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Shape-Memorable, Self-Healable, Recyclable, and Full-Color Emissive Ultralong Organic Phosphorescence Vitrimers with Exchangeable Covalent Bonds

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Polymeric materials displaying ultralong organic phosphorescence (UOP) have drawn much attention in the fields of optoelectronics, bioimaging, and information encryption. However, it is challenging to realize polymeric UOP materials with variable mechanical strength, self-healing, and superior processability. This work presents a low-cost strategy to achieve polymeric UOP with full-color-emission (doping vitrimers with different phosphorescent emitters) by introducing exchangeable covalent cross-linked bonds. These amorphous polymers show ultralong lifetimes up to 1.75 s under ambient conditions. Impressively, bright afterglow can be observed after soaking the different color films in water for 4 weeks. Furthermore, the polymeric UOP with exchangeable links exhibits self-healable, recyclable, and shape memory features due to the dynamic covalent networks. These results outline a fundamental strategy to construct multifunctional polymers and pave a way to expanding polymeric phosphorescence materials and their applications.

1. Introduction

Ultralong organic phosphorescence (UOP) emission is defined as emission lasting for more than 0.1 s after removal of the excitation source and can typically be detected by the naked eye, exhibiting long lifetimes, large stokes shifts, and significant signal-to-noise ratio.[1] Among all the UOP materials, UOP polymers have advantages in terms of amorphous, flexibility, stretchability, and low cost are better candidates for future applications of bioimaging, information encryption, and foldable electronic devices.[2] Nevertheless, long-lived triplets can be easily quenched via intermolecular collision or energy transfer and thus make it difficult to achieve efficient polymeric UOP.[3] Generally, the presupposition of polymer matrix is considered as follows: (i) perfect oxygen and moisture resistance to reduce triplet excitons quenching, (ii) rigid microenvironment with rich intermolecular interactions to restrict the nonradiative pathways, (iii) high singlet and triplet energy levels to suppress the reversed energy transfer from emission center to matrix, and (iv) good mechanical strength for wide applications.[4,5]

Regard to this, several linear polymers with abundant intra- and intermolecular hydrogen bond are successfully used in fabrication of amorphous UOP by doping or grafting organic phosphors into the rigid matrix, such as polyvinyl alcohol,[6] poly(lactic acid),[7] polymethyl methacrylate,[8] and polyacrylamids.[9] However, hydrogen bond in such polymers is very sensitive to humidity and unfavorable for long-term stability in air.[10] Compared to these processible thermoplastics, polymeric UOP materials with covalent cross-linked bond which can supply stronger interactions between the molecular chains exhibit superior environmental resistance, higher quantum efficiently (Φ_P), and longer lifetime (τ) due to efficient suppression of excited-state vibrations in the rigid networks.[2,11] Unfortunately, cross-linked polymers are regularly defined as traditional thermosets that lack recyclability, reprocessing, and environmental friendly features.[1b] Besides, the full-wavelength range color tuning with good purity in cross-linked polymeric UOP is rarely demonstrated.

In 2011, vitrimers which rely on reversible transesterifications in epoxy/acid and epoxy/anhydride polyester networks with dynamic bond exchange mechanism were developed by Leibler's group (**Figure 1**a and Figure S1, Supporting Information).[12] The exchangeable covalent bonds triggered above topology freezing transition temperature (T_v) enable covalent cross-linked thermosets with features such as self-healing,

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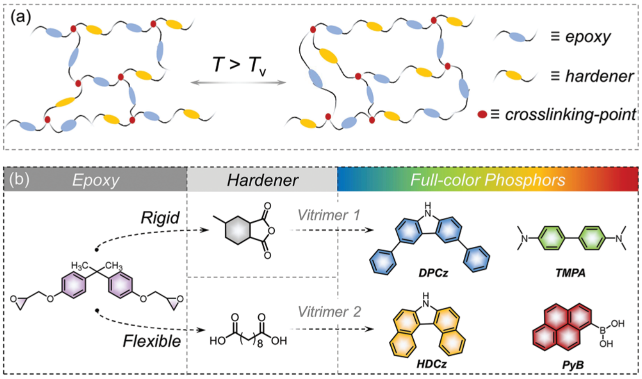

Figure 1. a) The mechanism of topological rearrangements via exchangeable covalent bonds in the epoxy-based vitrimer. b) The chemical structures of rigid (vitrimer 1, V1) and flexible (vitrimer 2, V2) ultralong organic phosphorescence (UOP) vitrimers with different color emission.

welding, reshaping, reprocessing, and recycle ability.[13] Inspired by this, the introduction of vitrimer feature into polymeric UOP will afford a better performance than that in traditional thermoplastics UOP. Notably, the reprocess ability of the vitrimer-based UOP can be maintained even though they are constructed by covalent cross-linked bonds.

2. Results and Discussion

To validate our hypothesis, we put forward a method to construct full-color emissive (from blue to green, yellow, and red) UOP by doping vitrimers with different phosphorescent emitters, and the lifetime varies from 0.36 to 1.75 s under ambient conditions by doping different phosphor emitters. Impressively, the dynamic transesterifications in vitrimers endow the cross-linked polymeric UOP with humidity resistant, recyclable, self-healing, and environmental friendly features. Moreover, due to the different rigidity of the hardener, vitrimer 1 and vitrimer 2 possess different elastic modulus which indicates the vitrimeric UOP can be applied in multiple scenarios to promote the further development of polymeric UOP materials in the future.

To obtain the covalent cross-linked UOP, two curing systems (epoxy/acid and epoxy/anhydride) were used to establish the polyester networks with vitrimer features. Generally, in doped polymeric UOP materials, the energy levels of the highest occupied molecular orbital and lowest unoccupied molecular orbital of the polymer matrix are crucial when acting as host material. Otherwise, the formation of exciplex between the host polymer and guest phosphors will reduce the color purity with a broad and structureless emission feature.[14] Therefore, the frontier orbitals and energy levels of the vitrimers and phosphors should be examined first. As shown in Figure S2 (Supporting Information), the energy gaps of two vitrimer matrices (5.13 eV for V1 and 5.45 eV for V2) are large enough to cover the gaps of four phosphors (DPCz, TMPA, HDCz, and PyB), avoiding the electron transfer between the polymer matrices and phosphors.[14a] These results indicate that these vitrimer matrices are ideal hosts for full-color emissive polymeric system preparation.

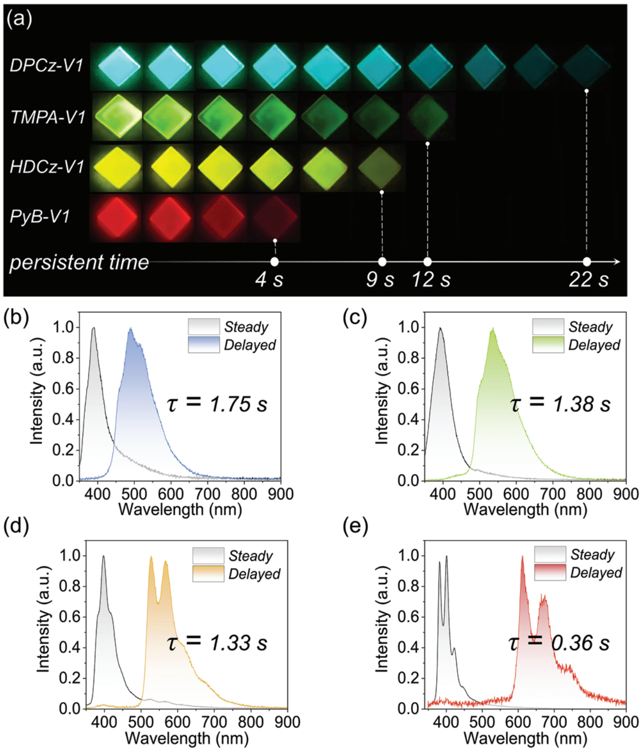

Figure 2. a) Photographs of V1 series taken upon turning a 365 nm lamp off under ambient conditions, the size of bulk UOPs is 1 × 1 × 0.15 cm. The steady and delayed spectra of b) DPCz-V1, c) TMPA-V1, d) HDCz-V1, and e) PyB-V1.

As anticipated, the long-lived polymeric UOP systems were successfully constructed by doping the four organic phosphors (0.5% w/w) into the two vitrimers (Figure 1b). The structureless features of X-ray diffraction indicate these vitrimers exhibiting amorphous phase (Figure S3, Supporting Information). After removal of 365 nm UV irradiation, these doping vitrimers with phosphorescent emitters exhibit intense full-color afterglow (from blue to red), which can be captured by naked eyes with a faded ultralong emission up to 22 s (**Figure 2**a). In order to evaluate the origin of the UOP in vitrimers, steady and transient spectra were recorded. All the polymeric UOP exhibit dual emission features as displayed in Figure 2b–e. For instance, a persistent lifetime up to 1.75 s can be recorded at 480 nm (sky blue) for DPCz-V1, with the prompt lifetime of 10.3 ns at 381 nm (Figure 2b and Figure S4–S6, Supporting Information). According to previous literature, the dual-emission characteristic can be assigned to fluorescence and phosphorescence of the dopant dispersed in polymer.[6c] This result can further be demonstrated by the phosphorescence spectra measured in dilute solutions at 77 K, which exhibit the same vibronic structures as that of polymers at room temperature (Figure S7, Supporting Information). Meanwhile, the green, yellow, and red afterglow emissions with long-lived lifetimes could be successfully achieved from TMPA-V1 (τ = 1.38 s), HDCz-V1 (τ = 1.33 s), and PyB-V1 (τ = 0.36 s), respectively (Figure 2c–e). Such slow radiations of the long-lived triplets demonstrate the rigid environment and oxygen barrier in the vitrimeric matrices. Furthermore, the phosphorescent lifetimes of these polymer

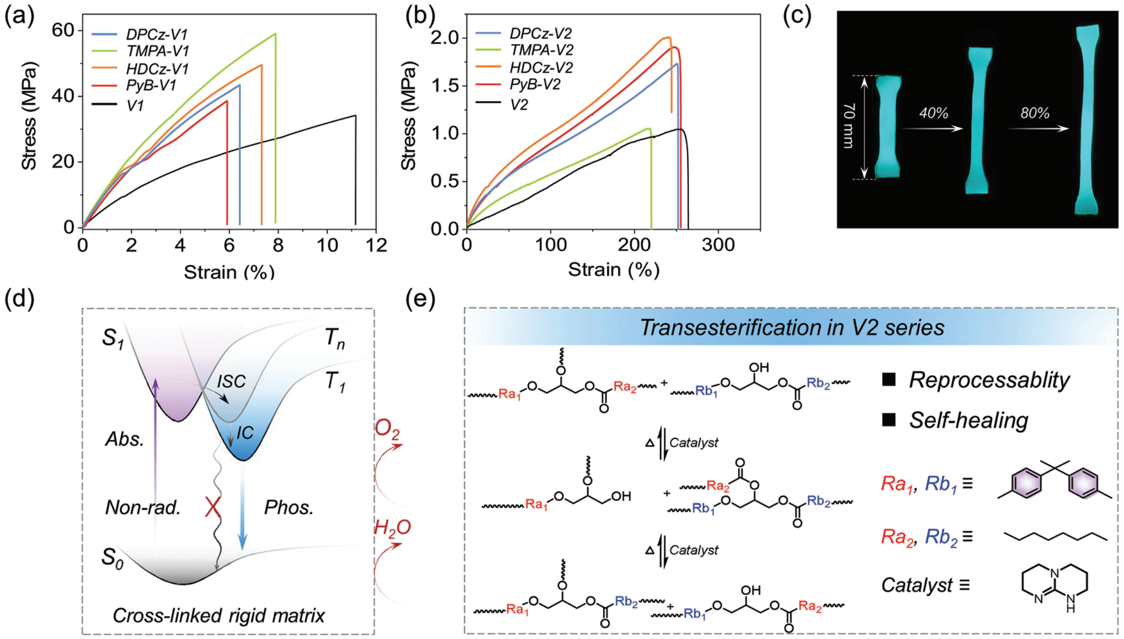

Figure 3. Tensile stress–strain curves of a) V1 series and b) V2 series, c) the afterglow photographs of dumbbell-shape specimen of DPCz-V2 with different elongation, d) proposed mechanism of ultralong organic phosphorescence (UOP) in epoxy vitrimers with oxygen and moisture resistance, and e) exchange process via transesterification in V2 series.

objects remained very stable when these polymers were soaked in water (Figures S8, S9, and Table S1, Supporting Information) and the bright persistent emissions were still easily captured by naked eyes (Figure S10, Supporting Information) for over 4 weeks, indicating the excellent humidity resistance of the cross-linked matrix. Such ability can be ascribed to the low water affinity of ester groups of the polymer matrices. Compared with previous studies where the long phosphorescence was achieved by crystal engineering or a tedious chemical synthesis,[15] it is highly significant that the full-color polymeric UOP was realized simply through a feasible doping methodology.

To understand the mechanism of colorful UOP, theoretical calculations were performed. Generally, triplet energy levels and spin-orbit coupling matrix (SOC) are the two key roles for obtaining efficient full-color UOP.[16] The lowest triplet energy level (T_1) of the phosphor regulates the color of UOP while the SOC of S_1-T_n and T_1-S_0 affect the efficiency of the UOP. As shown in Figure S11 (Supporting Information), the gradually decreased energy levels of T_1 in DPCz, TMPA, HDCz, and PyB are 3.06 , 3.01 , 2.46, and 2.09 eV, respectively, which are consistent with the redshifted color of long-lived phosphorescence. In addition, SOC matrices of the phosphors are evaluated to identify the possible intersystem crossing (ISC) channels. All these molecules exhibit abundant ISC channels for the large SOC constant between S_1 and lower-lying T_n, which can be ascribed to the existence of heteroatoms (nitrogen, oxygen, and boron) and aromatic skeleton.[17] This speculation can also be verified by the natural transition orbitals analysis (Figures S12–S15, Supporting Information). For instance, the electron configuration of S1 in blue emitter DPCz exhibits mixture of n–π^* and π–π^* while the T_1 is pure π–π^* transition. According to EI-Sayed rules,[18] the intense ISC transition occurs between the two excited states with a large SOC constant ($\xi_{(S1\text{-}T1)}$ = 0.91 cm^{-1}). Additionally, T_1 with $^3(\pi$–$\pi^*)$ configuration can show an extremely long-lived emission due to the forbidden transition.[17,18]

In order to further verify the influence of the matrix rigidity on the UOP features, the flexible hardener 1,10-decanedioic acid was selected as curing agent to construct soft vitrimers (namely V2 series, Figure 1b). As anticipated, V2 series also exhibit full-color UOP emissions with different phosphors doping (Figures S16–S19, Supporting Information). However, the phosphorescence lifetime of DPCz-V2, TMPA-V2, HDCZ-V2, and PyB-V2 are 0.76, 0.78, 0.53, and 0.28 s (Figure S20, Supporting Information), respectively, which are much shorter than that in V1 series. Generally, shortened lifetime indicates an enhanced nonradiation which is caused by excited-molecular motions at room temperature.[19] Thus, glass transition temperature (T_g) of these vitrimers was obtained by differential scanning calorimeter and shown in Figure S21 (Supporting Information). The T_g of V1 series are around 140 °C which are much higher than that in V2 series (29.63 °C ~ 36.98 °C), due to the different rigidity of the hardeners. The relatively low T_g in V2 series is very close to the room temperature and thus results in significant molecular motions.[11a] Meanwhile, the mechanical performance of these epoxy vitrimers were examined to evaluate the rigidity of the matrices. As displayed in **Figure 3**a, the modulus values of V1 series are 1113.65, 1222.69, 1157.01, and 991.06 MPa for DPCz-V1, TMPA-V1, HDCZ-V1, and PyB-V1, respectively. In contrast, the V2 series exhibit superior flexibility and elasticity as elastomers with much smaller modulus of 2.05, 1.01, 4.67, and 1.59 MPa for DPCz-V2, TMPA-V2, HDCZ-V2, and PyB-V2, respectively (Figure 3b). The epoxy vitrimers from relatively brittle materials (V1 series) to elastomers (V2 series), i.e., extensibility dramatically increased from 7% to 250%, has been achieved via varying hardeners (5-methylhexahydrophthalic anhydride and decanedioicacid). As a result, the shortened lifetimes in V2 series can be ascribed to the flexible matrices which is caused by the introduction of flexible hardener with reduced rigidity.

Intriguingly, the modulus of these objects varies with the emission color, which can be ascribed to the different cross-linking density in vitrimers caused by the catalytic or reaction activity of the doped phosphors.[20] Under external stress, the V2 series with lower modulus undergo more deformation than the V1 series with higher modulus. As shown in Figure 3c and Figure S22 (Supporting Information), the elastomer characteristic of V2 can be demonstrated with the reversibility deformed by mechanically stretching under ambient conditions and no significant afterglow changes are observed between the initial and deformed states. Additionally, complex shapes can be realized at elevated temperature without using molds for V2 series. A helical fusilli-like object of DPCz-V2 was obtained from a ribbon by twisting (**Figure 4**a), which can return to its original shape by simply heating over T_g. This result demonstrates the original ribbon shape can be memorized due to the permanently covalent cross-linked network in V2 series.

Furthermore, the networks of vitrimers are relied on associative exchange mechanism with bond-exchange reaction. The covalent bonds are only broken when new ones are formed, making these networks permanent as well as dynamic but exhibit a fixed cross-linked density. Therefore, the temperature-induced self-healing and reprocessability can be obtained because of the dynamic network rearrangement in vitrimers. As depicted in Figure 4b and Figure S23 (Supporting Information), the cross scratch can be healed rapidly in 1 h with pressure under 180 °C. The scratch cannot be captured by naked eyes. The result reveals the excellent self-healing ability of the vitrimer-based UOP material. It is noteworthy that the catalyst concentration is closely related to the healing efficiency.[20a] One of the most promising characteristic properties of vitrimers is the recyclability, which is difficult for traditional thermosets. Cutting into small fragments, DPCz-V2 shows to be capable of reforming and reshaping (Figure 4c). With hot pressing at 180 °C after 3 h, the comminuted DPCz-V2 sample can recover most of its initial state with slightly decreased UOP feature (Figure S24, Supporting Information).

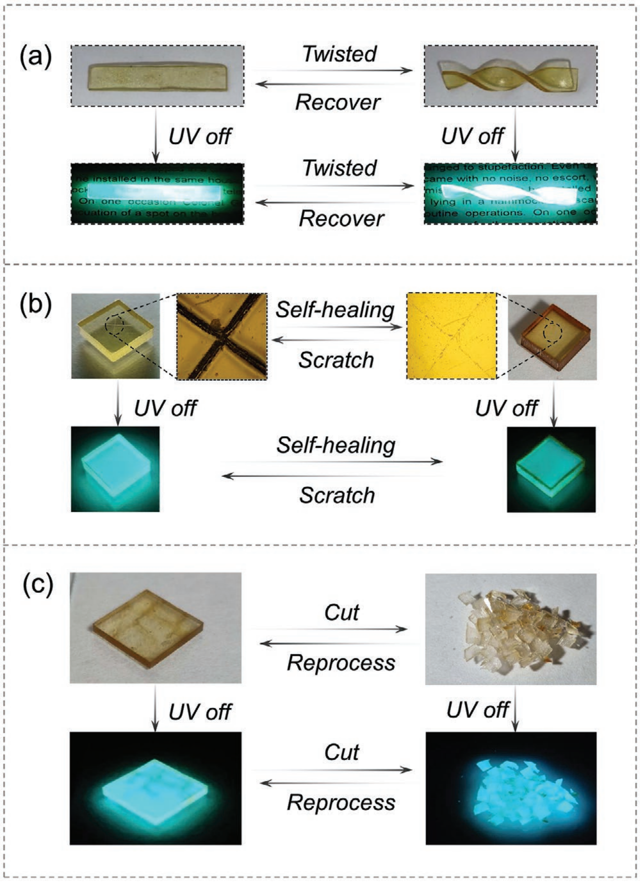

Figure 4. a) Fusilli-shaped DPCz-V2 and recovery by heating the ribbon, b) optical microscopy observations of the self-healing ability, c) the reprocess procedure of the shredded DPCz-V2 fragments. These photographs of DPCz-V2 were taken under daylight and turning off UV light.

3. Conclusion

To summarized, we present an efficient vitrimer-based UOP materials with full-color emission through a facial strategy. Impressively, the doped systems show a persistent emission over 22 s under ambient conditions. On the basis of experiments and theoretical calculations, it is found that the rigid environment constructed by the cross-linked covalent bonds in vitrimers restrict the excited molecular motions and prevent the quenching of triplet excitons by oxygen and moisture, thus boosting the UOP emission. Furthermore, because of the covalent cross-linkage and dynamic transesterification exchange features, the vitrimers with multifunction of shape memory, recyclable, and self-healing UOP are obtained. The proposed approach provides possibilities for method innovation in developing polymeric UOP materials with multifunction to expand their applications.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords

full color, polymeric phosphorescence, self-healing, shape memory, ultralong organic phosphorescence

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