Hydrogen Bonding-Induced Oxygen Clusters and Long-Lived Room Temperature Phosphorescence from Amorphous Polyolols

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Abstract

The study of non-conjugated luminescent polymers (NCLPs) with fluorescence and long-lived room-temperature phosphorescence is of great significance for revealing the essence of NCLPs luminescence, which has gradually attracted the attention of researchers in recent years. Herein, polymethylol (PMO) and poly(3-butene-1,2-diol) (PBD) with polyhydroxyl structures were prepared and their luminescence behaviors were investigated to further reveal the clusteroluminescence (CL) mechanism. Compared with the weak or even non-luminescent behavior of polyvinyl alcohol, PMO and PBD exhibit cyan-blue fluorescence with quantum yields of ca. 12% and green room-temperature phosphorescence with lifetimes of ca. 89 ms in the solid state. Both fluorescence and phosphorescence exhibit typical excitation-dependent CL behavior. Experimental and theoretical analyses show that the strong hydrogen-bonding interaction of PMO and PBD greatly promotes the formation of oxygen clusters and the through-space n-n interaction of oxygen atoms, enabling fluorescence and phosphorescence emission. The results of this work have important implications for understanding the clusteroluminescence mechanism of NCLPs and provide a new polymer design strategy for the rational design of novel NCLPs materials.

Introduction

Light is an important factor for human survival, health, and development, while fluorescence and phosphorescence are two types of light that humans simulate in nature and play a vital role in optoelectronic devices,[1] chemo-/bioprobes[2], biological imaging,[3] and other fields[4]. Conventional wisdom holds that chromophores with well-defined large conjugated groups are required to achieve fluorescence or/and phosphorescence emission[5]. However, in recent years, numerous studies have found that many natural and synthetic polymers or small molecules, in the absence of well-defined chromophores or conjugated structures, also exhibit fluorescence or/and even room temperature phosphorescence (RTP), such as polyether[6], polyester[7], natural products[8], poly(maleic anhydride) derivatives[9], tertiary amine derivatives[10],
poly(hydroxyurethane)\cite{11}, and polysiloxane\cite{12}. The structures of these molecules usually contain heteroatom groups (such as N, O, S, etc.), and their luminescence exhibits concentration-dependent, solid-state fluorescence, and excitation-dependent emission, i.e., typical clusterization-triggered emission (CTE) or clusteroluminescence (CL) properties\cite{13}. The classical through-bond conjugation theory is difficult to explain such non-conjugated luminescence molecules. In this case, CTE or CL has been widely recognized and concerned by researchers since it was proposed\cite{9a, 14}. However, owing to the inclusion of both n and π electrons in the molecular structure, the intrinsic CL mechanism remains obscure, although it has been tentatively uncovered in some previous works\cite{6, 7b, 15}. Therefore, it is urgent to construct a class of typical luminescent model molecules with simple and well-defined structures to further clarify the CL mechanism.

Phosphorescence is another aspect and channel to reveal the CL mechanism. But for spin-forbidden phosphorescence, the vibration and rotation of molecules and the effects of external conditions such as oxygen and moisture greatly limit the generation of phosphorescence, especially for RTP. To achieve phosphorescence emission, facilitating the singlet-to-triplet intersystem crossing (ISC) to populate the triplet and stabilizing the triplet excitons to inhibit the nonradiative transition pathways are key principles. The phenomenon of RTP has long been synonymous with metallic and inorganic complexes\cite{16}. Nonetheless, over the past few years, purely organic luminophores have gradually been endowed with long-lived RTP through precise molecular design. The main strategies to achieve its RTP are the introduction of heavy atoms (e.g., halogens)\cite{17}, crystallization\cite{18}, and host-guest interactions\cite{19}. For CL, crystallization is an effective and commonly used approach to achieve RTP emission, which can induce intramolecular motion restriction to generate rigid molecular conformations to suppress nonradiative decay\cite{6, 15a, 20}. However, the crystallinity of polymers tends to vary greatly depending on post-processing methods, which affects the emission intensity and lifetime of their RTPs and restricts their specific practical applications. Instead, hydrogen bonding (H-bonding) is a crystallization-like strategy that can be readily constructed in amorphous polymers to achieve conformational rigidification, and many RTP systems also select polymers with multiple hydrogen bonds (e.g., polyvinyl alcohol (PVA)) as a matrix\cite{21}. But developing amorphous RTP NCLPs and revealing their luminescence mechanism remains a challenge.

In this work, PMO and PBD with one hydroxyl group on each carbon atom in the backbone and side chain were designed and synthesized, and their luminescence properties were studied in detail to further understand the CL mechanism. The extremely strong H-bonding of PMO and PBD induces the generation of oxygen clusters and through-space n-n interactions of oxygen atoms, which is the source of the strong fluorescence and long-lived RTP. Theoretical calculation analysis shows that the distance between the large number of oxygen atoms is between 2.58–2.83 Å, which is less than twice the van der Waals radius of oxygen atom (r_H: 1.52 Å; r_O: 1.40 Å). The existence of oxygen clusters and through-space n-n interactions are further confirmed. The above results also fully demonstrate that even without crystallization and π electrons, CL can be realized through the action of H-bonding. And if the H-bonding is strong enough, nonradiative decays can also be suppressed to produce RTP.

**Results and Discussion**

Polyvinyl alcohol (PVA), a well-known polymer with a polyhydroxyl structure, possesses one dissociative -OH group on every two carbon atoms in the backbone. In contrast to PVA, PMO and
PBD have one -OH group on each carbon atom in the backbone and side chain (Figure 1). It is of considerable interest in view of strong H-bonding in the study of photophysical properties. To synthesize PMO and PBD, poly(vinylene carbonate) (PVC) and poly(vinylethylene carbonate) (PVEC) were firstly prepared by the radical polymerization of vinylene carbonate and vinylethylene carbonate using AIBN as a radical initiator, respectively (Schemes S1-S2)[22]. The proton nuclear magnetic spectroscopy (1H NMR) and gel permeation chromatography (GPC) data indicated that PVC and PVEC were successfully synthesized, and their number-averaged molecular weights (Mn) and polydispersity indexes (PDI) were 102.8 kg/mol, 1.4 for PVC and 52.1 kg/mol, 1.2 for PVEC, respectively (Figure S1-S4). Then, PVC and PVEC were hydrolyzed in strong alkaline solution to obtain pure white PMO and PBD powders according to literatures (Figure 1 and Schemes S1-S2)[23]. Fourier-transform-infrared (FT-IR) spectra showed that the C=O stretching vibrations of the five-membered cyclic carbonate of PVC and PVEC at ca. 1800 cm\(^{-1}\) disappeared completely, proving the successful synthesis of PMO and PBD (Figures S5-S6).

The glass transition temperatures (Tgs) of PMO and PBD can reach 183.3°C and 113°C, indicating amorphous rather than crystalline states (Figures S7-S8). However, owing to the extremely strong H-bonding, they can’t be dissolved in any solvent[24], which extremely limits the study of optical behaviors in solution.

As shown in the structure of Figure 1, there are no other heteroatoms and π electrons in PMO and PBD except oxygen atoms and n and σ electrons. Nonetheless, both PMO and PBD powders exhibited cyan-blue fluorescence and long-lived green RTP with a duration of 2.0 s, which belonged to the typical CL chromophores. To reveal the CL mechanism, PVA showing very weak fluorescence was chosen as a control owing to the similarity in molecule structure. The fluorescence and phosphorescence quantum yields (QYs) of PMO and PBD are 6.83%/5.32% and 6.94%/5.17%, respectively, which are relatively respectable values in NCLPs with RTP, especially for some NCLP systems with only oxygen atoms[6, 8, 25] Because PMO and PBD have similar optical properties, here the PMO is taken as an example for detailed description. The pure white PMO powder showed distinct excitation-dependent photoluminescence (PL) properties (Figure 2a), similar to many of CL chromophores reported before[13, 26] The spectrum covered an emission band from 350 to 600 nm, with an emission peak of 438 nm excited by 360 nm (Figure 2a). The fluorescence lifetime
measured at the emission peak of 438 nm was 3.95 ns (Figure 2b). Based on the theory of through-bond conjugation,[27] theoretically, there’s no fluorescence in PMO because there is no definite conjugation unit in the molecular structure of PMO. Although the presence of oxygen atoms results in n-σ* electronic transitions, the energy gap of the (n, σ*) transition is too high to emit visible light. For example, the energy gap of (n, σ*) transitions of methanol is around 6.7 eV,[28] corresponding to light with a wavelength of 183 nm. Also, the transitions are related to the promotion of an electron from a nonbonding n orbital to σ* antibonding orbital, which are forbidden transitions and therefore are weak intense. Therefore, the fluorescence of PMO does not originate from the (n, σ*) transition of oxygen atom. So, what is the origin of such unusual PL? Tang and Yuan at al.[13-14, 29] proposed the CTE mechanism and TSI from isolated aromatic rings and heteroatoms with lone-pair electrons to rationally reveal the PL origin of NCLPs. In this case, the only possibility is that the fluorescence originates from the through-space n-n interaction of oxygen. Owing to the overlap of n electrons of oxygen atoms in PMO, new orbitals with lower HOMO-LUMO gaps from oxygen clusters will be generated compared to single oxygen atoms, which can absorb and emit lower-energy (longer-wavelength) light. Furthermore, differences in TSI degree lead to the emergence of different HOMO-LUMO gaps from diverse oxygen clusters, leading to excitation-dependent emission characteristics. Meanwhile, green RTP emission with a maximum emission peak at 500 nm and a lifetime of 89.17 ms was observed (Figure 2c-2d), which is comparable to the lifetime of some crystalline small molecules.[30] Similar to the steady-state PL spectrum, the phosphorescence spectrum also shows excitation-dependent emission in the range of 462 to 500 nm at excitation wavelengths from 300 to 360 nm (Figure 2e). This further confirms the existence of diverse oxygen clusters with different conjugation degrees. And the excitation-dependent emission provides an efficient method to realize multicolor fluorescence and RTP emission.

For such long-lived RTP emission, polymerization and extremely strong H-bonding play a key role. As reported in our previous work,[31] polymerization is a very efficient method to achieve PL and RTP emission, namely polymerization-induced emission. When the degree of polymerization (DP) of the PMO is 1, 2 or 3, i.e., methanol, ethylene glycol, and glycerol, they emit no PL and RTP as we all known (Figures S9-S11). For erythritol, xylitol, D-mannitol/D-glucitol with DP of 4, 5 and 6, respectively, they are all crystalline. As reported by Yuan and coworkers,[6] crystalline xylitol showed weak blue fluorescence with a QY of 1.5 and an RTP, but not a long phosphorescence lifetime even at a low temperature of 77 K. This suggests that polymerization can induce stronger through-space interaction than crystallization to boost PL and RTP to some extent. Therefore, for amorphous PMO, there must be a critical DP (CDP) to achieve CL. However, owing to the polydispersity of polymers, it is difficult to synthesize monodisperse PMO. So here we can’t get the value of CDP experimentally, but it must exist. Another factor that should be emphasized is H-bonding. In fact, polymerization is only a prerequisite for the generation of oxygen clusters and TSI. The H-bonding is the key to fluorescence and RTP, and the H-bonding strength must be strong enough. For example, for PVA with one less hydroxyl group in the building block, the very weak emission signal in the PL spectrum is consistent with what we observed with the naked eye (Figures 1 and 2f). To some extent, the H-bonding strength can be reflected by solubility and Tg. PVA is soluble in hot water and the highest Tg can reach up to 85 °C.[32] Compared to insoluble PMO with a Tg of 183.3°C, the H-bonding strength of PVA is much lower than that of PMO. Therefore, only strong H-bonding can induce the through-space n-n interactions of oxygen atoms and further orbital splitting, showing PL emission. In addition, strong H-bonding promotes conformational
rigidification and significantly blocks nonradiative deactivation channels, conferring long-lived RTP emission. Like many traditional chromophores or PL materials without RTP, RTP appears once they diffuse into PVA or other polymers with strong H-bonding.[21, 33] This work provides another avenue to understand the mechanism of PL and RTP.

Figure 2. (a) PL spectra of PMO in the solid state at different excitation wavelengths. (b) Luminescent decay curve of PMO in the solid state at 438 nm (λ_{ex}=360 nm). (c) Time-resolved spectra of PMO at different delay times in the solid state. (phosphorescence mode: λ_{ex}=360 nm). (d) phosphorescence decay curve of PMO in the solid state at 500 nm (λ_{ex}=360 nm). (e) Time-resolved spectra of PMO at different excitation wavelengths in the solid state. (delay time: 1 ms). Inset: normalized time-resolved spectra of PMO at different excitation wavelengths in the solid state. (f) PL spectra of PVA in the solid state at different excitation wavelengths.

The similar optical properties were observed in PBD with neighboring hydroxyl groups in the side chain (Figure 3), confirming the significance of neighboring hydroxyl groups for fluorescence and RTP. As shown in Figure 3a, it also exhibits excitation-dependent PL emission and emits the same emission peak at 438 nm excited by 360 nm. The RTP peak position and lifetimes of fluorescence and phosphorescence are close to those of PMO (Figure 3b-3d). Therefore, whether the neighboring hydroxyl groups are located in the backbone or side chain has no effect on their luminescent properties. The strong intra-/intermolecular H-bonding interactions of PBD also results in insolvability in most solvents. In other words, when monomers with adjacent hydroxyl groups are polymerized, strong H-bonding can induce physical crosslinking, exhibiting strong intra-/intermolecular interactions. It is further demonstrated the through-space interaction between the oxygen atoms.
Figure 3. (a) PL spectra of PBD in the solid state at different excitation wavelengths. (b) Time-resolved spectra of PBD at different delay times in the solid state. (phosphorescence mode: $\lambda_{ex}=$360 nm). (c, d) Luminescent (c) and phosphorescence (d) decay curves of PBD in the solid state at 438 and 510 nm ($\lambda_{ex}=$360 nm).

To further fully confirm that the fluorescence and RTP originate from the through-space n-n interaction of oxygen atoms, optimized conformations of PMO, PBD and PVA based on single polymer chains with fourteen constitutional units were calculated by density functional theory (DFT) at B3LYP/6-31(d, p) level (Figure 4a-4c). Ethylene glycol and 1,2-propanediol, as repeating building blocks of PMO and PBD, were selected as controls and optimized at the same level (Figure 4d-4e). Theoretical calculation analysis shows that the distance between most of the oxygen atoms in PMO and PBD is between 2.58–2.83 Å (Figure 4a, 4c and Tables S1-S2), which is less than twice the van der Waals radius of the oxygen atom ($d_0$) ($r_b$: 1.52 Å; $r_f$: 1.40 Å). But for PVA, there are almost no short contacts between oxygen atoms, and most of the oxygen atoms are at a distance greater than $d_0$ (Figure 4b and Table S3). Furthermore, for ethylene glycol and 1,2-propanediol, the distance between adjacent hydroxyl groups is about 3.6 Å, which is much larger than $d_0$. Indeed, no fluorescence was detected in ethylene glycol and 1,2-propanediol (Figures S10 and S12). The importance of polymerization for TSI is well demonstrated, and the above results fully confirm that the fluorescence and RTP of PMO and PBD are ascribed to the through-space n-n interaction between oxygen atoms. In this case, the overlap of electron clouds of oxygen atoms leads to the splitting and coupling of the orbitals and the generation of new molecular orbitals with smaller energy gaps for visible light emission (Figure 4f). The resulting molecular orbitals correspond to the blue visible light of PMO and PBD. Owing to the difference in the distance between the oxygen atoms, the degree of electron cloud overlap and TSI is also different. Thus, it results in the
generation of molecular orbitals with different energy gaps and the emergence of excitation-dependent PL and RTP emission. That is, the excitation-dependent PL and RTP emission are attributed to diverse oxygen clusters with different conjugated degrees, as detailed schematic diagram is shown in Figure 4f.

Figure 4. (a-c) Optimized conformations of PMO (a), PVA (b), and PBD (c) based on single polymer chains with fourteen constitutional units at (DFT) B3LYP/6-31(d, p) level. (d, e) Optimized conformations of ethylene glycol (d) and 1,2-propanediol (e) at (DFT) B3LYP/6-31(d, p) level. (f) A schematic diagram of TSI for PMO and PBD, and the orbital splitting induced by TSI, where $E_0$ is the energy gap of the oxygen and $E_{OC}$ is the energy gap of the oxygen cluster.

Conclusion

In summary, a novel class of amorphous polyols with fluorescence and long-lived RTP properties was prepared. Experimental results and theoretical calculations prove that the through-space n-n interaction of oxygen atoms is the fundamental cause of fluorescence and RTP. Results from controls (ethylene glycol, 1,2-propanediol, and PVA) confirmed that polymerization and H-bonding
play key roles in the generation of oxygen clusters and TSI. The difficulty of studying the photophysical behavior of PMO and PBD in solution limits the in-depth understanding of through-space n-n interactions to a certain extent. Our ongoing efforts are to seek a soluble strong H-bonded NCLP and to develop NCLPs with better optical performance. This work not only provides a new strategy for the design and construction of fluorescence and RTP materials, but also sheds new light on the CL mechanism of NCLPs.

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Conflicts of interest
There are no conflicts to declare.

Notes and references


Through-space n-n interaction

Intramolecular oxygen clusters

Intermolecular oxygen clusters

H-bonding

Polymerization

Intramolecular oxygen clusters