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Revealing Oxygen Clusters in Polyethers

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Electronic Supplementary Information

Abstract The investigation of organic luminescent materials has spanned more than a century, and molecular design strategies based on π-electron conjugation remain dominant. Recently, however, the discovery of clusteroluminescence (CL) in non-conjugated, heteroatom-rich, non-aromatic systems has provided an entirely new perspective for understanding the emission mechanisms. Through-space conjugation (TSC) is believed to play a crucial role in the generation of excited states through the clustering of heteroatoms. In our previous work, poly(ethylene glycol) (PEG) was found to exhibit two types of emission behavior in the aggregated state: Type I emission around 400 nm, a short-wavelength, excitation-independent luminescence arising from the negative hyperconjugation effect of the polymer backbone itself, and Type II emission, a long-wavelength, excitation-dependent emission attributed to "oxygen clusters" formed by aggregated oxygen atoms. Nevertheless, direct experimental evidence confirming the decisive role of cluster structures in governing these luminescent behaviors is lacking. Herein, we selected poly(propylene glycol) (PPG), which possesses a similar molecular backbone but contains methyl side groups, and systematically compared the photophysical properties of PEG and PPG with different molecular weights to elucidate the influence of methyl group steric hindrance on oxygen cluster formation. Our results reveal that Type II emission completely disappears in PPG, directly verifying that oxygen cluster structures are indispensable for generating long-wavelength CL.

Keywords Clusteroluminescence; Through-space conjugation; Oxygen clusters; Negative hyperconjugation; Polyether

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INTRODUCTION

Organic luminescent materials are of immense importance in diverse fields, such as optoelectronics, sensing, and biological imaging.[1–4] Over more than a century of development, π-electron-based through-bond conjugation (TBC) has consistently been regarded as the fundamental principle for designing organic luminophores.[5,6] Nevertheless, in recent years, unconventional emissions from non-TBC systems, or even from systems completely lacking π electrons, have been increasingly reported by many research groups.[7–10] For instance, dendrimers based on poly(amino amine)s and poly(amino ester)s were found to exhibit blue photoluminescence (PL), and subsequent studies confirmed that the emission originated intrinsically from the polymers themselves, rather than from impurities.[11–13] In addition to synthetic aliphatic polymers, several natural macromolecules, including starch, sodium alginate, and bovine serum albumin, have also been reported to possess intrinsic PL.[14–17] The unconventional luminescence observed in natural systems is particularly intriguing and potentially valuable for practical applications. However, such phenomena did not initially attract widespread attention, largely because natural materials are more difficult to purify and structurally define than are synthetic systems. Over the past decade, an increasing number of non-TBC polymers and small molecules exhibiting PL have been discovered. Tang *et al.* subsequently coined the term "clusteroluminescence" (CL) based on their studies on poly[(maleic anhydride)-*alt*-(vinyl acetate)].[18,19] Investigations using model small

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molecules, particularly multiarylalkanes (MAAs), have led to the establishment of the through-space conjugation (TSC) mechanism.[20–24] However, when extending this mechanism from small molecules to polymeric systems, a fundamental challenge remains unresolved: what is the exact structure of the clusters responsible for CL, and how can the existence of such clusters be directly demonstrated?

To address this challenge, many research groups have devoted substantial efforts using a variety of strategies, among which the representative contributions of Tang and Yuan are particularly notable.[25–27] Over the past five years, Zhang *et al*. conducted a series of systematic studies on aliphatic polyester systems. Full-color PL was successfully achieved by manipulating both the primary and secondary structures of aliphatic polyesters, representing a major breakthrough in the development of CL materials.[28–31] Within these systems, it has been demonstrated that the regulation of hierarchical structures essentially corresponds to the modulation of ester cluster assemblies. More recently, our investigations of poly(ethylene glycol) (PEG), a purely aliphatic polymer completely devoid of π electrons, revealed that its aggregated-state luminescence can be classified into two distinct categories.[32] Type I is a short-wavelength excitation-independent emission with fine structures at 375, 395, and 417 nm. Further studies have demonstrated that this emission originates from the negative hyperconjugation effect within the polymer backbone. Type II is a long-wavelength excitation-dependent emission (EDE). Oxygen clusters serve as a structural prerequisite, whereas TSC constitutes the electronic consequence responsible for the observed Type II emission. Although our previous work mainly focused on elucidating the negative hyperconjugation effect in PEG, the relationship between EDE and cluster formation has not yet been systematically investigated. Therefore, a fundamental question remains unanswered: Are the oxygen clusters truly the origin of excitation-dependent emission?

To answer this question, in the present work, we designed a comparative study between PEG and its derivative poly(propylene glycol) (PPG) (Fig. 1 and Figs. S1–S10 in the electronic supplementary information, ESI). In contrast to PEG, the introduction of methyl groups into PPG is expected to intensify both intra- and inter-chain steric hindrance, thereby influencing the formation of oxygen clusters. High- and low-molecular-weight PEG samples and their corresponding PPG counterparts were systematically investigated through comprehensive photophysical analyses. This study is the first to unequivocally confirm the existence of excitation-independent short-wavelength emission induced by negative hyperconjugation. More importantly, this reveals that the long-wavelength excitation-dependent emission observed in high-molecular-weight PEG completely disappears in high-molecular-weight PPG, despite the latter possessing an even higher molecular weight. The disappearance of this type-II emission in PPG strongly suggests the absence of oxygen cluster formation within the polymer system. These findings provide more direct experimental evidence for the existence of cluster structures in clusteroluminescent materials and establish a new foundation for advancing the fundamental understanding and future development of the clusteroluminescence field.

EXPERIMENTAL

All experimental synthetic details and characterization data are available in ESI.

RESULTS AND DISCUSSION

A systematic comparison of the photophysical properties of low-molecular-weight PEG (PEG-L, M_w=26 kDa) and high-molecular-weight PEG (PEG-H, M_w=266 kDa) revealed similar ground-state absorption behaviors, with both exhibiting maximum absorption peaks at 275 nm (Fig. S11 in ESI); however, their excited-state emission characteristics diverged remarkably. In addition to preserving the 275 nm excitation band attributable to the n-σ^* transition, its excitation spectrum displayed a new emergent peak at 335 nm, signifying the formation of a new excited-state species (Fig. S12 in ESI). Upon excitation within the range of 270–350 nm, PEG-L presented a set of sharp emission peaks with well-resolved fine structures at 375, 395, and 417 nm that remained unaltered with varying excitation wavelengths, as illustrated in Fig. 2(a). This steady, short-wavelength luminescence was classified as Type I emission. Concentration-dependent experiments (Figs. S13–S15 in ESI) demonstrated that the emission intensity increased progressively with increasing concentration, manifesting a typical aggregation-induced emission (AIE) effect. The excitation-inde-

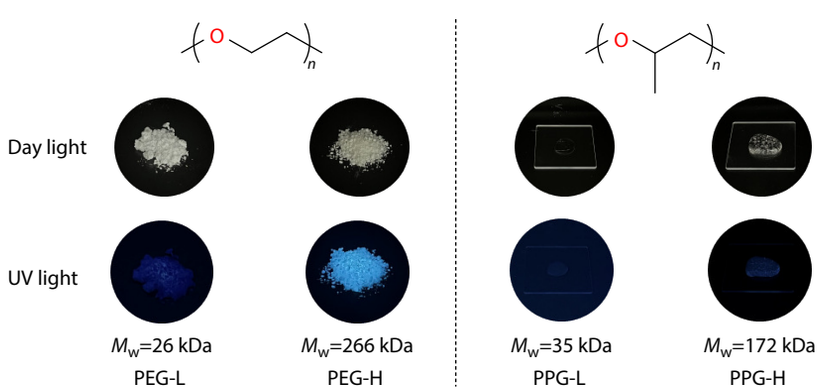


Fig. 1 Chemical structures of poly(ethylene glycol) (PEG) and poly(propylene glycol) (PPG), along with photographs of their bulk state under daylight and UV irradiation.

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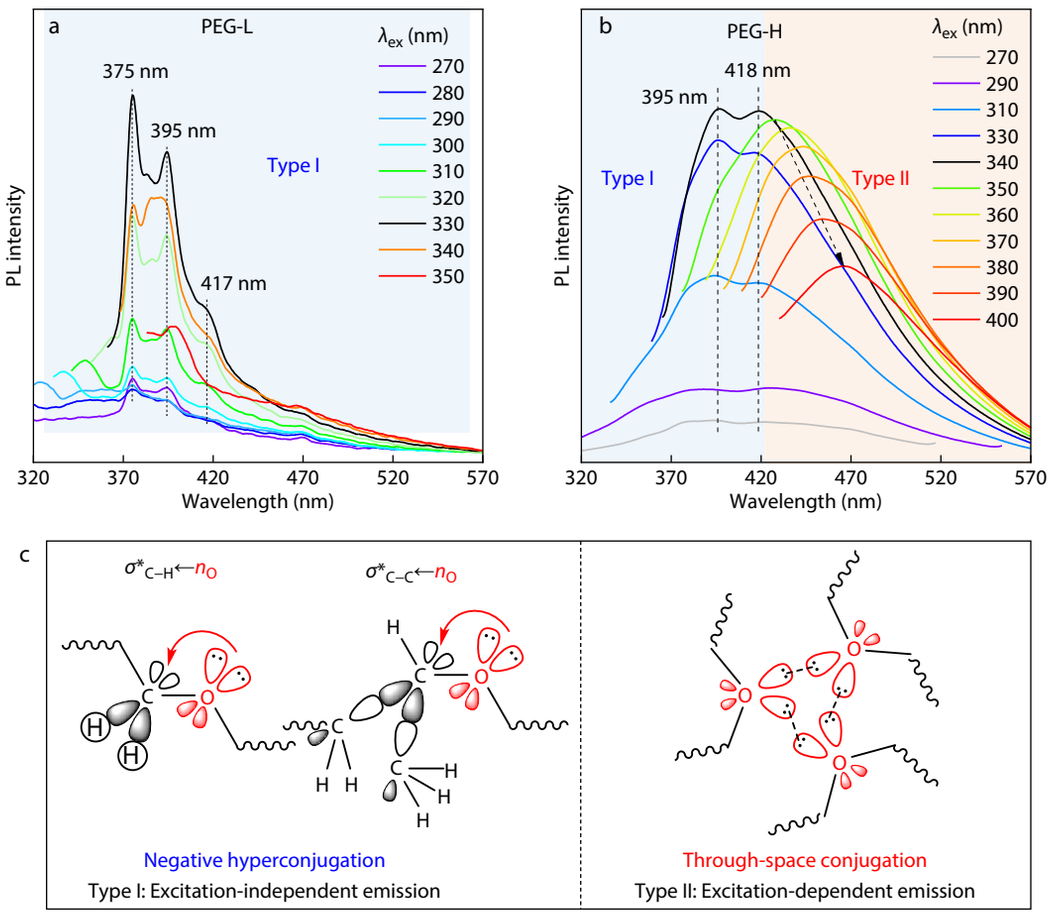


Fig. 2 Photoluminescence (PL) spectra of (a) PEG-L and (b) PEG-H in aqueous solution (concentration: 1 mol/L) under different excitation wavelengths (λ_{ex}). (c) The proposed mechanism of negative hyperconjugation and through-space conjugation corresponds to the Type I and Type II emission, respectively (Reproduced with permission from Ref. [32]; Copyright (2025), Springer Nature).

pendent nature and the structured spectral profile indicate that this emission originates from a distinct and stable luminescent species along the polymer chain, which we ascribed to the negative hyperconjugation between the oxygen lone-pair electrons and the σ^* orbitals of the adjacent C—H and C—C bonds (Fig. 2c).

When the molecular weight was increased to 266 kDa (PEG-H, Fig. 2b, Figs. S16–S18 in ESI), the emission behavior became more complex. Under short-wavelength excitation, Type I emission was still clearly observable, featuring dual emission peaks at 395 and 418 nm. The short-wavelength peak at 375 nm was also present but merged into a broad peak. This Type I emission shares the same negative hyperconjugation mechanism with that of PEG-L. More significantly, when the excitation wavelength was extended beyond 350 nm, a distinctly different, broad, excitation-dependent long-wavelength emission gradually emerged and underwent a continuous redshift. This was designated as Type II emission and was attributed to through-space conjugation within the oxygen clusters in the aggregated state. The coexistence of Type I and Type II emissions in high-molecular-weight PEG, along with their respective mechanistic assignments, accurately recapitulates the key experimental findings previously reported by our group.

Both intra- and inter-molecular interactions exerted a profound influence on the photophysical properties, prompting us to chemically modify the structure to perturb the formation of oxygen clusters and the corresponding CL. Generally, PEG exhibits a certain degree of crystallinity because of its relatively strong interchain interactions, which serve as driving forces for cluster formation. Notably, the introduction of a methyl group into the side chain of PEG weakens its interchain interaction, as demonstrated by its viscous oil-like state, even at high molecular weights. Because the methyl group is positioned close to the oxygen atoms in the main chain, it significantly increases the distance between the two oxygen atoms due to steric hindrance, ultimately disrupting the formation of oxygen clusters.

Accordingly, methyl side groups were introduced, and two PPG samples with distinct molecular weights, low-molecular-weight PPG-L (M_w=35 kDa) and high-molecular-weight PPG-H (M_w=172 kDa), were synthesized to compare their luminescent performance with that of PEG and evaluate whether the incorporated methyl side groups impact Type I and Type II emissions. As shown in Fig. 3(a), the UV-Vis absorption spectra of PPG-L in DMF showed pronounced concentration dependence, with an absorption peak centered around 270–280 nm, assigned to the n-σ^* transition of the oxygen

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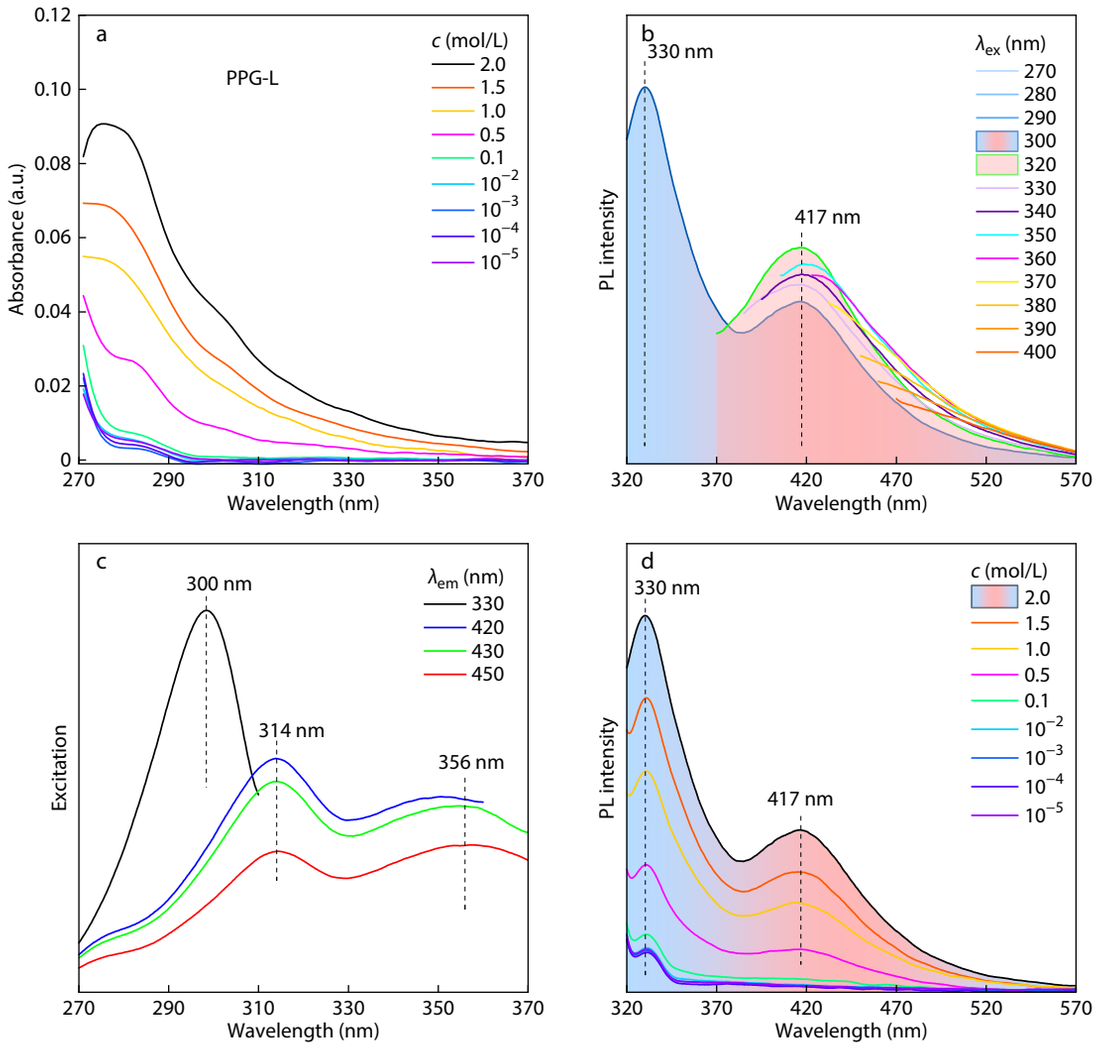


Fig. 3 (a) Absorption and (d) PL spectra of PPG-L in DMF with different concentrations; The excitation wavelength in panel d is 300 nm. (b) PL and (c) excitation spectra of PPG-L in DMF with a concentration of 1 mol/L.

atoms, which is almost the same as that of PEG. Over the excitation wavelength range of 270–400 nm, the emission spectra of PPG-L displayed two principal emission peaks at 330 and 417 nm (Fig. 3b and Figs. S19–S25 in ESI). The peak at 330 nm appeared relatively sharp, with an optimal excitation wavelength of 300 nm, whereas the peak at 417 nm was somewhat broader and reached its maximum intensity at an excitation wavelength of 320 nm. It is noteworthy that the two emission peaks exhibited no appreciable shift with varying excitation wavelengths, displaying no EDE effect, suggesting that the two peaks are derived from fixed emissive species within the polymer chain.

As shown in Fig. 3(c), the emission peak at 330 nm exhibits an excitation band at approximately 300 nm, which can be attributed to the n-σ^* transition of the oxygen atoms, in accordance with the absorption spectra. However, when monitoring the emission peaks at 420, 430, and 450 nm, identical excitation peaks at 314 and 356 nm were observed, further confirming the presence of fixed emissive species. Based on previous studies of PEG, this emission can be attributed to negative hyperconjugation. Concentration-dependent emission spectra (Fig. 3d) revealed that the emission intensity of PPG-L increased significantly with increasing concentration, exhibiting a typical AIE effect. The PL properties of PPG-L further support the proposed negative hyperconjugation mechanism responsible for the intrinsic and stable emission of polyethers at approximately 400 nm. Similar to PEG-L, the EDE effect associated with cluster formation is absent.

Because the oxygen-cluster-induced Type II emission was observed only in high-molecular-weight PEG-H but was absent in low-molecular-weight PEG-L, it was essential to determine whether such Type II emission also exists in high-molecular-weight PPG. Therefore, the photophysical behavior of the high-molecular-weight PPG-H was further investigated (Figs. S26–S33 in ESI). As shown in Fig. 4(a), the absorption spectra of PPG-H were analogous to those of PPG-L, exhibiting a dominant absorption peak at 278 nm, the intensity of which increased with concentration. Notably, in a concentrated DMF solution (c=1.0 mol/L), the excitation-dependent PL spectra displayed emission peaks at 330 and 417 nm, while the position of the 417 nm peak remained essentially unchanged upon varying the excitation wavelength (Fig. 4b).

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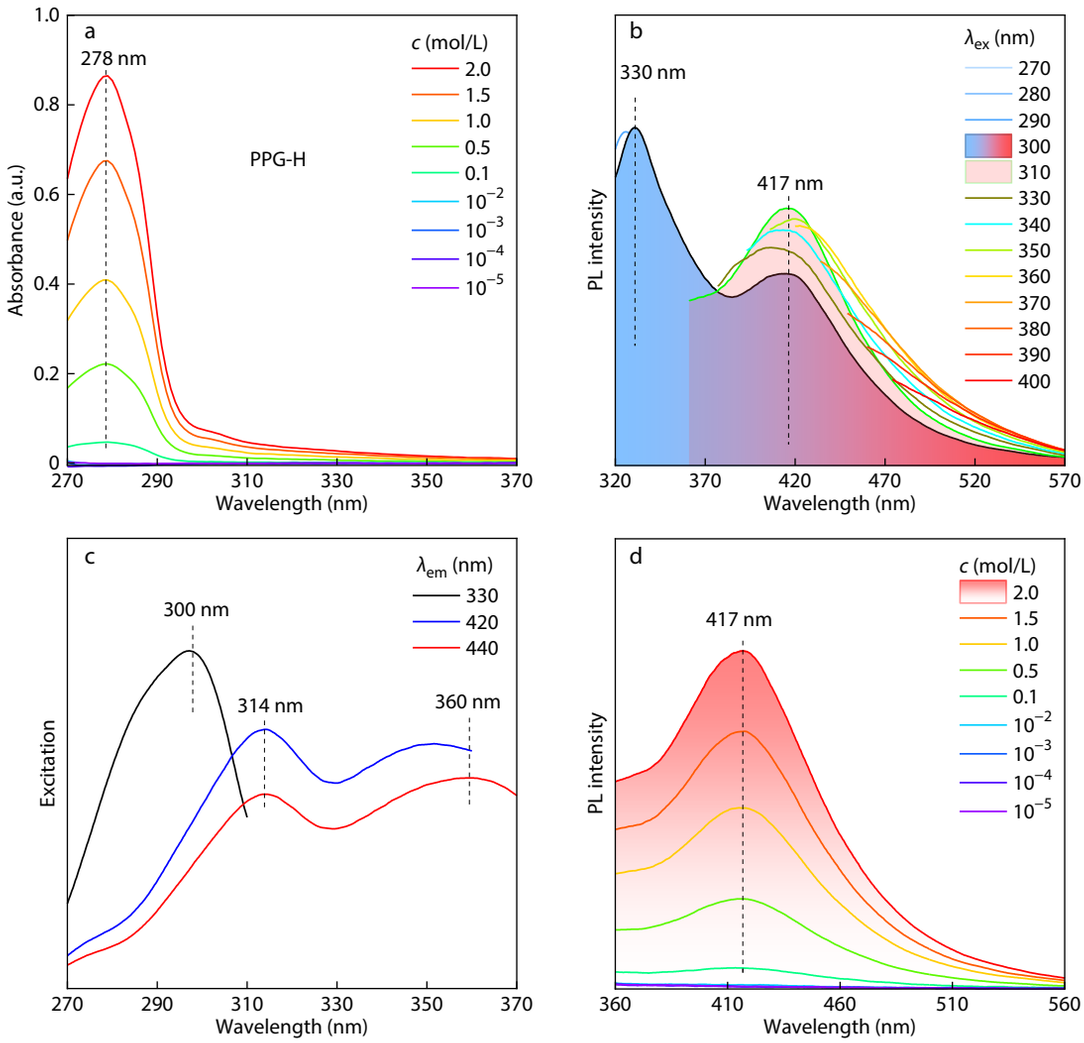


Fig. 4 (a) Absorption and (d) PL spectra of PPG-H in DMF with different concentrations. The excitation wavelength in panel d is 310 nm. (b) PL and (c) excitation spectra of PPG-H in DMF with a concentration of 1 mol/L.

The excitation spectra revealed that the optimal excitation peak for monitoring the 330 nm emission was located at 300 nm, whereas the excitation peaks corresponding to the 420 and 440 nm emissions appeared at 314 nm and 360 nm, respectively, which were almost identical to those of PPG-L (Fig. 4c). Concentration-dependent measurements (Fig. 4d) further demonstrated that the emission intensity of PPG-H increased dramatically with increasing concentration, whereas the emission wavelength remained fixed at 417 nm.

The above photophysical properties of PPG-H showed clear differences from those of PEG-H, as no long-wavelength EDE effects were detected. This result suggests that Type II emission governed by oxygen cluster-induced through-space conjugation was completely absent in PPG-H.

The concentration-dependent absorbance at 300 nm and the PL intensity at 417 nm were plotted to quantitatively compare the influence of molecular weight on the photophysical properties of PPG. As shown in Fig. 5(a), the absorbance of both PPG-H and PPG-L increased with increasing concentration, and at the same concentration, PPG-H consistently exhibited a higher absorbance than PPG-L. Regarding the emission behavior (Fig. 5b), the relative emission intensity ($I_{417nm}/I_{0\text{-}417nm}$) of PPG-H increased more steeply with increasing concentration than that of PPG-L, and the difference became particularly pronounced when the concentration exceeded 0.1 mol/L. According to our previous studies on CL and the relevant concept of critical cluster concentration (CCC),[33] the CCC of PPG-H was obviously lower than that of PPG-L, suggesting that longer polymer chains enable PPG-H to aggregate more readily than PPG-L. These findings indicate that high-molecular-weight PPG can more effectively form emissive aggregated structures; however, this enhanced clustering does not lead to the emergence of Type II emission characteristic of clusteroluminescence.

As mentioned above, the 417 nm emission in PPG is assigned to negative hyperconjugation, which is a local electronic effect along the polymer backbone. The concentration-induced PL enhancement reflects the role of aggregation in restricting the molecular motion and suppressing the nonradiative decay. Specifically, as PPG chains aggregate at higher concentrations, the increased local viscosity and reduced molecular mobility favor radiative decay from the negative

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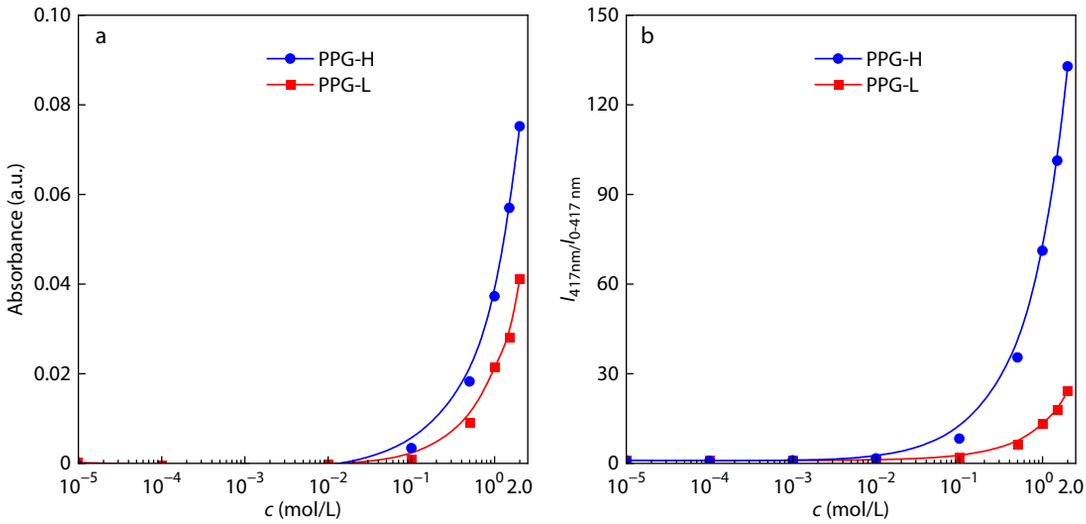


Fig. 5 (a) Absorbance change at 300 nm and (b) emission intensity (I) change at 417 nm versus the concentration of PPG-L and PPG-H. λ_{ex}=300 and 310 nm for PPG-L and PPG-H, respectively, $I_{0\text{-}417\ nm}$: emission intensity at c=1×10^{-5} mol/L

hyperconjugation-excited state, thereby enhancing the emission intensity. Importantly, unlike PEG, the CCC behavior observed in PPG is not associated with the formation of oxygen clusters that enable through-space conjugation. Instead, it reflects the AIE effect, where cluster formation primarily rigidifies the polymer backbone and restricts molecular motion without introducing new electronic interactions. This distinction is crucial: in PEG, oxygen clusters not only restrict molecular motion, but also generate new through-space conjugation pathways that give rise to Type II emission with the EDE effect; in PPG, methyl side groups prevent effective oxygen cluster formation, so aggregation only enhances the pre-existing Type I emission *via* a classic restriction of intramolecular motion (RIM) mechanism.

We can conclude that two factors govern oxygen cluster formation in polyethers: chain length (molecular weight) and backbone flexibility/steric environment. Chain length influences the probability of intrachain and interchain contacts; longer chains have more conformational degrees of freedom and a higher density of oxygen atoms, which increases the likelihood of forming multiple conformationally diverse oxygen clusters. This is evident from the observation that PEG-H exhibits a Type II EDE, whereas PEG-L does not. However, the chain length alone is insufficient, and the steric environment around the oxygen atoms is equally critical. In PPG-H, the methyl side groups impose significant steric hindrance that prevents the oxygen atoms from approaching each other closely enough to form effective through-space conjugation pathways. Thus, while longer chains promote cluster formation, the presence of methyl groups effectively isolates individual oxygen atoms, rendering cluster-mediated electronic interactions impossible, regardless of the chain length. This distinction is key to understanding why Type II emission is present in PEG-H but completely absent in PPG-H, despite the latter having a higher molecular weight.

To gain a deeper insight into the physical mechanisms underlying these phenomena, theoretical calculations and molecular structure analyses were performed. As illustrated in Fig. 6(a), PEG and PPG exhibit markedly different molecular conformations. The PEG backbone, which lacks side groups, allows the oxygen atoms to approach each other closely, thereby facilitating through-space conjugation. In contrast, the introduction of methyl side groups in PPG effectively separates adjacent oxygen atoms and favors a more extended polymer chain conformation. This structural difference directly determines their ability to form oxygen clusters; PEG readily forms oxygen clusters, whereas PPG does not.

As shown in Fig. 6(b), when oxygen atoms aggregate into clusters, long-wavelength clusteroluminescence accompanied by an EDE effect can arise through through-space conjugation. Conversely, when oxygen atoms are isolated by methyl side groups, through-space conjugation is disrupted, leaving only localized n-σ^* negative hyperconjugation associated with individual oxygen atoms, which gives rise to excitation-independent short-wavelength emission. The experimental results obtained for PPG are in excellent agreement with this "isolated oxygen atom" model. Specifically, its short-wavelength emission at 417 nm originates from negative hyperconjugation, while the complete absence of long-wavelength emission directly confirms that effective oxygen clusters cannot or can hardly be formed within the PPG chains. These findings provide direct and compelling experimental evidence that clusteroluminescence originates from through-space conjugation within oxygen clusters while simultaneously demonstrating the feasibility of regulating clusteroluminescence behavior through side-group engineering of the polymer backbone.

CONCLUSIONS

Through a systematic comparison of the photophysical properties of PEG and PPG systems, which possess nearly identical structures, except for the additional methyl group in PPG, negative hyperconjugation was further confirmed as the origin of the short-wavelength emission with well-defined fine structures (Type I emission). More importantly, Type II emission was absent in both PPG-L and PPG-H, suggesting that the polymerization-induced clusteroluminescence mechanism does not occur

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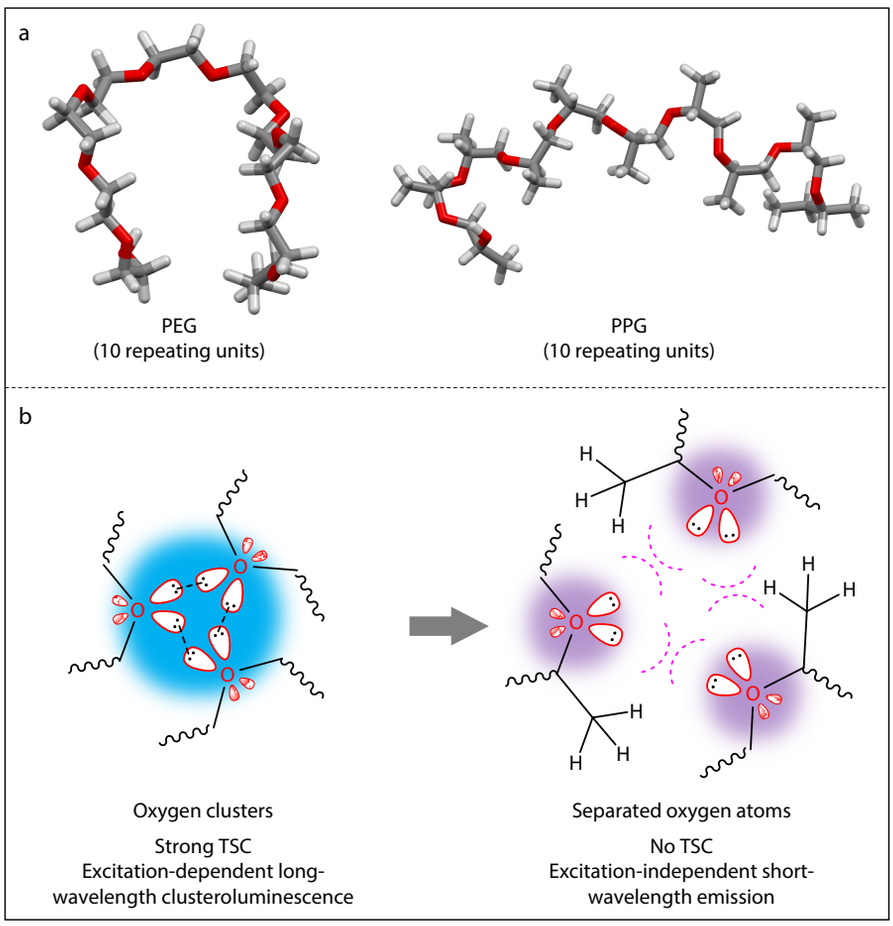


Fig. 6 (a) Simulated conformation of a single molecular chain of PEG and PPG with 10 repeating units; (b) Schematic illustration of the evolution from oxygen cluster in PEG to separated oxygen atoms in PPG.

in PPG systems. We revealed that because of the steric hindrance effect of the methyl side groups, adjacent oxygen atoms along the PPG chains were effectively isolated, thereby preventing the formation of oxygen clusters and leading to the complete disappearance of Type II emission. This result provides direct experimental evidence that long-wavelength clusteroluminescence accompanied by the EDE effect originates from through-space conjugation within the oxygen clusters. Furthermore, it demonstrates the feasibility of precisely regulating clusteroluminescence behavior through side-group engineering of the polymer backbone.

Conflict of Interests

Ben Zhong Tang is an editorial board member for *Chinese Journal of Polymer Science* and was not involved in the editorial review or the decision to publish this article. All authors declare that there are no competing interests.

Electronic Supplementary Information

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Data Availability Statement

The related data of this paper can be obtained from the author for reasonable reasons. The authors' contact information: Haoke Zhang (zhanghaoke@zju.edu.cn).

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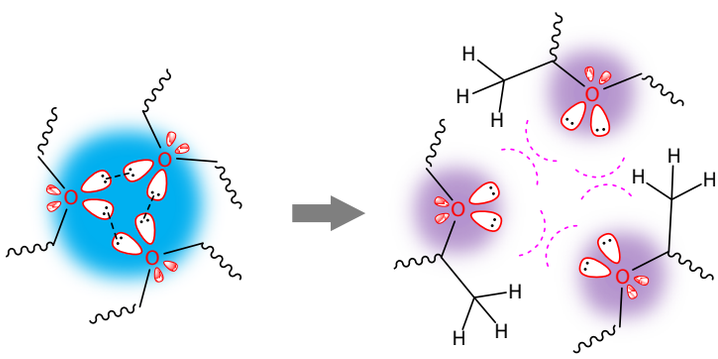
Graphical Abstract

Revealing Oxygen Clusters in Polyethers

Kailuo Chen, Ziyi Yang, Chengjian Zhang, Jianyu Zhang, Yuping Wang, Jing Zhi Sun, Haoke Zhang, Xing Hong Zhang, and Ben Zhong Tang

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Direct experimental evidence that through-space conjugation within oxygen clusters governs the excitation-dependent emission of polyether clusteroluminogensis presented herein.



Oxygen clusters

Strong TSC

Excitation-dependent long-wavelength clusteroluminescence

Separated oxygen atoms

No TSC

Excitation-independent short-wavelength emission

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