that ion-amplified photochemical filtering preserves polymer-dependent compositional features while constraining the surviving DOM toward partially convergent, redox-relevant formula-level endpoints.

Carbon-normalized structural indices were used to evaluate how UV/Ion-driven filtering reshapes the surviving formula space of microplastic-derived dissolved organic matter (DOM). **(a, b)** Distributions of C-1-DBE/C for lignin-like, lipid-like and protein/amino sugar-like assigned formulae derived from PE and PBAT, reflecting condensation- and carbon-chain-related structural descriptors. **(c, d)** Distributions of carbon-normalized modified aromaticity index (AI_{mod}/C), used to assess aromaticity-associated formula density. **(e, f)** Distributions of DBE/C, used to compare unsaturation density across functional formula classes. Together, these distributions show that UV/Ion filtering constrains structural endpoints through decreased aromaticity-associated formula density and class-dependent unsaturation rebalancing, rather than through uniform loss of all condensed or unsaturated formulae.

Redox-mediation potential of photoaged MP-DOM

Electron paramagnetic resonance (EPR) spectroscopy, theoretical electronic structure calculations and Cr(VI) probe experiments were used to verify whether molecular simplification under UV/Ion screening corresponds to the redox activity of photoaged microplastic-derived DOM. EPR tests confirmed that all photoaged DOM samples could generate ROS, and ROS production levels were strongly controlled by polymer type and ionic matrix conditions. Hydroxyl radicals were the main detected radical species. Compared with blank controls, $\bullet\text{OH}$ generation was 6.41-fold and 7.18-fold higher in PE-derived DOM under UV-only and UV/Ion conditions, respectively, while that in PBAT-derived DOM was 8.72-fold and 10.39-fold higher. Superoxide radicals followed the same polymer-dependent trend, with 2.85-fold and 3.94-fold increases for PE-derived DOM and 4.80-fold and 5.98-fold increases for PBAT-derived DOM. Singlet oxygen production also showed consistent polymer and matrix dependence. PE-derived DOM increased 4.75-fold under UV-only treatment and 5.77-fold under UV/Ion treatment, while PBAT-derived DOM increased 6.88-fold and 8.20-fold, respectively (Fig. 9a). Thus, PBAT-derived DOM always exhibited stronger ROS generation capacity than PE-derived DOM, and UV/Ion treatment further enhanced the photosensitive redox response for both polymers.

Electronic structure calculations provided molecular-level interpretation for the observed redox behavior without assigning unique molecular structures to individual FT-ICR-MS formulae. Electrostatic potential distribution showed negative potential regions concentrated around oxygen-rich functional groups, while HOMO distribution indicated electron-donating domains related to oxygenated groups and conjugated π -structures (Fig. 9b). These structural features supported sustained ROS generation even with reduced aromatic formula abundance under UV/Ion treatment, indicating that oxygenated functional groups are key drivers of photoinduced electron and energy transfer^{2,4,13,28,29}. The Cr(VI) redox probe was used to evaluate the electron-transfer potential of photoaged DOM, rather than to obtain quantitative reduction kinetic data. Photoexcited DOM promotes electron and energy transfer to dissolved oxygen to generate ROS^{2,13,28,29} and directly transfers electrons to aqueous Cr(VI) oxyanions^{30,31}. The reduced Cr(III) can be stabilized through coordination with oxygen-containing DOM ligands^{30,31} (Fig. 9c, d). This proposed redox mediation pathway reflects the coupling relationship between ROS generation and DOM electron-donating properties, rather than conclusive evidence for a complete electron shuttle cycle or definite Cr(III) coordination structure. Together, the EPR and electronic-structure results indicate that photoaged MP-DOM retained redox activity. PBAT-derived DOM showed greater photosensitive reactivity than PE-derived DOM, and this response was further enhanced under UV/Ion conditions^{13,28,29,32}. These redox characteristics are consistent with the conceptual model of ion driven DOM molecular evolution shown in Fig. 10.

Electron paramagnetic resonance (EPR) measurements and representative electronic-structure calculations were used to evaluate the redox-mediation potential of photoaged microplastic-derived dissolved organic matter (DOM). **(a)** EPR spectra showing the formation of reactive oxygen species (ROS), including hydroxyl radicals ($\cdot\text{OH}$), singlet oxygen ($^1\text{O}_2$) and superoxide radicals ($\text{O}_2\cdot^-$), under UV-only and UV/Ion conditions for polyethylene (PE)- and poly(butylene adipate-co-terephthalate) (PBAT)-derived DOM. **(b)** Electrostatic potential (ESP) and HOMO distributions of a representative oxygenated DOM model, highlighting electron-rich regions and potential electron-donor motifs rather than uniquely identified FT-ICR-MS structures. **(c)** Proposed photoinduced redox-mediation pathway, in which photoexcited DOM may mediate electron- and energy-transfer reactions with dissolved O_2 , promoting ROS generation, while potentially transferring electrons to aqueous Cr(VI) oxyanions as a probe metal-redox acceptor. **(d)** Proposed stabilization of reduced Cr(III) through coordination with oxygen-containing DOM ligands. Together, ROS generation and the Cr(VI) probe response support the emergence of redox-relevant functionality in photoaged microplastic-derived DOM, with polymer-dependent responses reflecting differences in redox-mediation potential.

Conceptual schematic illustrating the formation and molecular evolution of dissolved organic matter (DOM) released from polyethylene (PE) and poly(butylene adipate-co-terephthalate) (PBAT) microplastics under photo-oxidative forcing. **(a)** Continuous 254 nm UV irradiation promotes solid-phase photo-oxidation of PE and PBAT, forming oxygenated surface functionalities and releasing oxygenated assigned formulae. **(b)** Under UV-only exposure in ultrapure water, released DOM is dominated by CHO assigned formulae, whereas the freshwater ionic matrix drives a UV/Ion molecular-filtering pathway that

alters the distribution of CHO, CHNO and CHOS assigned formula classes while selectively removing part of the formula pool, reducing formula richness from 320 to 145 for PE-derived DOM and from 422 to 262 for PBAT-derived DOM. (c) The UV/Ion-filtered DOM retains polymer-specific molecular fingerprints: PE-derived DOM is biased toward an aliphatic survivor pool, whereas PBAT-derived DOM extends toward more oxygenated formula space. The resulting endpoint is a simplified, redox-relevant DOM pool shaped by selective retention and redistribution of assigned formulae rather than by uniform product accumulation.

Discussion

Microplastic-derived dissolved organic matter (MP-DOM) has emerged as a chemically active component of aquatic organic matter, yet the molecular mechanisms governing the conversion of recalcitrant polymer carbon into persistent and reactive dissolved products remain incompletely resolved^{11–13,24–29,32}. Previous studies have demonstrated that sunlight promotes microplastic photodissolution and generates chemically diverse DOM, with polymer-dependent release rates, molecular signatures and photoreactivity^{10–13,24–29,32}. Inorganic ions can further regulate radical chemistry and alter microplastic photoageing pathways^{14,15}. However, existing interpretations have largely focused on dissolved-carbon release, parent-polymer degradation or bulk optical changes, treating MP-DOM primarily as an accumulated endpoint of photo-oxidation^{10,11,14,15,24–27}. Such a view provides limited insight into how aqueous environments regulate the persistence, continued transformation and functional dominance of individual photoproducts after release^{12,13,27–29,32}. By integrating optical spectroscopy, molecularly resolved FT-ICR-MS profiling^{33,34}, pool-overlap analysis, formula-inferred transformation networks, EPR measurements and representative electronic-structure calculations, this study reframes MP-DOM evolution as a coupled process of molecular generation and post-release selection. We show that ionic conditions do not simply accelerate plastic degradation; instead, they impose a molecular filtering effect that contracts heterogeneous photoproduct pools and increases the relative dominance of specific survivor formulae within the observable molecular pool. Thus, MP-DOM represents not merely released plastic carbon, but a selectively assembled molecular pool jointly shaped by polymer inheritance and aqueous-matrix constraints.

The molecular contraction induced by ionic conditions indicates that post-release selection is a fundamental process controlling MP-DOM evolution. Rather than producing a distinct population of ion-specific products, UV/Ion exposure primarily reshaped molecular populations already accessible through polymer photo-oxidation by altering their persistence and relative abundance. This selective restructuring may arise from the combined effects of ionic regulation on radical speciation, intermediate stability, molecular association and secondary oxidation pathways^{14,15,35–38}. Highly reactive intermediates may undergo further oxidation, fragmentation or loss from the observable molecular pool, whereas comparatively persistent formulae become relatively enriched^{35–39}. Such filtering explains why photoaged plastic carbon does not continuously accumulate as an increasingly complex mixture, but instead evolves towards a more restricted molecular domain. Importantly, this interpretation refers to

formula-level persistence within the analytical window and does not imply complete chemical destruction of undetected compounds, given the potential influences of extraction selectivity, ionisation bias, residual ion suppression and signal attenuation^{21,22,33,34}.

Polymer architecture determines the molecular trajectories available for this filtering process. PE consists predominantly of a saturated hydrocarbon backbone and lacks intrinsic ester linkages and aromatic chromophores. Its transformation is therefore initiated mainly at structural defects, pre-existing oxidised sites or photoactive impurities, followed by hydrogen abstraction, hydroperoxide formation, carbonyl accumulation and chain cleavage, favouring hydrogen-rich aliphatic products^{8,9,35}. PBAT, by contrast, contains hydrolysable ester bonds, carbonyl groups and terephthalate-derived aromatic units, providing additional reaction centres for hydrolysis, oxidation and Norrish-type photochemical pathways^{36–38,40–42}. Consequently, PE-derived DOM preferentially retained high-H/C, lipid-like molecular features, whereas PBAT-derived DOM occupied a broader oxygen-rich molecular space enriched in carbonyl-bearing and protein/amino sugar-like formula regions. These Van Krevelen classifications represent operational elemental-ratio domains rather than definitive molecular identities^{19,21–23}. Transformation networks further indicate that ionic forcing refined molecular composition without erasing polymer-specific chemical inheritance. Although PE and PBAT followed distinct molecular succession pathways, their survivor pools converged towards overlapping nominal oxidation-state distributions. PE approached this oxidation-state window through progressive oxygen incorporation into an initially reduced hydrocarbon framework, whereas PBAT reached it through ester cleavage, further oxygenation and preferential loss of reactive products. This convergence therefore reflects distinct transformation routes towards a similar formula-level carbon oxidation state, rather than equivalence in molecular identity, measured redox potential or thermodynamic stability²⁰. Polymer architecture thus defines the accessible photoproduct space, whereas aqueous-matrix filtering determines the composition of the surviving DOM pool.

A key implication of this molecular restructuring is that photochemical activity cannot be inferred from bulk aromaticity alone. Aromatic and extensively conjugated structures are traditionally regarded as major DOM photosensitisers because their π -electron systems absorb radiation and can generate reactive excited states^{2,4,39,43,44}. However, previous MP-DOM studies have shown that photochemical reactivity and ROS formation are not necessarily positively correlated with aromatic abundance^{13,27–29,45,46}. Here, declining SUVA₂₅₄ and aromaticity-associated formula density coincided with stronger ROS-related EPR responses, indicating that photo-oxidation redistributed rather than simply diminished photochemical functionality. Molecular transformation likely shifted part of the activity from extended aromatic domains towards carbonyl-centred, quinone-/semiquinone-like and locally conjugated oxygenated structures. Such motifs can support $n \rightarrow \pi^*$ excitation, triplet-state formation and subsequent energy- or electron-transfer reactions, thereby contributing to the generation of $\cdot\text{OH}$, $\text{O}_2^{\cdot-}$ and $^1\text{O}_2$ ^{2,4,29,39,43–46}. Importantly, not all oxygen-containing groups possess photosensitising capability; isolated hydroxyl and carboxyl groups generally absorb weakly within the relevant spectral range^{2,39,44}.

Rather, oxygenated functionalities become photochemically important when incorporated into electronically coupled carbonyl-centred or locally conjugated environments^{44–46}. Their selective formation or retention may therefore partially compensate for the loss of extended aromatic chromophores^{45,46}. The stronger ROS-related responses of PBAT-derived DOM likely reflect the coexistence of ester-derived carbonyl centres, residual terephthalate-associated conjugation and a broader oxygenated molecular reservoir, whereas PE-derived DOM remained dominated by more saturated aliphatic survivors^{13,29,36–38,40–42}. Electronic-structure calculations support the plausibility of these reactive domains but do not assign specific structures to individual FT-ICR-MS formulae.

The emergence of redox-active MP-DOM demonstrates that molecular simplification does not necessarily entail functional attenuation. The Cr(VI) probe response, together with EPR and electronic-structure evidence, indicates that photoaged MP-DOM retains electron-transfer potential and may participate in the photochemical transformation of contaminants and redox-active elements^{16,28,30,31,45}. Photochemical filtering therefore did not generate an inert degradation residue, but a compositionally restricted survivor pool that retained substantial photochemical and electron-transfer potential. This finding broadens the environmental significance of MP-DOM beyond the amount of dissolved carbon released or changes in bulk optical properties, highlighting the importance of which molecular domains persist and whether they contain electronically active chromophores. Nevertheless, the Cr(VI) assay provides functional evidence rather than proof of quantitative reduction kinetics, complete electron-shuttling cycles or specific Cr(III)–DOM coordination structures. The present framework was also established under accelerated 254 nm irradiation and a simplified ionic matrix, which cannot fully reproduce natural sunlight spectra, complex water chemistry or interactions with indigenous DOM and minerals. Validation under natural irradiation and realistic aquatic matrices, together with ion-resolved experiments and structural identification of key photoreactive molecules, will be required to establish its environmental generality. Overall, parent-polymer chemistry defines the accessible photoproduct space, whereas aqueous ionic conditions regulate molecular persistence and redox activation under the tested conditions. Ion-amplified photochemical filtering therefore provides a molecular framework linking polymer-specific carbon transformation, aqueous-matrix selection and the emergence of redox-active dissolved organic matter.

Methods

Photo-ageing experiments and MP-DOM collection

Polyethylene (PE) and poly(butylene adipate-co-terephthalate) (PBAT) were selected as representative microplastics to compare dissolved organic matter (DOM) formation from a saturated polyolefin and an ester-containing biodegradable polyester^{35,36}. Pristine microplastic powders (mean particle diameter approximately 150 µm; purity > 99%; Shanghai Fengtai Polymer Co.) were sequentially washed with ultrapure water, methanol and dichloromethane to remove loosely bound additives and surface contaminants. The cleaned particles were dried under clean airflow and stored in combusted amber-

glass vials. Solvent-processing blanks without microplastics were subjected to the same pretreatment procedure.

A synthetic freshwater ionic matrix was prepared in ultrapure water (18.2 M Ω cm, Milli-Q) using trace-analytical grade salts and contained 6 mM NaCl, 3 mM NaHCO₃, 1.5 mM CaSO₄ and 0.6 mM (NH₄)₂SO₄. All glassware used for photo-ageing and DOM collection was acid-leached with 10% HNO₃, rinsed thoroughly with ultrapure water and combusted at 450 °C for 6 h before use.

For each polymer, two irradiation treatments were established: UV-only, in which microplastics were suspended in ultrapure water, and UV/Ion, in which microplastics were suspended in the synthetic freshwater ionic matrix. Each reactor contained 300 mg of microplastics in 30 mL of solution (10 g L⁻¹). Suspensions were exposed to continuous UV irradiation at 254 nm and 25 ± 1 °C. The 254 nm treatment was used as accelerated mechanistic photochemical forcing rather than as a direct simulation of natural sunlight. Light-field monitoring, mixing and control procedures are provided in Supplementary Method 1.

At 7, 14 and 28 days, suspensions were filtered through pre-rinsed 0.22 μ m polyethersulfone membranes to remove particles and collect MP-DOM. Filtrates were stored at 4 °C in combusted amber-glass vials before optical, mass-spectrometric and redox analyses.

Optical characterization and dissolved organic carbon analysis

UV–visible absorbance spectra of MP-DOM were measured from 200 to 800 nm using a Shimadzu UV-2600 spectrophotometer and quartz cuvettes. Ultrapure-water and ionic-matrix blanks were used as matrix-matched references, and spectra were blank-corrected before calculation of optical indices. Specific ultraviolet absorbance at 254 nm (SUVA₂₅₄) was calculated by normalizing absorbance at 254 nm to dissolved organic carbon (DOC) concentration and was used as an operational descriptor of chromophoric character¹⁷. The E2/E3 ratio was calculated as A_{254}/A_{365} and used as a treatment-consistent indicator of chromophore redistribution¹⁸.

DOC concentrations were quantified by high-temperature catalytic oxidation using a Shimadzu TOC-L analyser with multipoint calibration and check standards⁴⁷. Optical indices were calculated from blank-corrected spectra and normalized to DOC where applicable.

Solid-phase extraction and FT-ICR-MS analysis

MP-DOM samples were desalted and concentrated by PPL solid-phase extraction and subsequently analysed by negative-mode electrospray-ionization FT-ICR-MS^{21,22,34,48–51}. Carbon recovery ranged from 40% to 55% and was used as a quality-control criterion rather than as a normalization target. Detailed extraction, instrumental acquisition, calibration, blank filtering and formula-assignment procedures are provided in Supplementary Method 2.

Assigned formulae were used for formula-level comparisons and were not interpreted as unique molecular structures. Intensity-weighted H/C, O/C, N/C and S/C ratios were calculated to compare the elemental composition of MP-DOM among treatments. Van Krevelen diagrams were constructed from H/C and O/C ratios to visualize formula-level saturation and oxygenation patterns^{21,22,52}.

Molecular descriptors and formula classification

Molecular descriptors were calculated from assigned elemental formulae to evaluate structural and redox-related properties of MP-DOM. Double bond equivalents (DBE) were calculated as $DBE = 1 + C - H/2 + N/2$, where C, H and N denote the numbers of carbon, hydrogen and nitrogen atoms in the assigned formula⁵³.

The modified aromaticity index (AI_{mod}) was calculated as $AI_{mod} = [1 + C - O/2 - S - (H + N)/2] / [C - O/2 - N - S]$, where O and S denote the numbers of oxygen and sulfur atoms, respectively¹⁹. AI_{mod} was used as a formula-level descriptor of aromaticity-associated molecular character rather than as direct structural proof of aromatic rings.

The nominal oxidation state of carbon (NOSC) was calculated as $NOSC = -H/C + 2O/C + 3N/C + 2S/C$, where each term represents the elemental ratio of the assigned formula²⁰. NOSC was used to describe formula-level redox state and should not be interpreted as a direct measure of biodegradability or microbial utilization.

Carbon-normalized descriptors were calculated as needed to compare structural density across formula classes. C-1-DBE was used as an operational approximation of C-C single-bond capacity⁵³. Because formula-level information cannot distinguish C = C from other double bonds, this value may underestimate the number of C-C single bonds. The normalized indices $(C - 1 - DBE)/C$, DBE/C and AI_{mod}/C were used to compare condensation-related, unsaturation and aromaticity-associated formula density, respectively^{19,53}.

Formulae were classified in Van Krevelen space into lipid-like, lignin-like, protein/amino sugar-like, carbohydrate-like and other operational groups using established H/C and O/C domains⁵². These categories describe elemental-ratio regions and do not confirm compound identity^{23,52}.

Formula-pool and transformation-network analyses

Formula richness was defined as the number of unique assigned formulae detected within a sample or formula group. Relative intensity was calculated from blank-corrected FT-ICR-MS peak intensities and used to estimate the cumulative signal contribution of elemental and functional formula classes. Two-dimensional mass–intensity density maps were generated to visualize the joint distribution of molecular mass and relative signal intensity across total DOM and class-resolved formula pools.

Pool-overlap analysis was used to distinguish shared and treatment-specific formulae between UV-only and UV/Ion treatments for each polymer. Core formulae were detected under both conditions, whereas

UV-only and UV/Ion-only formulae were detected exclusively under the corresponding treatment. Formula richness, relative intensity and Van Krevelen distributions were compared among these pools.

Formula-inferred transformation networks were reconstructed from FT-ICR-MS formula lists using a rule-based formula-pair matching framework^{54,55}. The networks were interpreted as ensemble-level formula-difference associations rather than direct bond-level reaction mechanisms. Density calculation, matching rules, transition weights and class-fidelity calculation are described in Supplementary Method 3.

Redox assays and representative electronic-structure calculations

Photo-induced hydroxyl radicals, superoxide-derived radicals and singlet oxygen were evaluated by EPR spin trapping and selective-quenching controls^{13,28,56,57}. Integrated signals were expressed relative to identically processed blanks. Reagent concentrations, irradiation conditions and EPR acquisition settings are provided in Supplementary Method 4.

Representative electronic-structure calculations were used to visualize electrostatic-potential and highest-occupied-molecular-orbital distributions in oxygenated DOM-like structures. Cr(VI) was used as a probe metal-redox acceptor to evaluate the redox-mediation potential of photo-aged MP-DOM^{30,31}. Computational settings and probe-assay conditions are provided in Supplementary Method 5. The calculations did not assign unique structures to FT-ICR-MS formulae, and the Cr(VI) assay was not interpreted as quantitative remediation kinetics or confirmation of Cr(III) coordination chemistry.

Quality assurance and statistical analysis

Quality-control samples included ultrapure-water blanks, ionic-matrix blanks, filter blanks, SPE procedural blanks, solvent-processing blanks and instrument blanks. Peaks detected in SPE procedural blanks were removed using the criterion described in Supplementary Method 2. Experiments were conducted in independent triplicates unless otherwise stated, and data are reported as mean $\pm$ standard deviation. Statistical comparisons, where performed, were conducted using one-way or two-way analysis of variance as appropriate, followed by Tukey's honestly significant difference post hoc test. Normality and homoscedasticity were assessed using the Shapiro–Wilk and Levene tests, respectively. Statistical significance was reported as $*P < 0.05$, $**P < 0.01$ and $***P < 0.001$. PCA, density plotting, Sankey visualization and statistical analyses were performed using OriginPro 2025 and IBM SPSS Statistics 26.0, unless otherwise specified. No statistical inference was made for comparisons where the corresponding test was not performed.

Data availability

Data will be made available on request.

Declarations

Competing interests

The authors declare no competing interests.

Additional information

Supplementary information is available with this paper.

Author contributions

X.W., P.T., H.Y. and S.W. conceived the idea and designed the experiments. M.Y., D.R., S.Y. and S.P. performed the experiments. M.Y., D.R., S.Y., S.P., X.W., P.T., H.Y. and S.W. analyzed the data and discussed the results. M.Y. and D.R. wrote the original manuscript. X.W., P.T., H.Y. and S.W. revised the manuscript. All authors reviewed and approved the final manuscript.

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Figures

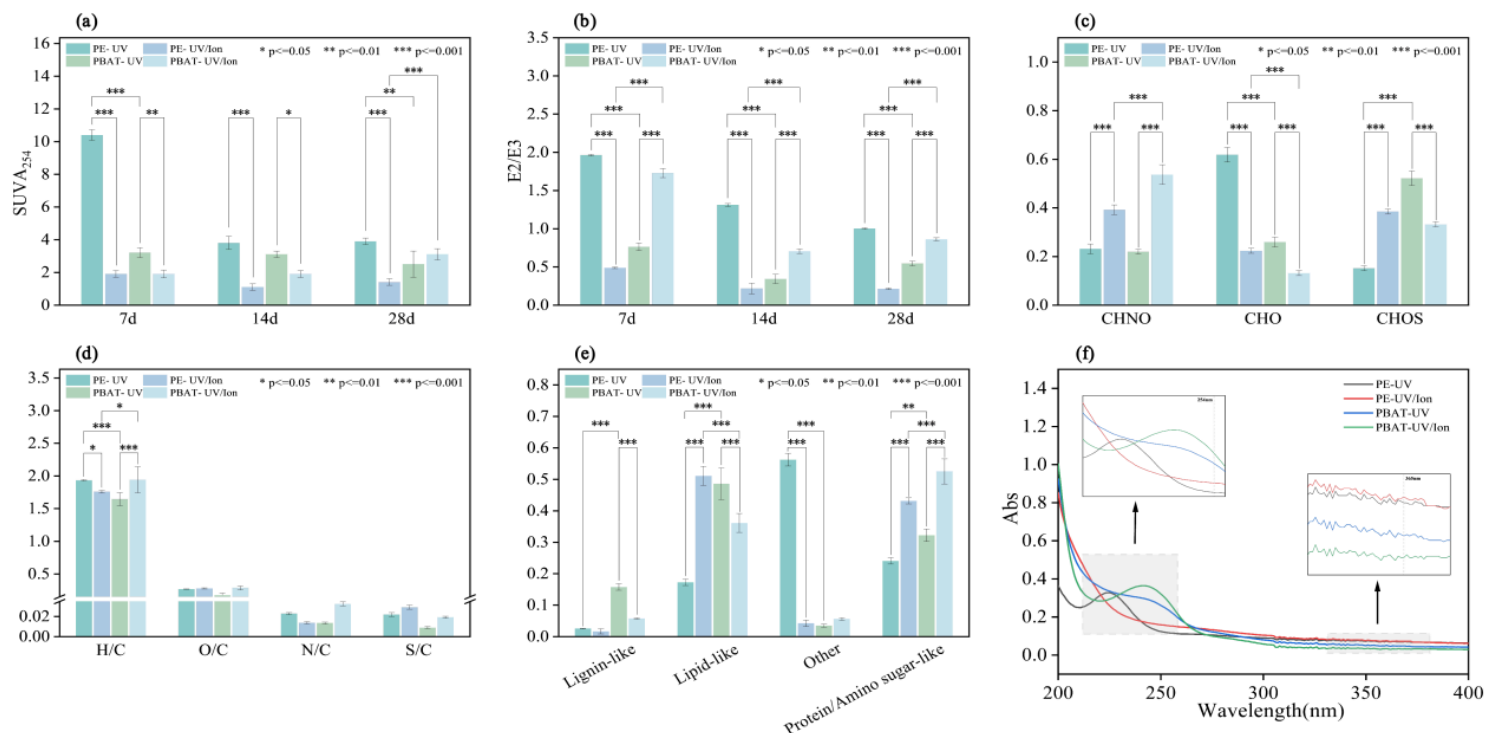


Figure 1

UV/Ion forcing reshapes optical and molecular signatures of microplastic-derived DOM.

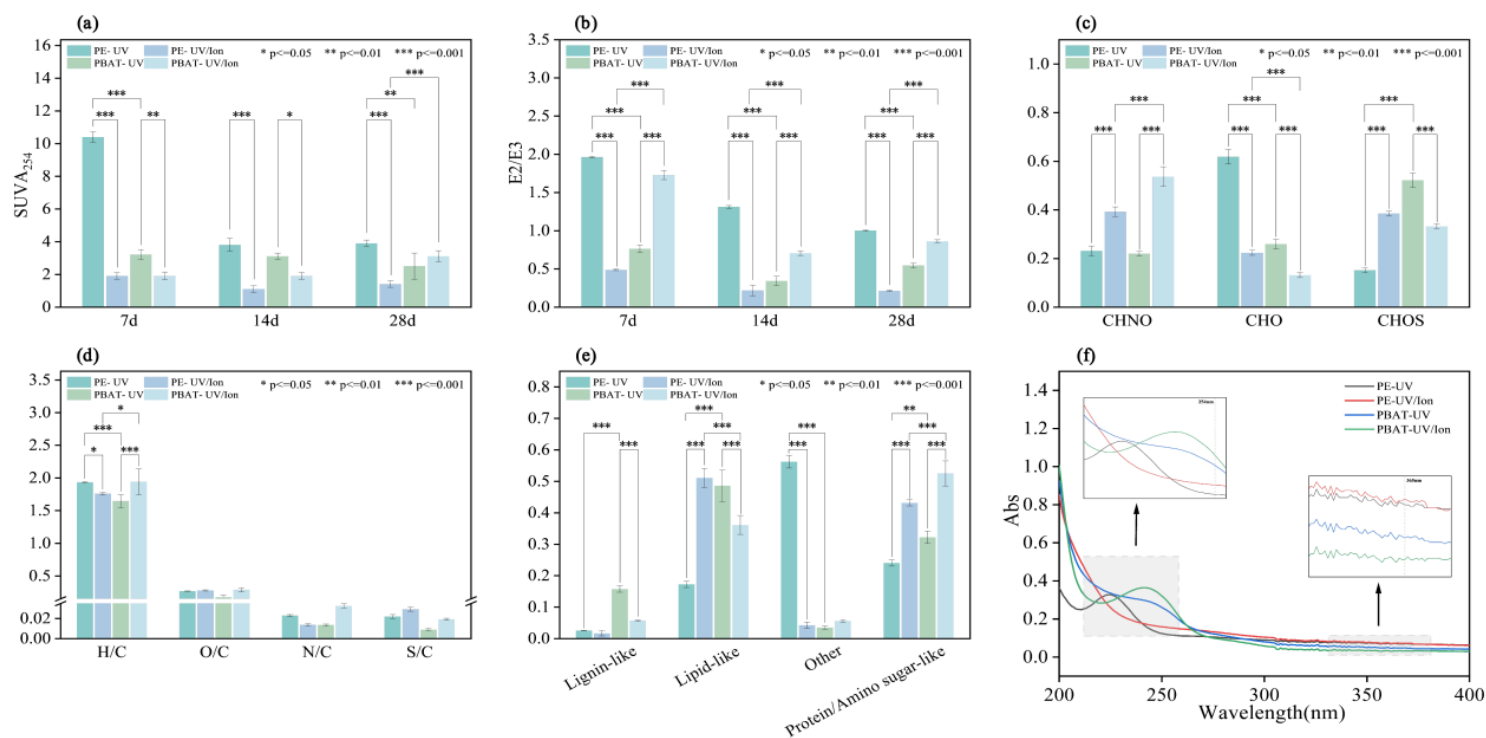


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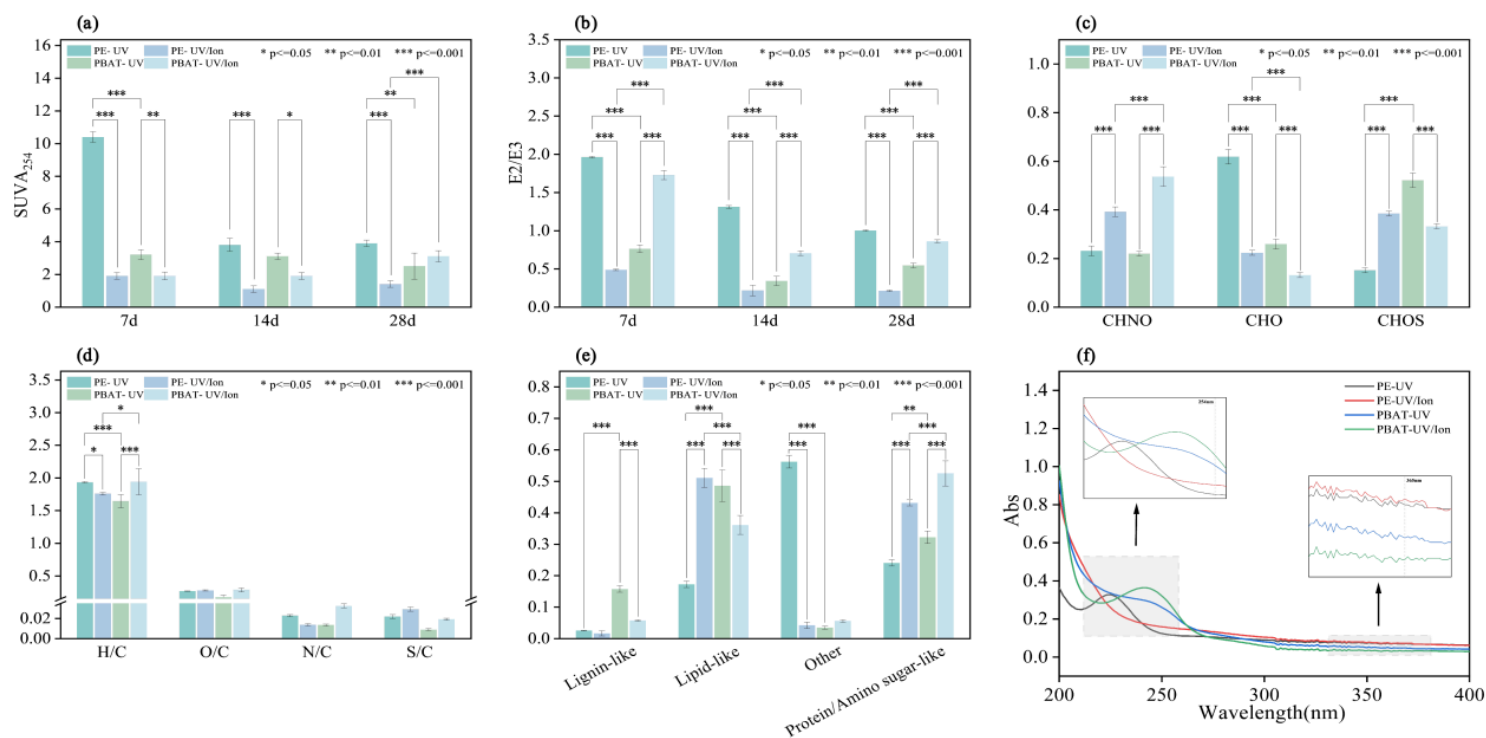


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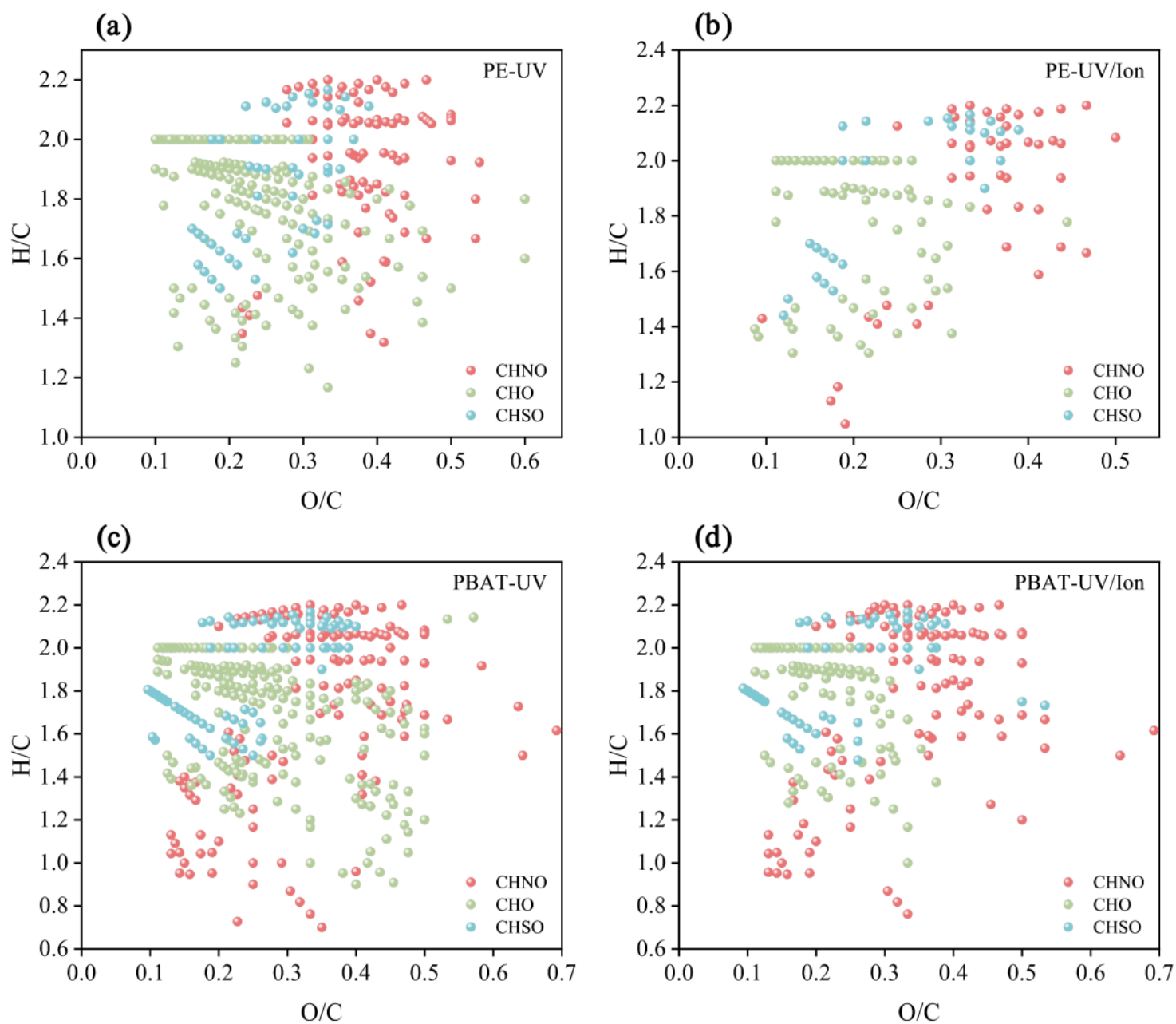


Figure 2

Van Krevelen maps reveal ion-amplified molecular filtering and polymer-specific routing.

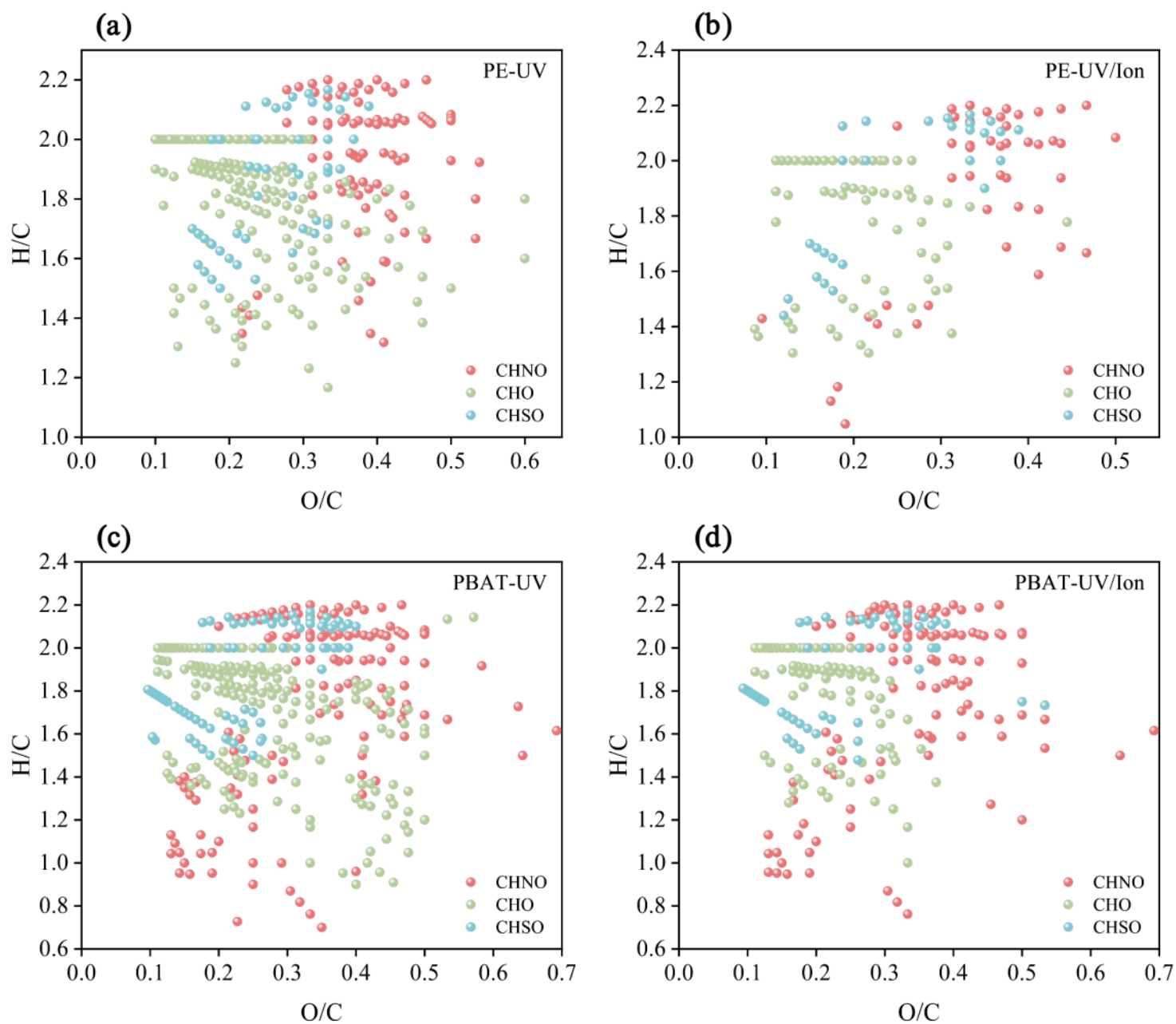


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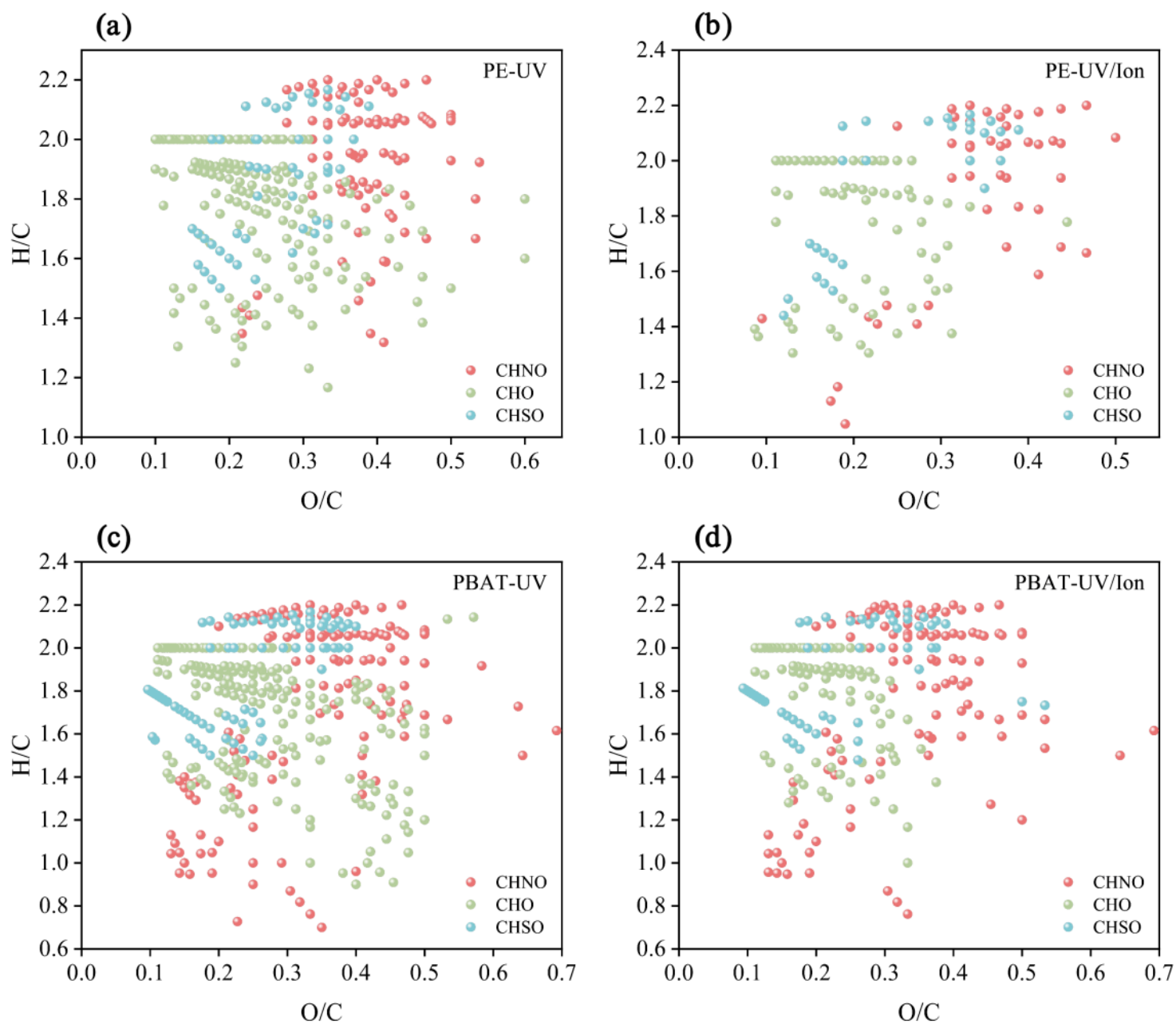


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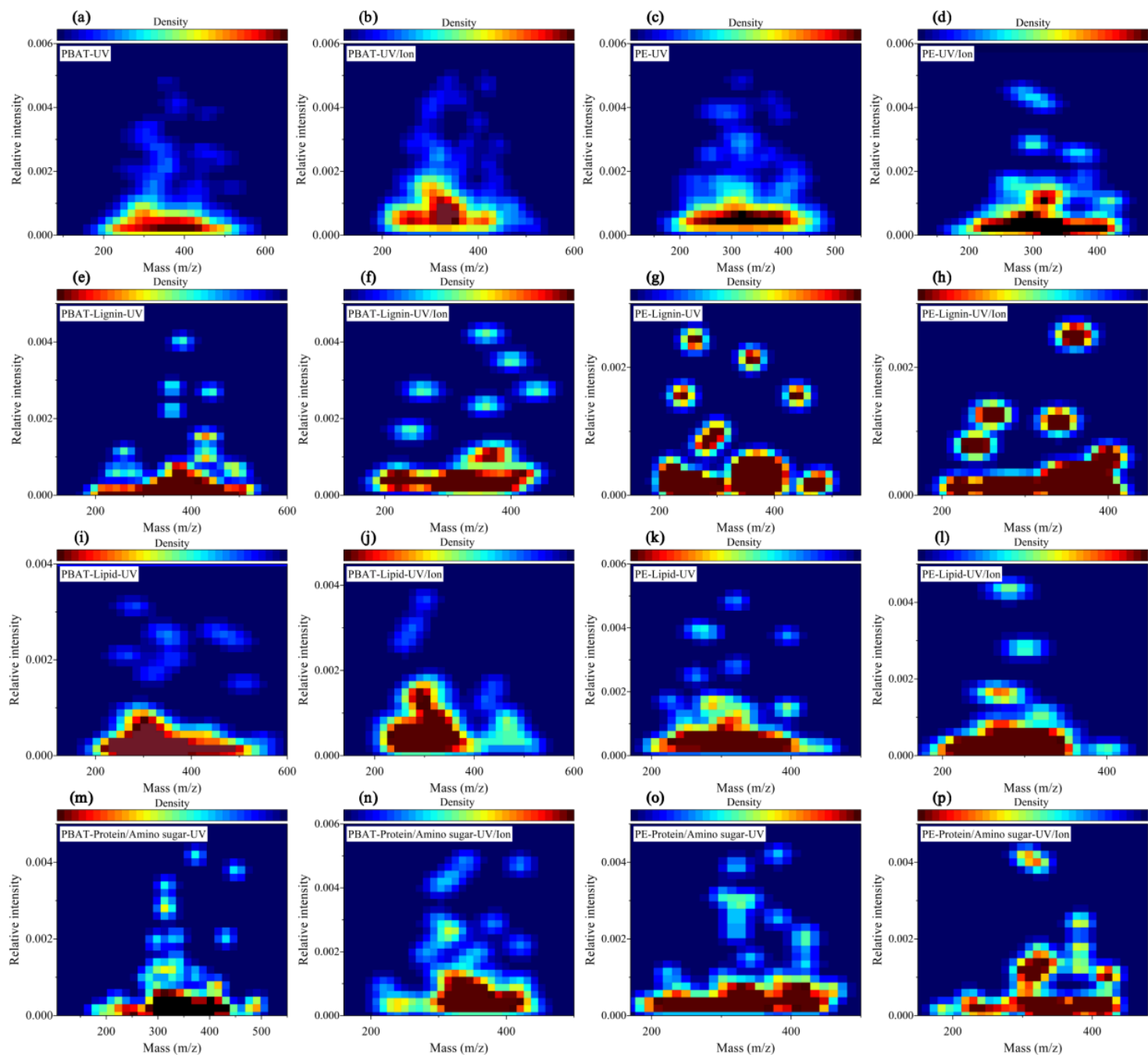


Figure 3

UV/Ion forcing concentrates surviving formulae into class-specific mass–intensity cores.

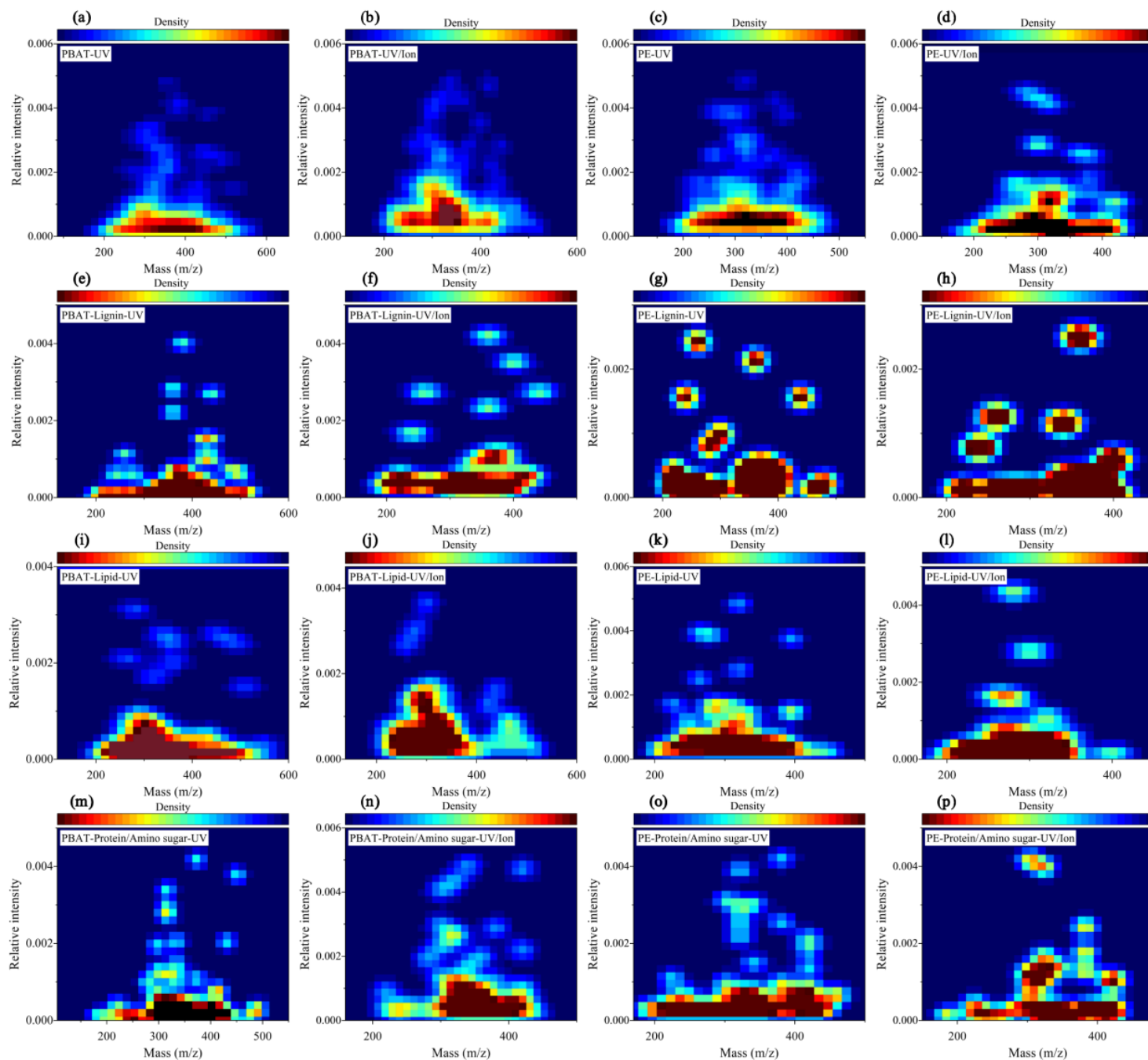


Figure 3

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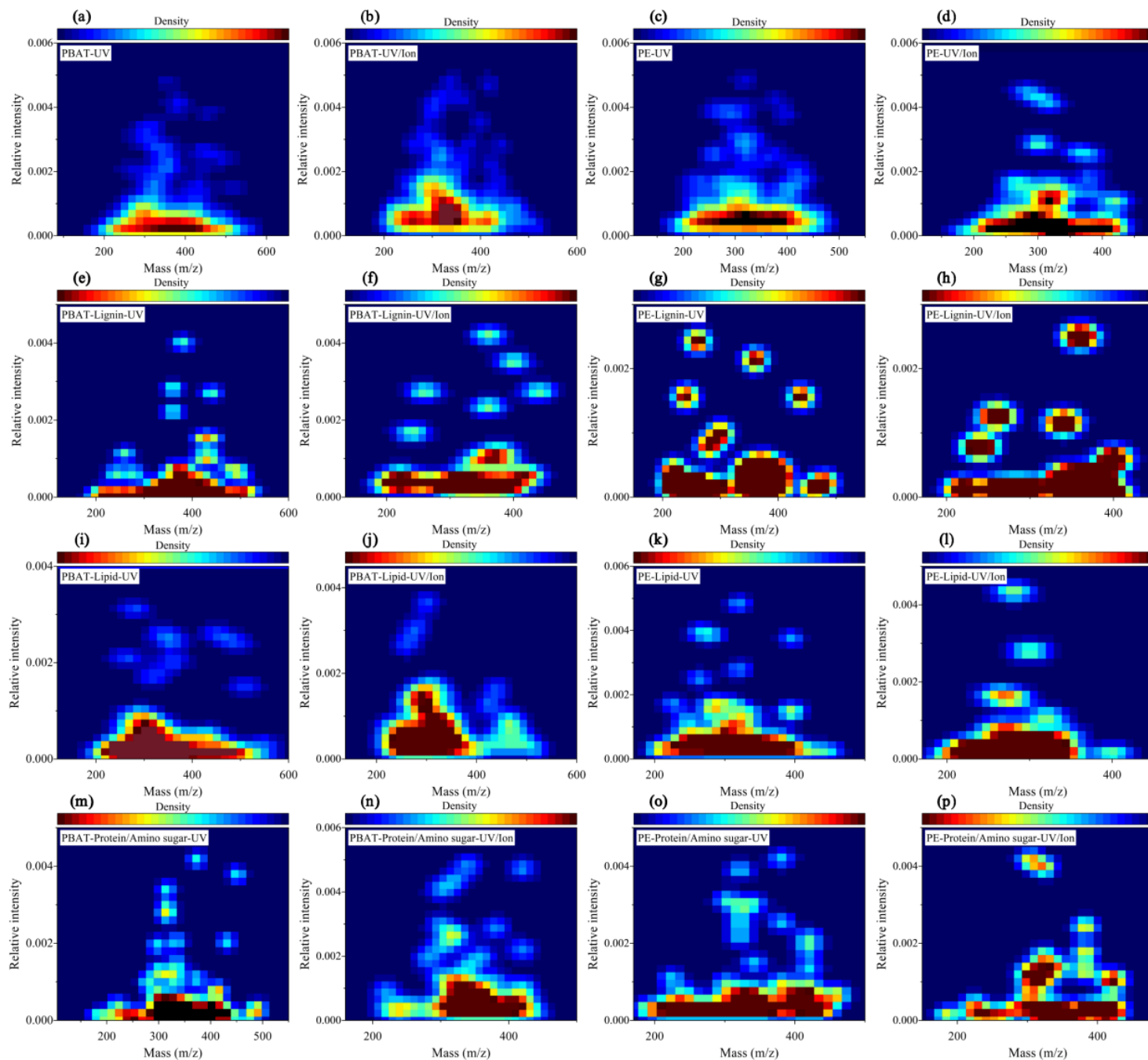


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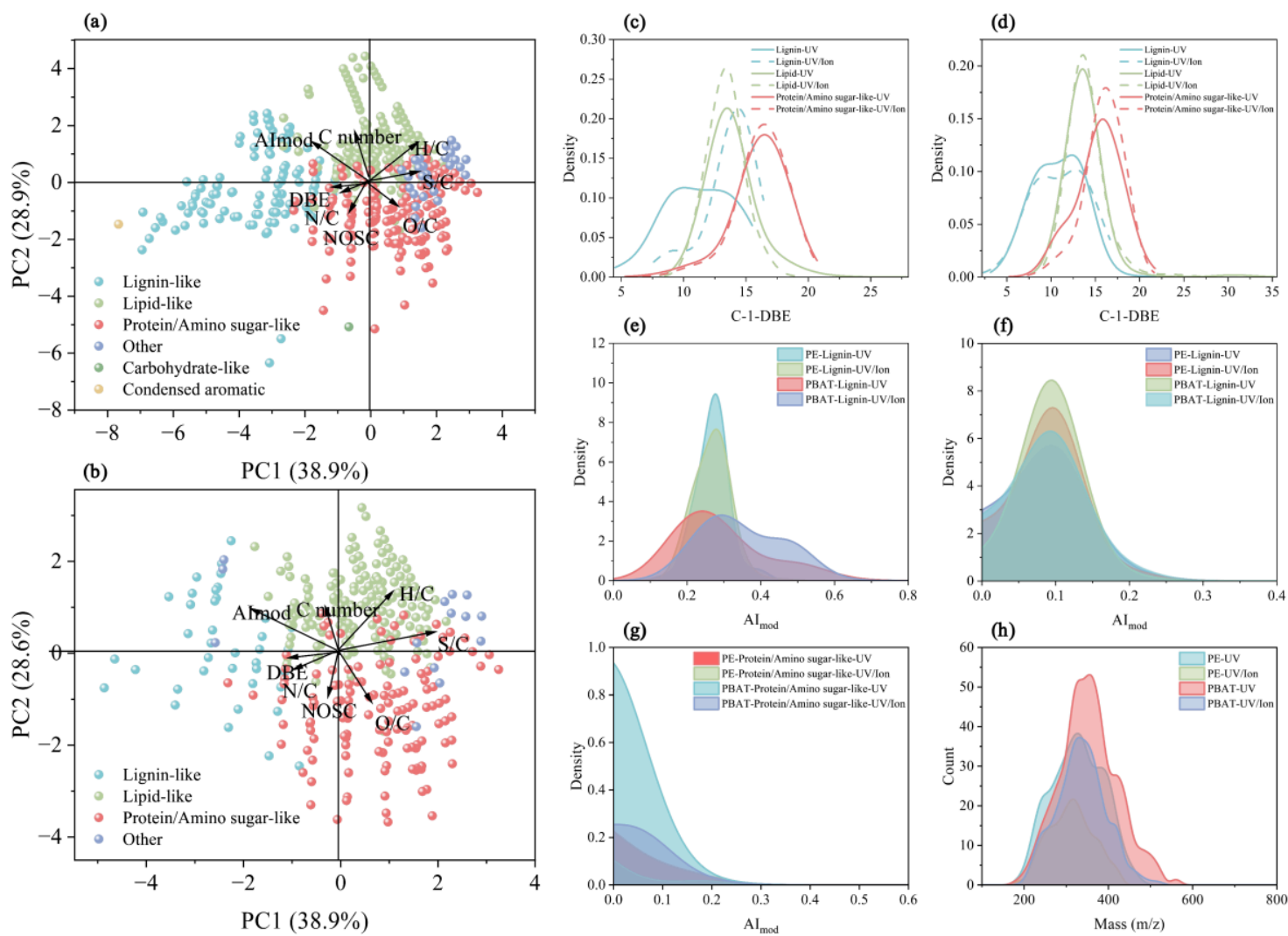


Figure 4

Formula-level structural indices define streamlined molecular endpoints under UV/Ion forcing.

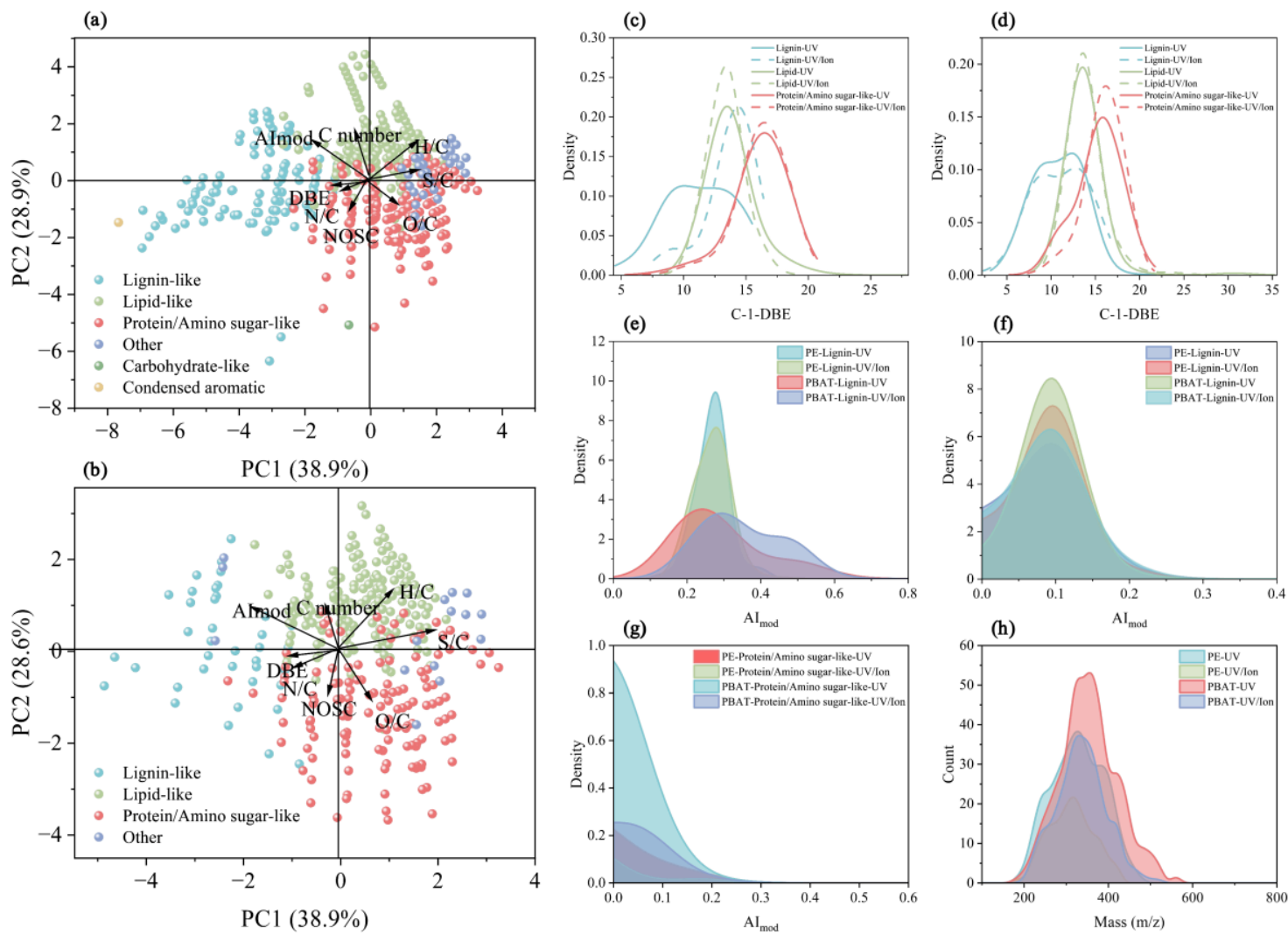


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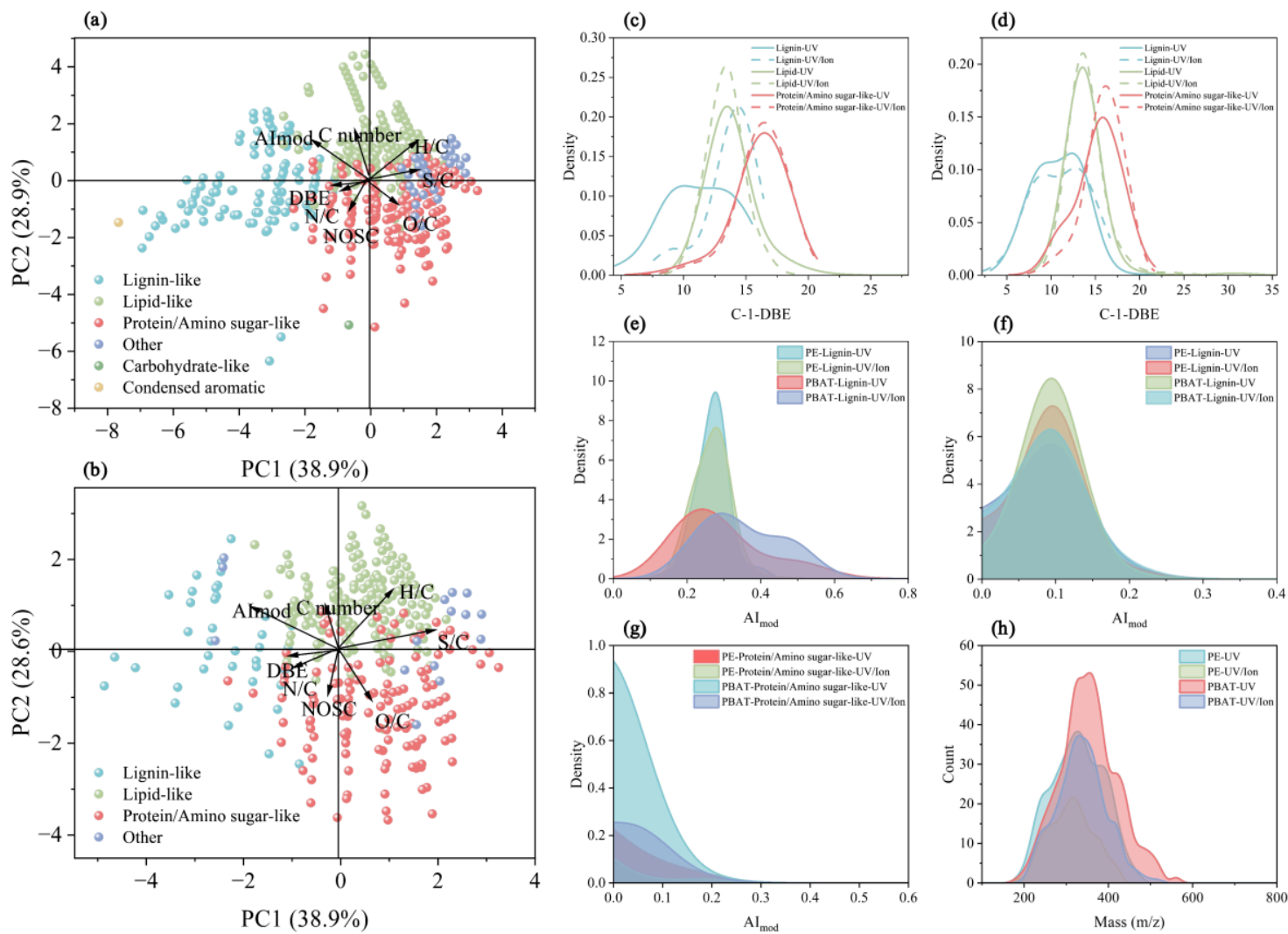


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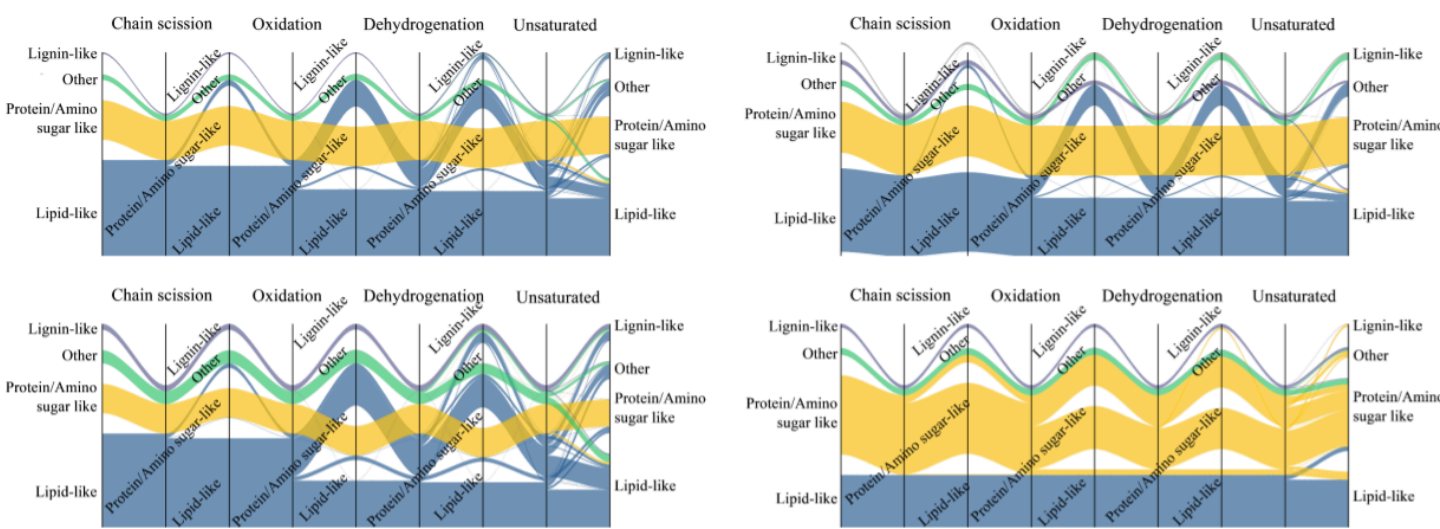


Figure 5

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Formula-inferred transformation networks reveal class-conserved refining of microplastic-derived DOM.

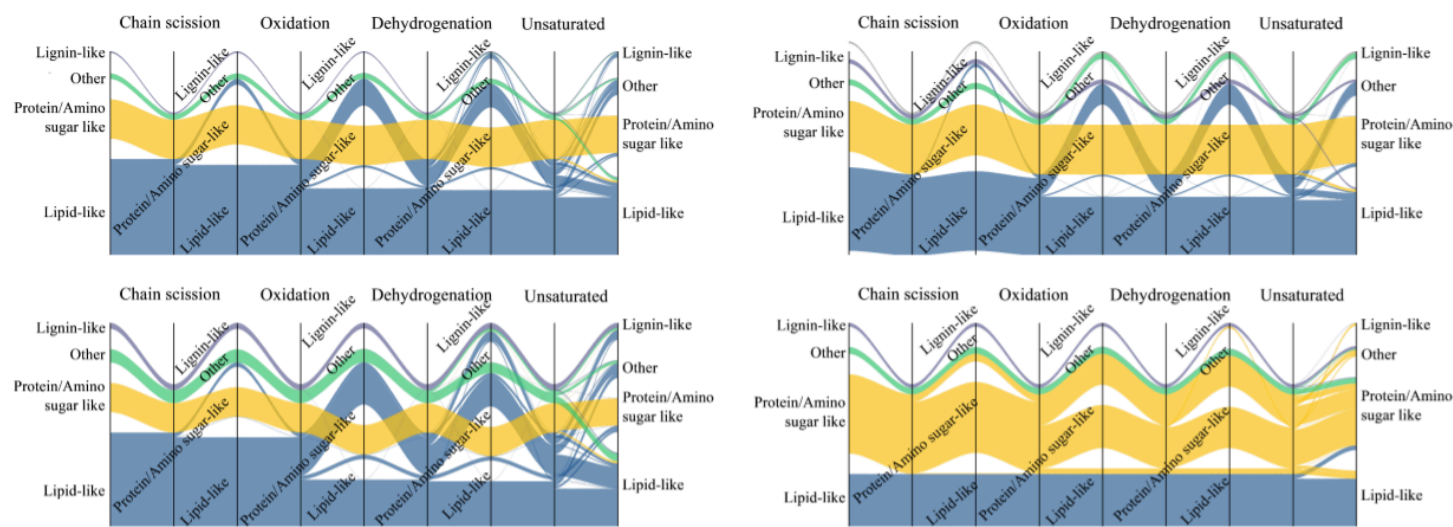


Figure 5

Formula-inferred transformation networks reveal class-conserved refining of microplastic-derived DOM.

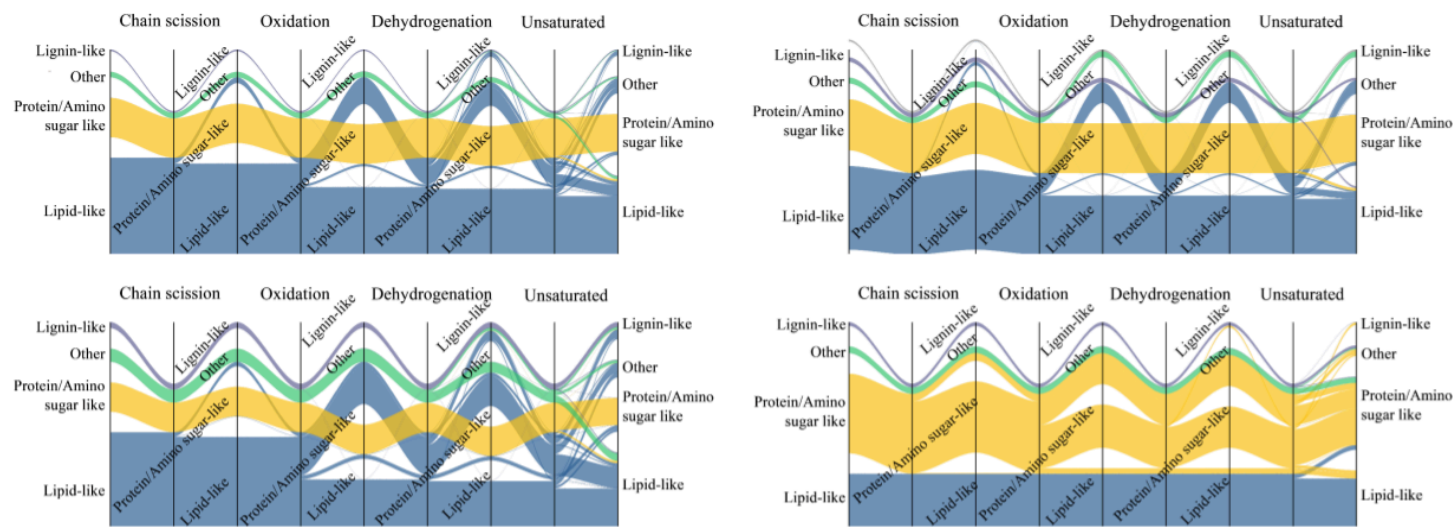


Figure 5

Formula-inferred transformation networks reveal class-conserved refining of microplastic-derived DOM.

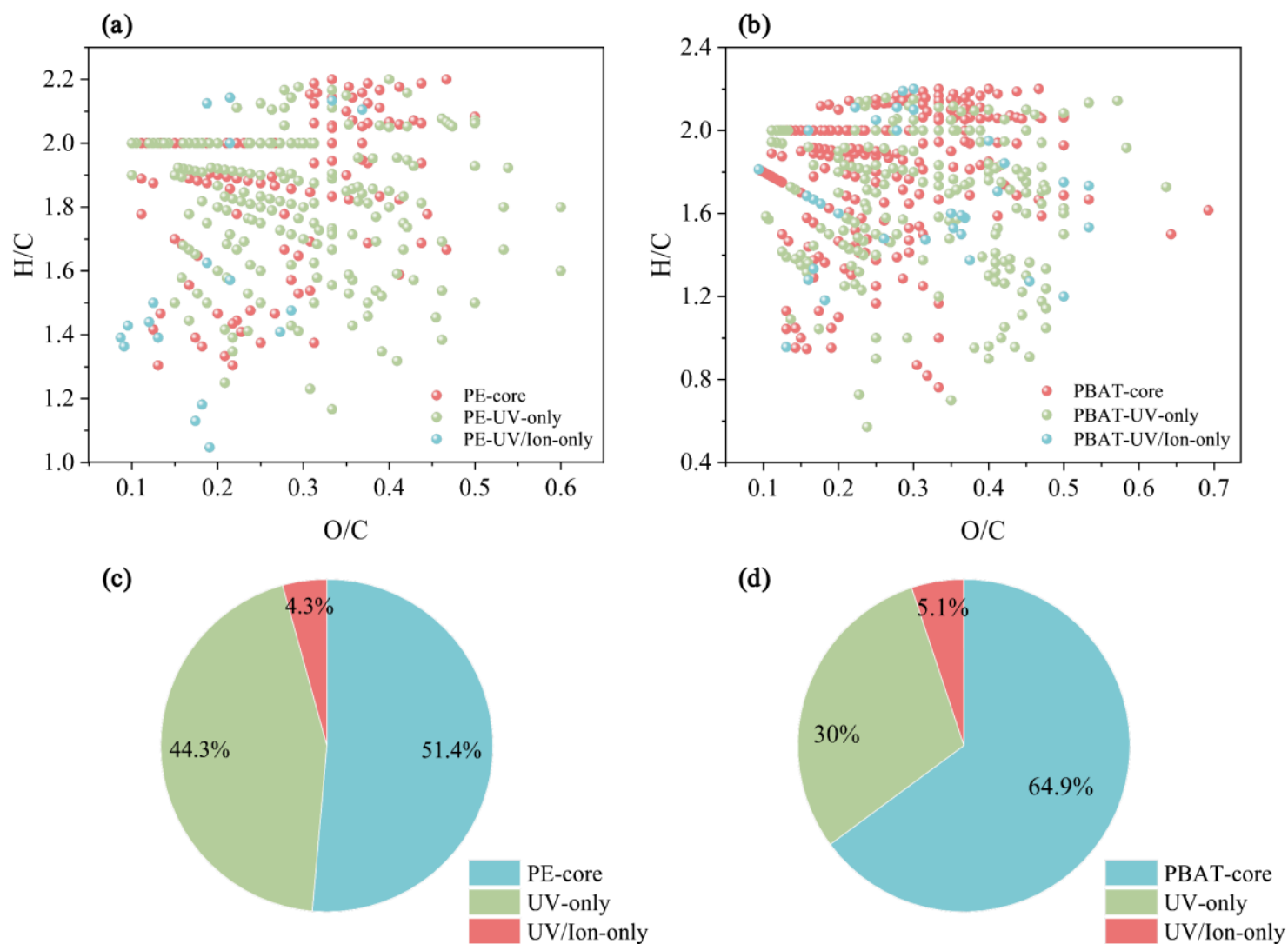


Figure 6

Pool-overlap analysis separates shared molecular cores from condition-specific formulae.

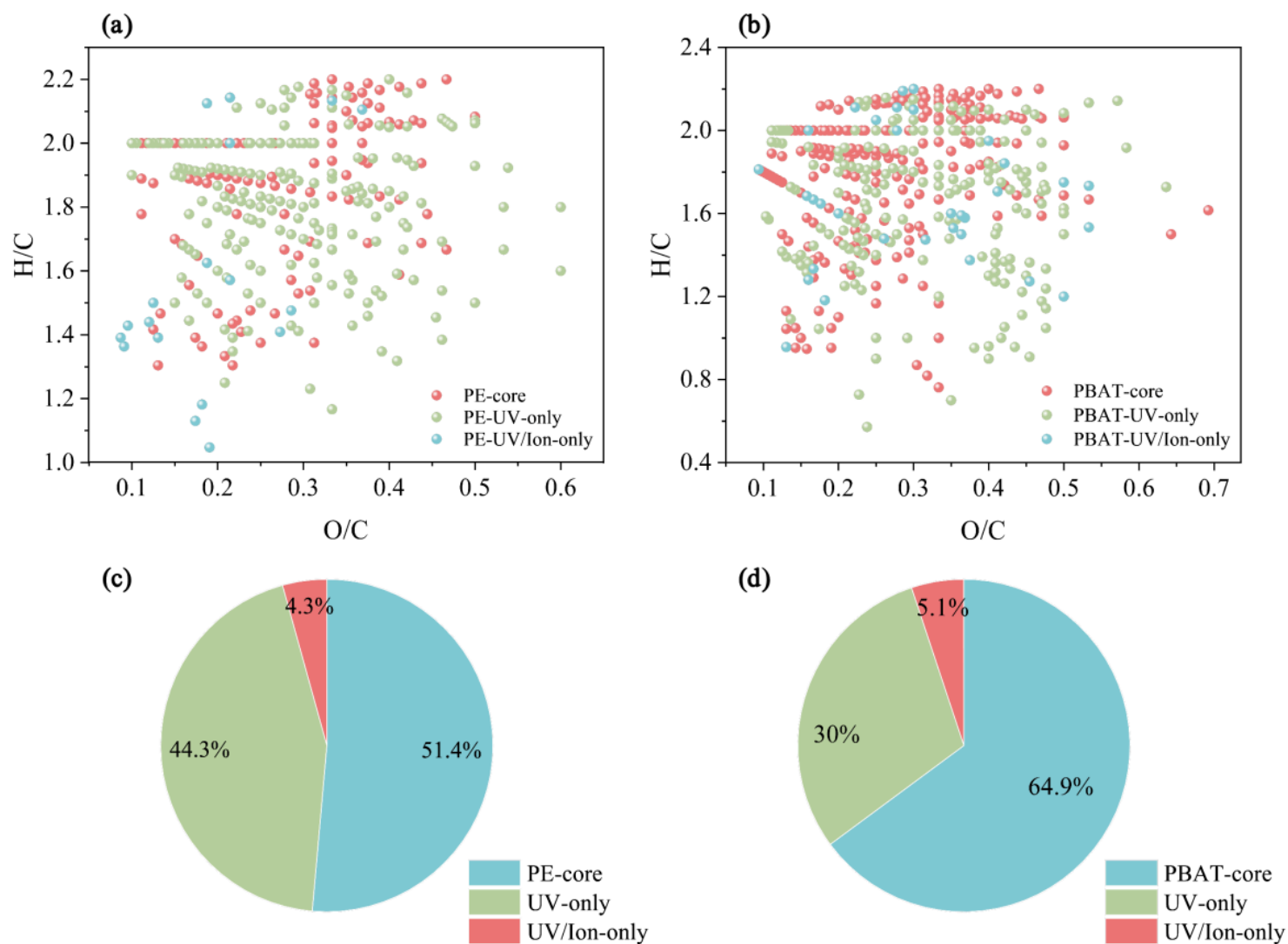


Figure 6

Pool-overlap analysis separates shared molecular cores from condition-specific formulae.

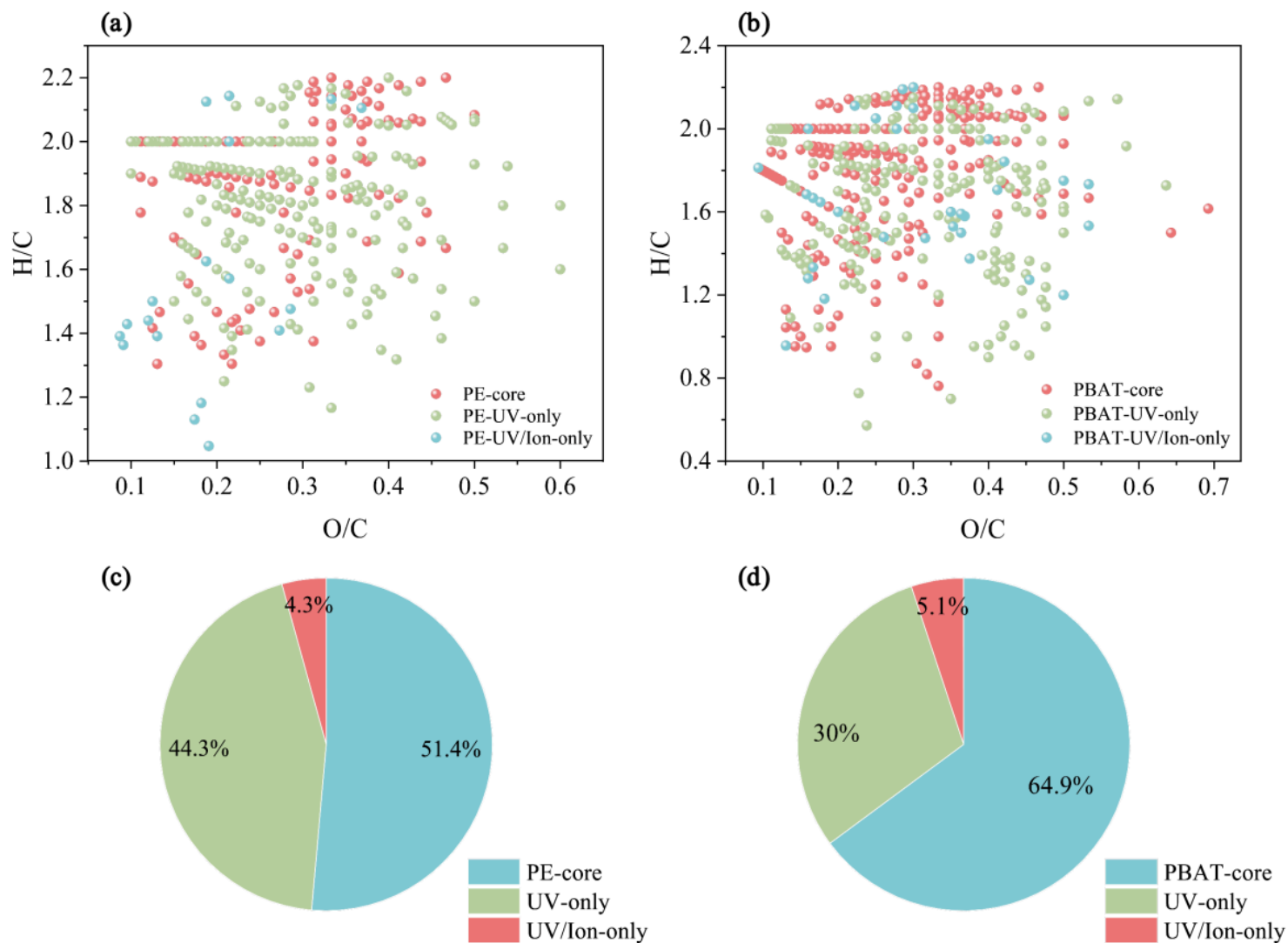


Figure 6

Pool-overlap analysis separates shared molecular cores from condition-specific formulae.

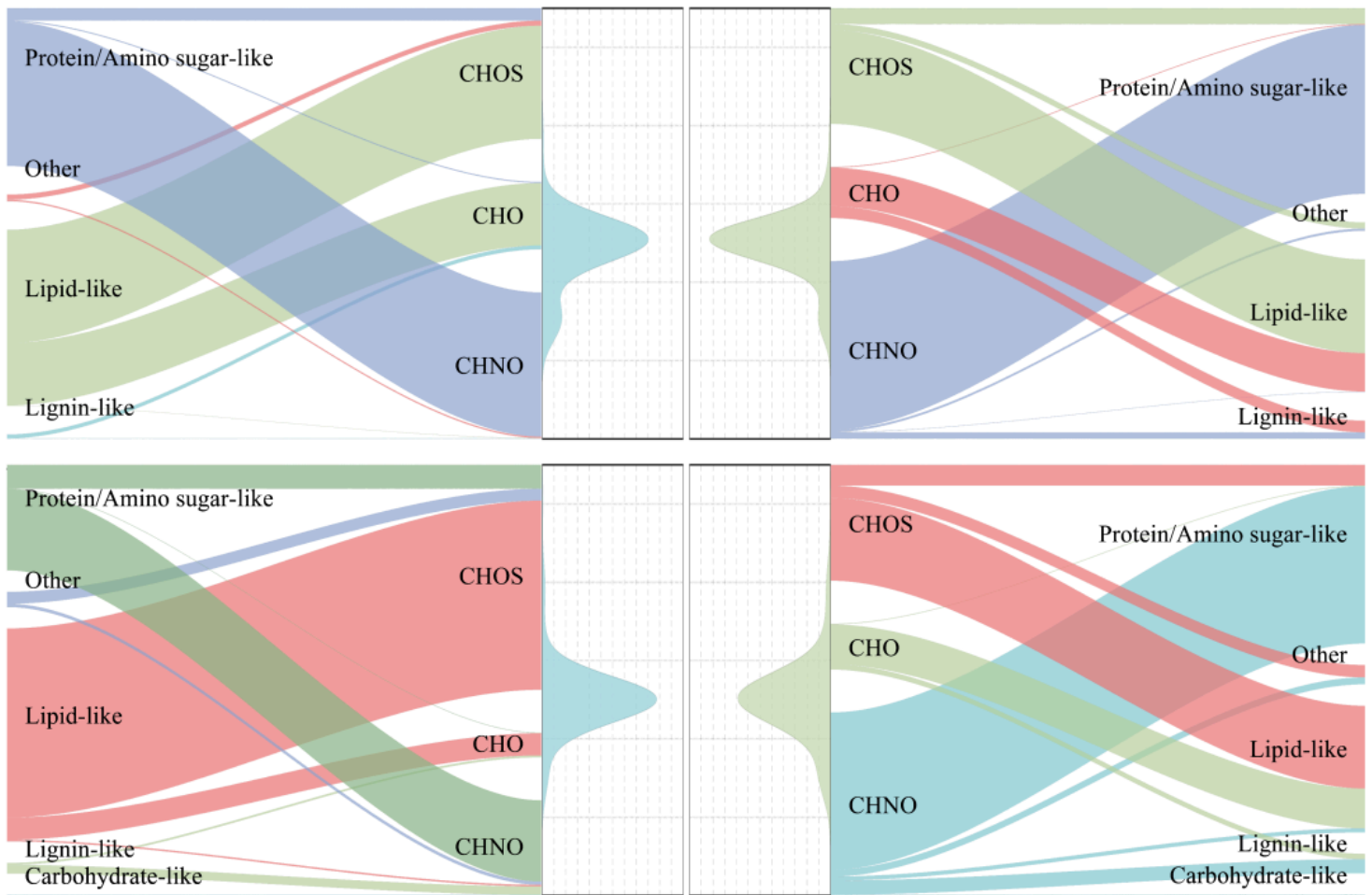


Figure 7

UV/ion forcing promotes functional-class and redox-state convergence of plastic-derived DOM.

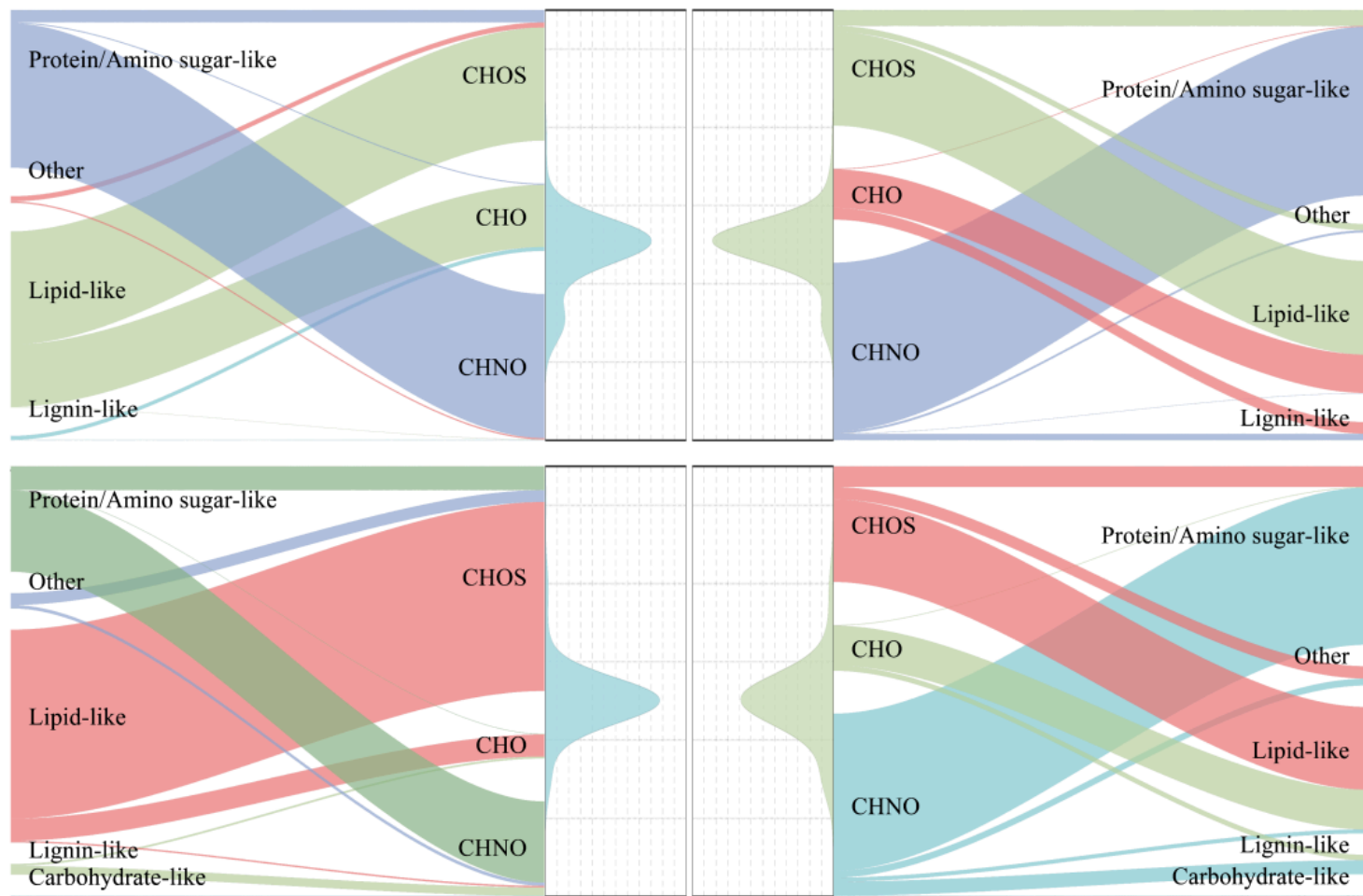


Figure 7

UV/ion forcing promotes functional-class and redox-state convergence of plastic-derived DOM.

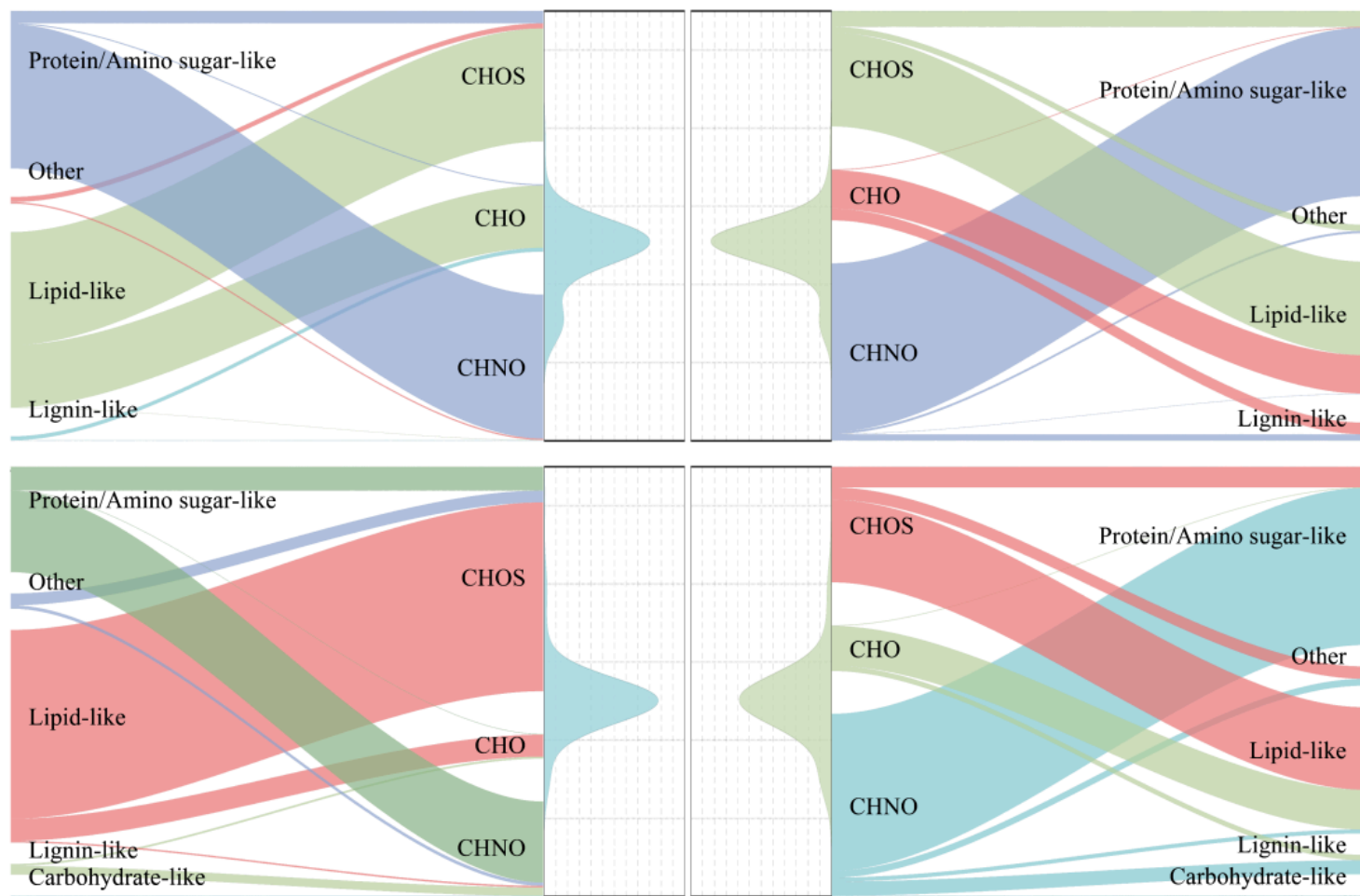


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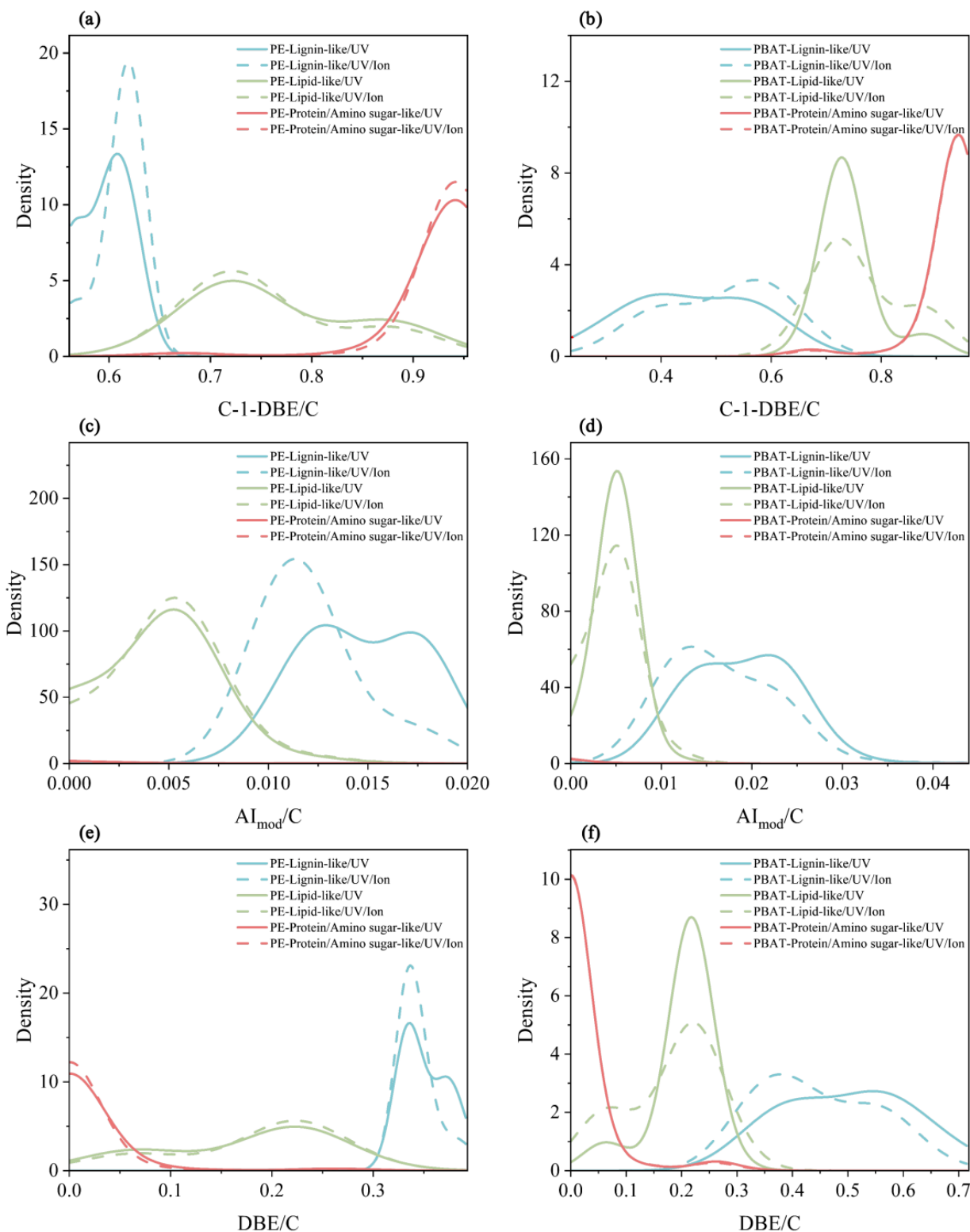


Figure 8

UV/Ion filtering redistributes aromaticity and unsaturation density across functional formula classes.

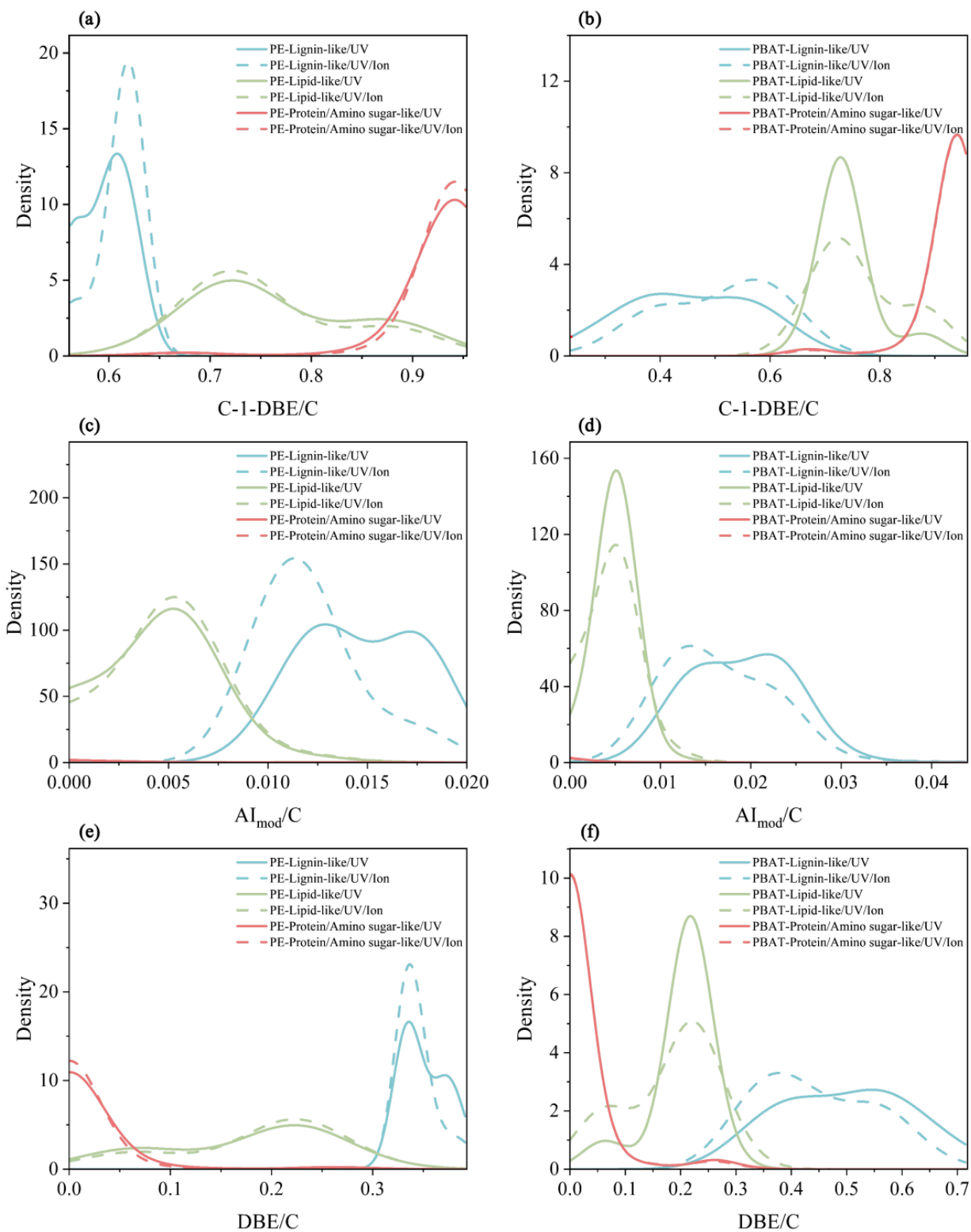


Figure 8

UV/Ion filtering redistributes aromaticity and unsaturation density across functional formula classes.

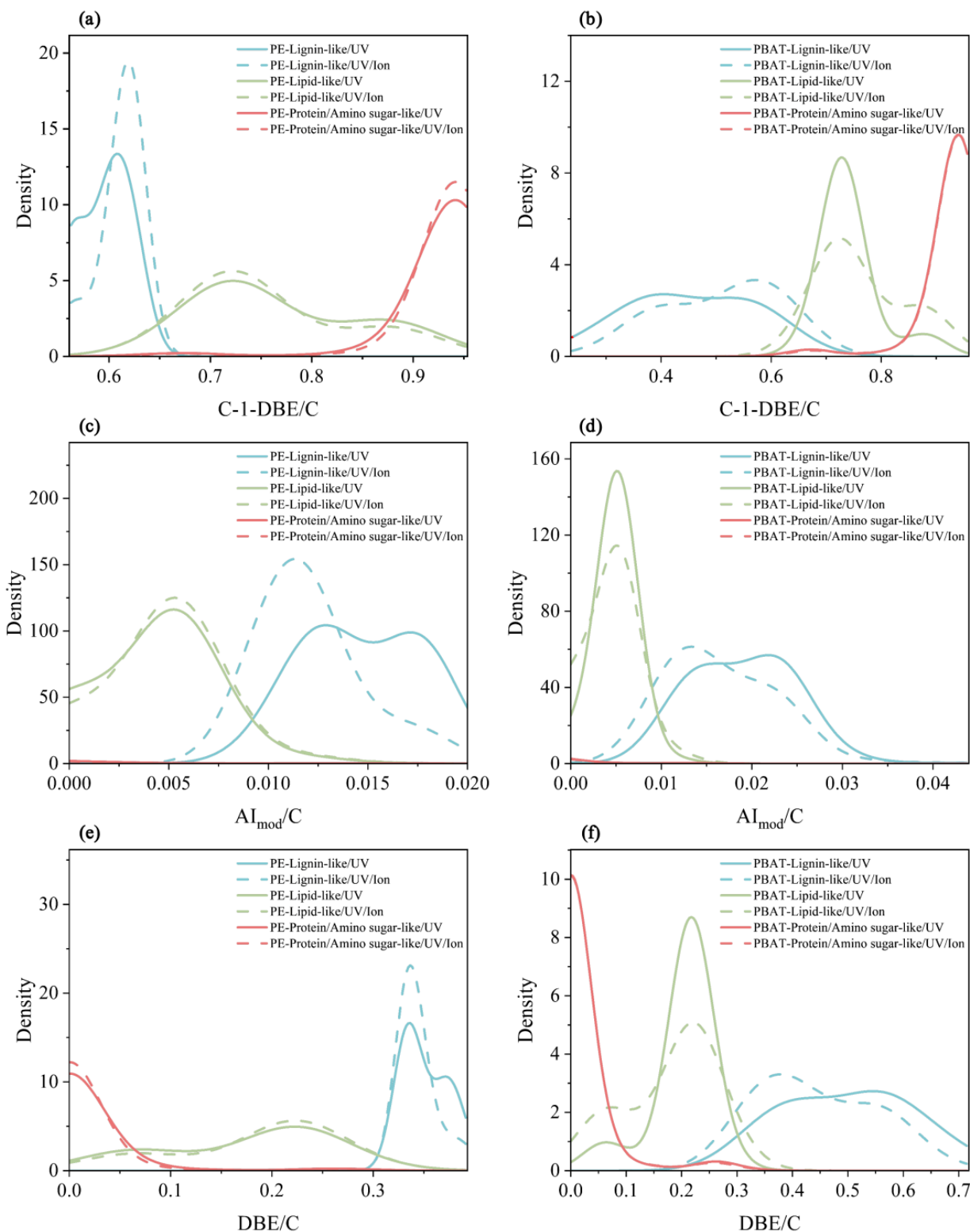


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UV/Ion filtering redistributes aromaticity and unsaturation density across functional formula classes.

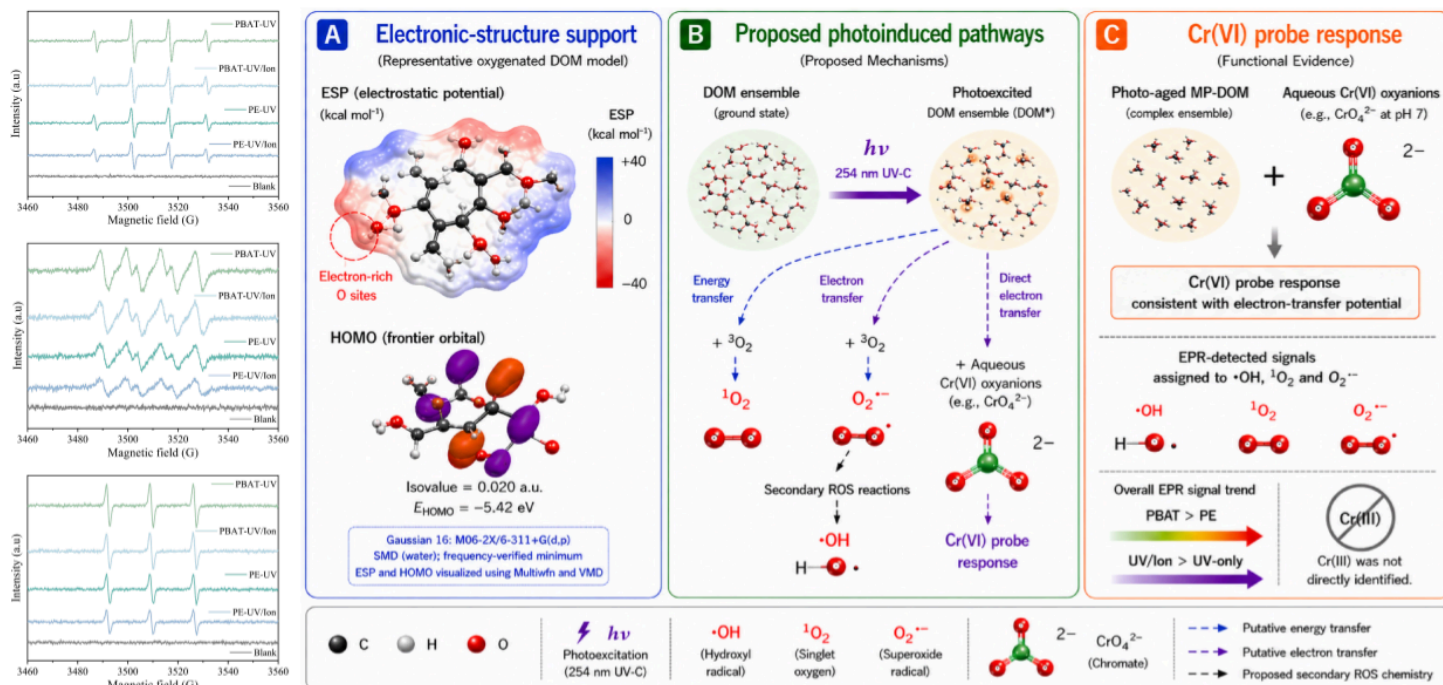


Figure 9

Proposed redox-mediation pathway of photoaged microplastic-derived DOM.

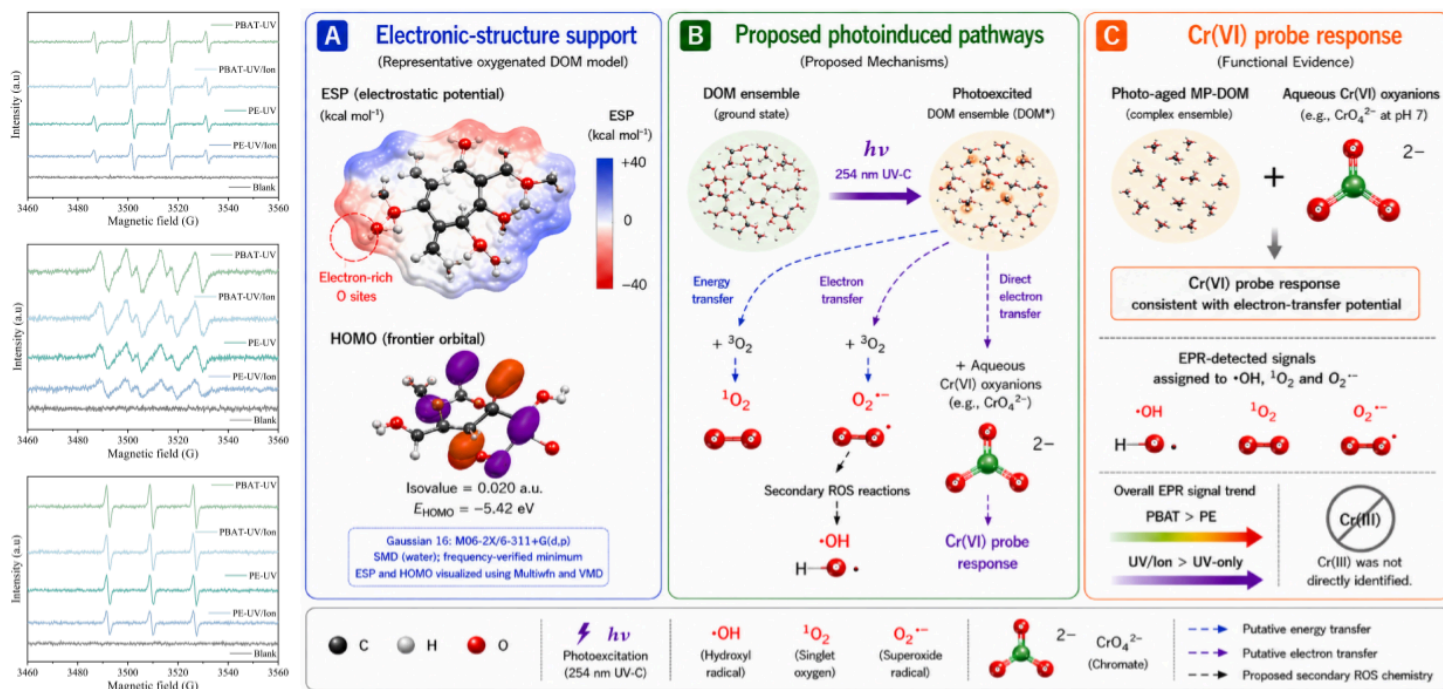


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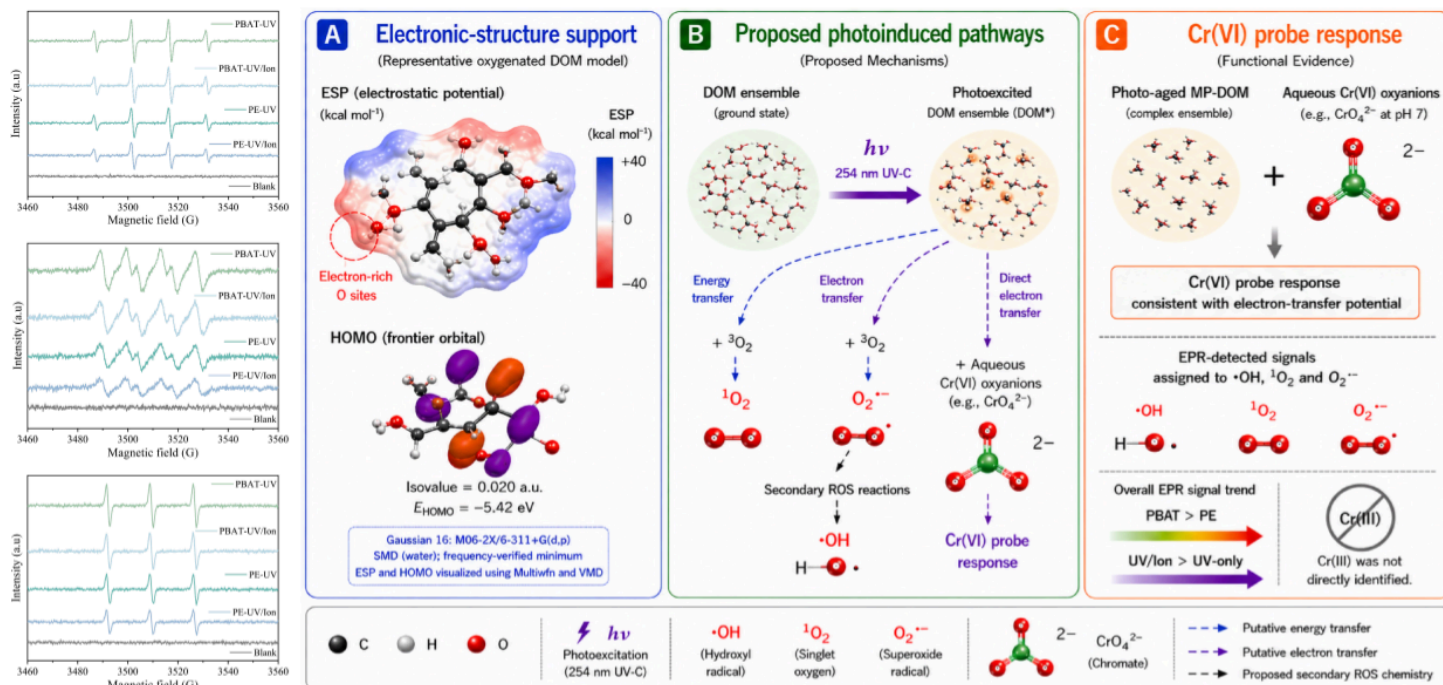


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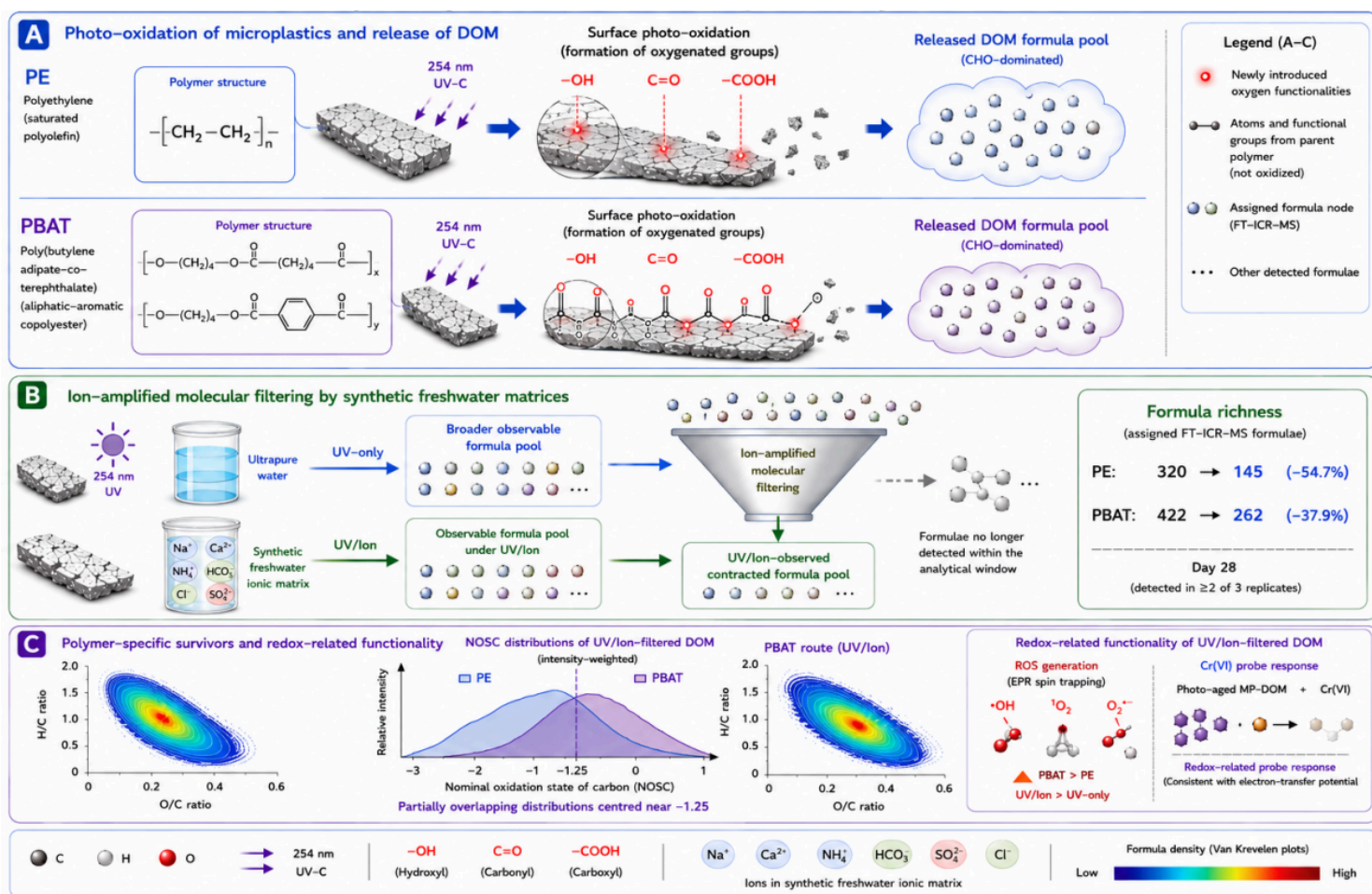


Figure 10

Conceptual model of ion-amplified photochemical filtering of microplastic-derived DOM.

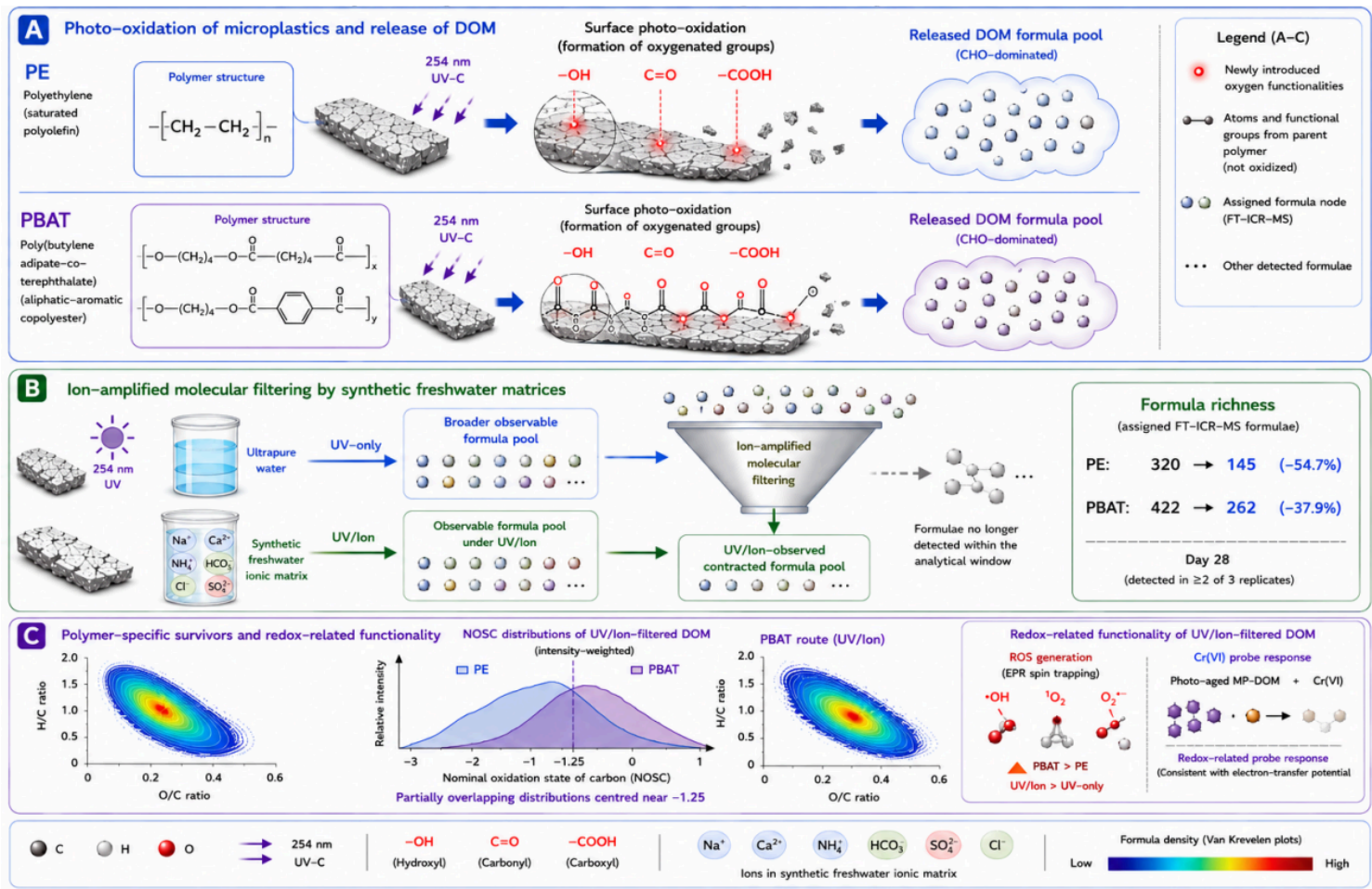


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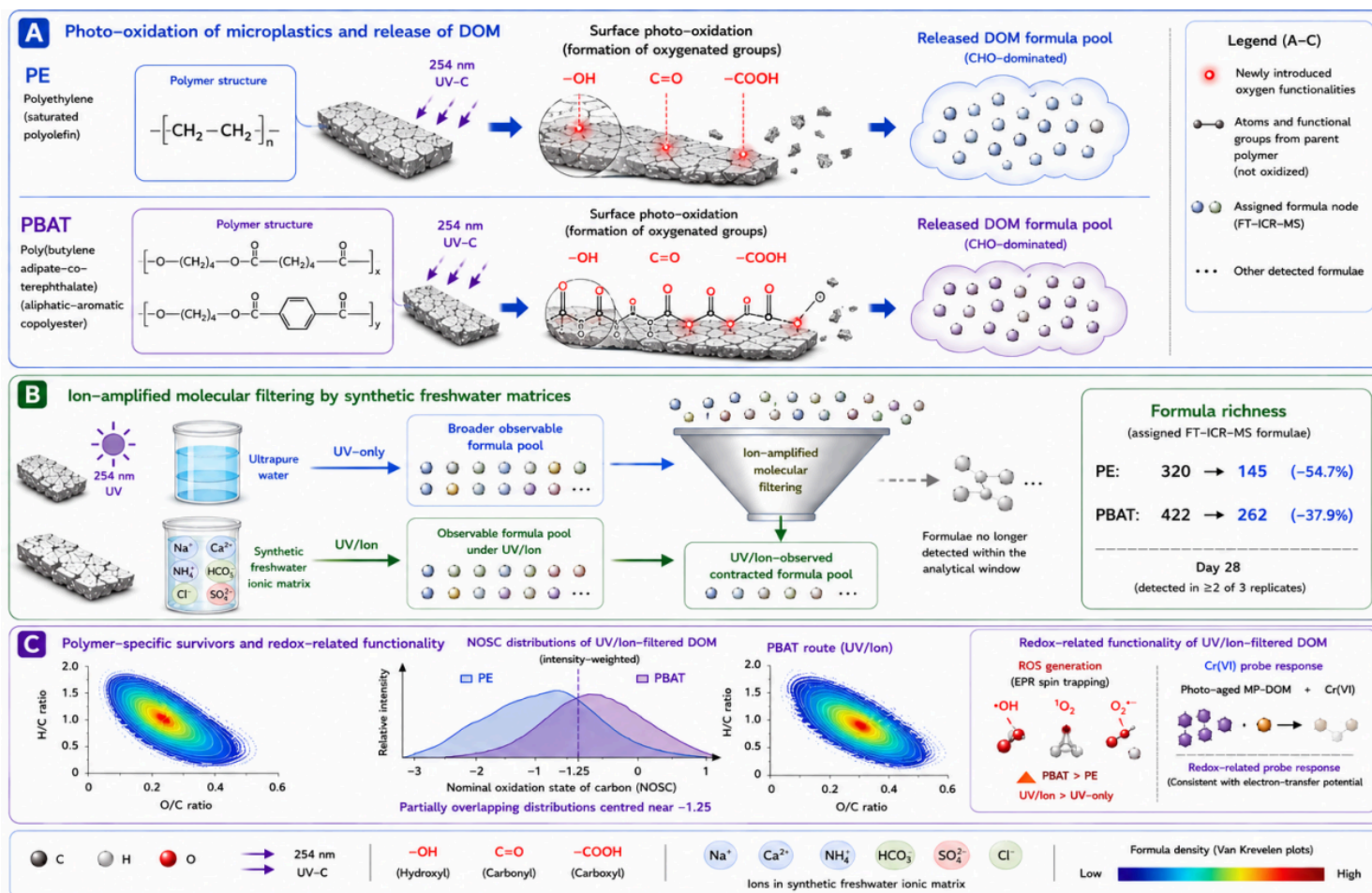


Figure 10

Conceptual model of ion-amplified photochemical filtering of microplastic-derived DOM.

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