

Utilizing d- $\pi$  Bonds for Ultralong Organic PhosphorescenceShuai Tian<sup>+</sup>, Huili Ma<sup>+</sup>, Xuan Wang, Anqi Lv, Huifang Shi, Yun Geng, Jie Li, Fushun Liang,\*  
Zhong-Min Su,\* Zhongfu An,\* and Wei Huang

**Abstract:** Developing pure organic materials with ultralong lifetimes is attractive but challenging. Here we report a concise chemical approach to regulate the electronic configuration for phosphorescence enhancement. After the introduction of d- $\pi$  bonds into a phenothiazine model system, a phosphorescence lifetime enhancement of up to 19 times was observed for DOPPMO, compared to the reference PPMO. A record phosphorescence lifetime of up to 876 ms was obtained in phosphorescent phenothiazine. Theoretical calculations and single-crystal analysis reveal that the d- $\pi$  bond not only reduces the (n,  $\pi^*$ ) proportion of the T<sub>1</sub> state, but also endows the rigid molecular environment with multiple intermolecular interactions, thus enabling long-lived phosphorescence. This finding makes a valuable contribution to the prolongation of phosphorescence lifetimes and the extension of the scope of phosphorescent materials.

Phosphorescence has attracted intense attention in diverse applications such as anti-counterfeiting,<sup>[1]</sup> molecular sensing,<sup>[2]</sup> and displays<sup>[3]</sup> due to their long-lived emission lifetimes.<sup>[4]</sup> For instance, phosphorescence can eliminate background fluorescence interference via the time-gate technique in the biological field.<sup>[5]</sup> Until now, most luminescent materials with phosphorescence are confined to inorganic and precious metal complexes with distinct shortcomings such as

high cost, biological toxicity, and instability in aqueous solutions.<sup>[6]</sup> Comparatively, pure organic phosphorescent substances are inexpensive, relatively safe to the environment, and the intrinsic structures are easy to modulate.<sup>[7]</sup> However, the development of efficient and ultralong organic phosphorescence (UOP) still remains a great challenge. The key issues involve the inefficient intersystem crossing (ISC) caused by weak spin-orbit coupling (SOC) and the rapid non-radiative decay due to molecular motions and oxygen quenching, among other things.<sup>[8]</sup> In this regard, the development of organic phosphorescent substances with efficient UOP needs to satisfy at least the following two factors: i) incorporating functional groups such as carbonyls, heavy atoms, as well as heteroatoms (N, S, P, etc.) to promote ISC through SOC enhancement;<sup>[9]</sup> ii) constructing a rigid environment to suppress the non-radiative decay of triplet excitons by a series of feasible approaches such as crystallization,<sup>[10]</sup> hydrogen bonding,<sup>[11]</sup> halogen bonding,<sup>[12]</sup> self-assembly,<sup>[13]</sup> H-aggregation,<sup>[14]</sup> hydrogen-bonded organic aromatic frameworks (HOAFs),<sup>[15]</sup> etc. Through the tremendous efforts of scientists, many organic phosphorescent substances with ultralong lifetimes have been developed along with the proposed mechanism.<sup>[16]</sup> Among those, most work focuses on creating a more rigid external environment to suppress the non-radiative pathways and thereby prolong the phosphorescence lifetime, while less attention was paid to the engineering of the intrinsic molecular structure. Hence, a concise yet efficient chemical strategy to prolong the lifetime is attractive and practical.

The d- $\pi$  bond is widely distributed in transition-metal complexes and oxyacids, but it is very rare in common organic compounds.<sup>[17]</sup> It mainly exists in molecules containing S=O and P=O bonds. Different from the normal  $\pi$ -bond that stems from the overlap of two p orbitals (for example, C=C, C=O), the d- $\pi$  bond is formed by the conjugation between a d orbital and a p orbital (for example, d<sub>xz</sub>-p<sub>z</sub>).<sup>[18]</sup> As exemplified in Figure 1 (top), the energy level of the 3d orbital is much higher than that of the 2p orbital, so it is not beneficial to delocalize electrons on the oxygen atoms. Meanwhile, the d- $\pi$  bond leads to a nonplanar conformation between the sulfonyl group and the phenyl ring. From the viewpoint of electronic and steric effects, the communication between the non-bonding electron pairs on the oxygen and the adjacent  $\pi$  orbital will be weakened, which may regulate the n-orbital contribution of the lowest excited triplet state (T<sub>1</sub>).

Based on the above understanding, we speculated that some organic phosphors with d- $\pi$  bonds could prolong the organic phosphorescence lifetime in crystals under ambient conditions. To confirm this hypothesis, organic compounds containing phenothiazine units were chosen as model systems, because phenothiazine with its unique non-planar butterfly

[\*] S. Tian,<sup>[†]</sup> J. Li, Prof. F. Liang  
Institute of Organic Luminescent Materials (IOLM)  
College of Chemistry, Liaoning University  
66 Chongshan Mid. Road, Shenyang 110036 (China)  
E-mail: fsliang@lnu.edu.cn

Dr. H. Ma,<sup>[†]</sup> X. Wang, A. Lv, Dr. H. Shi, Prof. Z. An, Prof. W. Huang  
Key Laboratory of Flexible Electronics (KLOFE) & Institute of Advanced Materials (IAM)  
Nanjing Tech University (NanjingTech)  
30 South Puzhu Road, Nanjing 211800 (China)  
E-mail: iamzfan@njtech.edu.cn

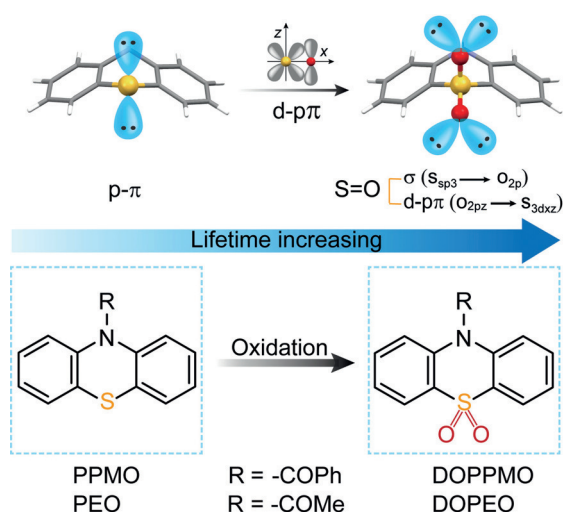
Prof. F. Liang, Prof. Z.-M. Su  
School of Chemistry and Environmental Engineering  
Changchun University of Science and Technology  
7089 Weixing Road, Changchun 130022 (China)  
E-mail: zmsu@nenu.edu.cn

Dr. Y. Geng, Prof. Z.-M. Su  
Department of Chemistry, Northeast Normal University  
5268 Renmin St., Changchun 130024 (China)

Prof. W. Huang  
Institute of Flexible Electronics (IFE)  
Northwestern Polytechnical University (NPU)  
127 West Youyi Road, Xi'an 710072 (China)

[†] These authors contributed equally to this work.

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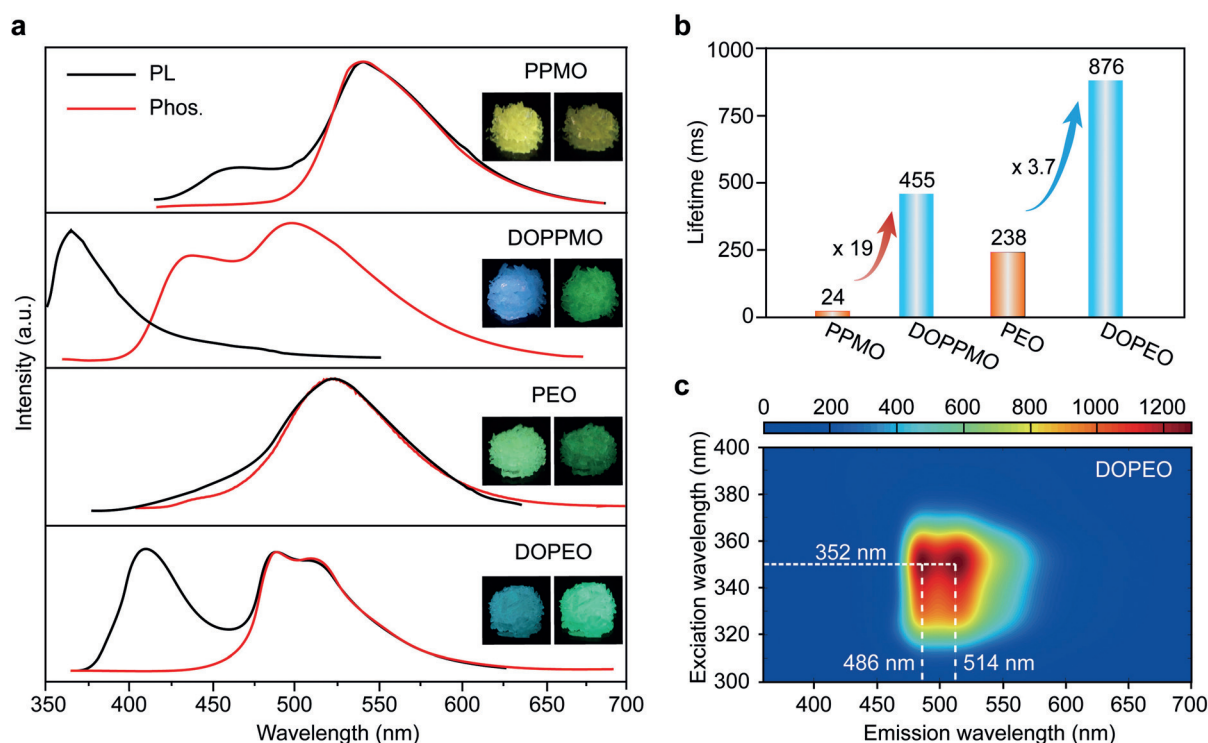
**Figure 1.** Top: Illustration of the phosphorescence lifetime enhancement by the introduction of d- $\pi$  bonds. Bottom: Structures of the compounds investigated in this work.

structure could hinder a possible intensive intermolecular  $\pi$ - $\pi$  stacking, which is beneficial for the inhibition of excited triplet-triplet annihilation (Supporting Information, Scheme S1 and Table S1).<sup>[19]</sup> We synthesized two N-acyl phenothiazine derivatives, namely, (10*H*-phenothiazin-10-yl) (phenyl)methanone (PPMO) and 1-(10*H*-phenothiazin-10-yl)ethan-1-one (PEO). Through subtle chemical modification, that is, a one-step sulfur oxidation, a d- $\pi$  bond was introduced into the luminogens (Figure 1, bottom). As expected, all compounds show phosphorescence under ambient conditions. A remarkable increase in the phosphorescence lifetime (up to 19 times) was observed when d- $\pi$  bonds were introduced. Particularly, DOPEO exhibits a balanced long phosphorescence lifetime of 876 ms (Table S2) and a phosphorescence quantum yield of 8.2%, which represent the highest values among phenothiazine-based phosphorescent substances. Furthermore, crystal analysis and theoretical calculations reveal that d- $\pi$  bonds play a significant role in manipulating the electronic configuration and molecular stacking of these compounds. A nearly pure ( $\pi$ ,  $\pi^*$ ) configuration of  $T_1$  and a more rigid molecular environment in the crystal state were attained, which gave rise to a substantial increase of the phosphorescence lifetime.

The synthetic routes for PPMO, DOPPMO, PEO and DOPEO are outlined in Scheme S2. Luminogens DOPPMO and DOPEO were obtained in overall yields of 77% and 86%, respectively, by two-step reactions from phenothiazine and the corresponding acyl chloride. All compounds were fully characterized by <sup>1</sup>H and <sup>13</sup>C NMR (Figures S1–S8). The phase purity and molecular packing were confirmed by powder XRD (Figure S9) and single-crystal analysis. PPMO, DOPPMO, and DOPEO show a good thermal stability and high melting points (Figure S10), while PEO was found to decompose before melting.

The photophysical properties of the phenothiazine derivatives were systematically investigated in both solution and the crystalline state. In a dilute THF solution ( $5 \times 10^{-5}$  M), both PPMO and DOPPMO have the same  $\pi$ - $\pi^*$  absorption

bands at around 230 nm, but different n- $\pi^*$  absorption bands with peaks at 273 and 303 nm, respectively. For PEO and DOPEO, the absorption peaks corresponding to the n- $\pi^*$  transition also show a 30 nm blue-shift (Figure S11). All systems have fluorescence peaks generated by the excited state of phenothiazine at around 360 nm (Table S3), which is slightly affected by the polarity of the solvents (Figure S12). We also investigated the emission behavior of the single molecules at 77 K. When excited at 290 nm, PPMO and PEO show similar profiles with peaks at 442 nm owing to their identical and effective chromophoric components. However, a significant blue-shift was observed for DOPPMO and DOPEO, indicating that the sulfonyl group has a great impact on the excited states of luminogens on the single-molecule level (Figure S13a). Furthermore, photoluminescence (PL) and phosphorescence spectra of these compounds in crystals at 298 K are shown in Figure 2. When irradiated at 330 nm, a large overlap can be observed in the PL and phosphorescence spectra of PPMO and PEO, implying sufficient ISC in  $S_1$ - $T_n$  transitions. DOPPMO exhibits an intense fluorescence peak centered at 353 nm and phosphorescence peak of relatively low intensity around 400–510 nm due to its low quantum yield. We also found phosphorescence peaks located at 435 and 490 nm with different lifetimes (234 ms and 455 ms, respectively), suggesting that they are likely to be produced by different excited states. Additionally, we investigated the emission spectra of DOPPMO at 77 K both in dilute solution and in 5% PPMA (Figure S13b). Similar emission behavior was observed, which was attributed to the single molecule.<sup>[16c]</sup> DOPEO exhibits dual emissions with almost equal intensity. The prompt PL spectrum shows fluorescence signals at 380–450 nm and phosphorescence emission at 460–600 nm, respectively. The phosphorescence spectra of the four compounds change when measured in vacuum or oxygen atmosphere, indicating the phosphorescence nature of the emission (Figure S14). Inset pictures show photographs taken before and after the excitation source was turned off. It can be seen that there is an obvious change in the emission color after oxidation, indicating that the sulfonyl group may vary the energy gap between  $T_1$  and  $S_0$ . The Commission Internationale de l'Éclairage (CIE) coordinate corresponding to the prompt emission of PEO, DOPEO, PPMO, and DOPPMO is shown in Figure S15. Interestingly, when the excitation light source was switched off, a bright blueish-white color for DOPEO was observed by the naked eye, which can last for more than 5 seconds (Supporting Information, Video SV1). Figure 2b shows the phosphorescence lifetimes of the four compounds as crystals under ambient conditions. Obviously, a highly enhanced lifetime was observed when sulfur was oxidized (Figures S16 and S17). These results indicate that the d- $\pi$  bond has a significant influence on the prolongation of the phosphorescence in the crystalline state. Typically, the lifetime of DOPPMO shows a huge increase by 19 times compared to that of PPMO. Among the compounds, DOPEO exhibits a balanced long phosphorescence lifetime of 876 ms (Table S2) and a phosphorescence quantum yield of 8.2%. The phosphorescence signal in the spectrum of solid-state DOPEO remains at the same position when the excitation wavelength is varied from 300 to 400 nm, and the



**Figure 2.** Photophysical properties of phenothiazine derivatives in the crystalline state under ambient conditions (298 K): a) Steady-state photoluminescence (black solid lines) and phosphorescence spectra (red solid lines). Insets show photographs under 365 nm UV light and after removal of the light source. b) Phosphorescence lifetimes of the emission bands at 539 nm (PPMO), 490 nm (DOPPMO), 521 nm (PEO), and 514 nm (DOPEO). c) Excitation–phosphorescence mapping of DOPEO.

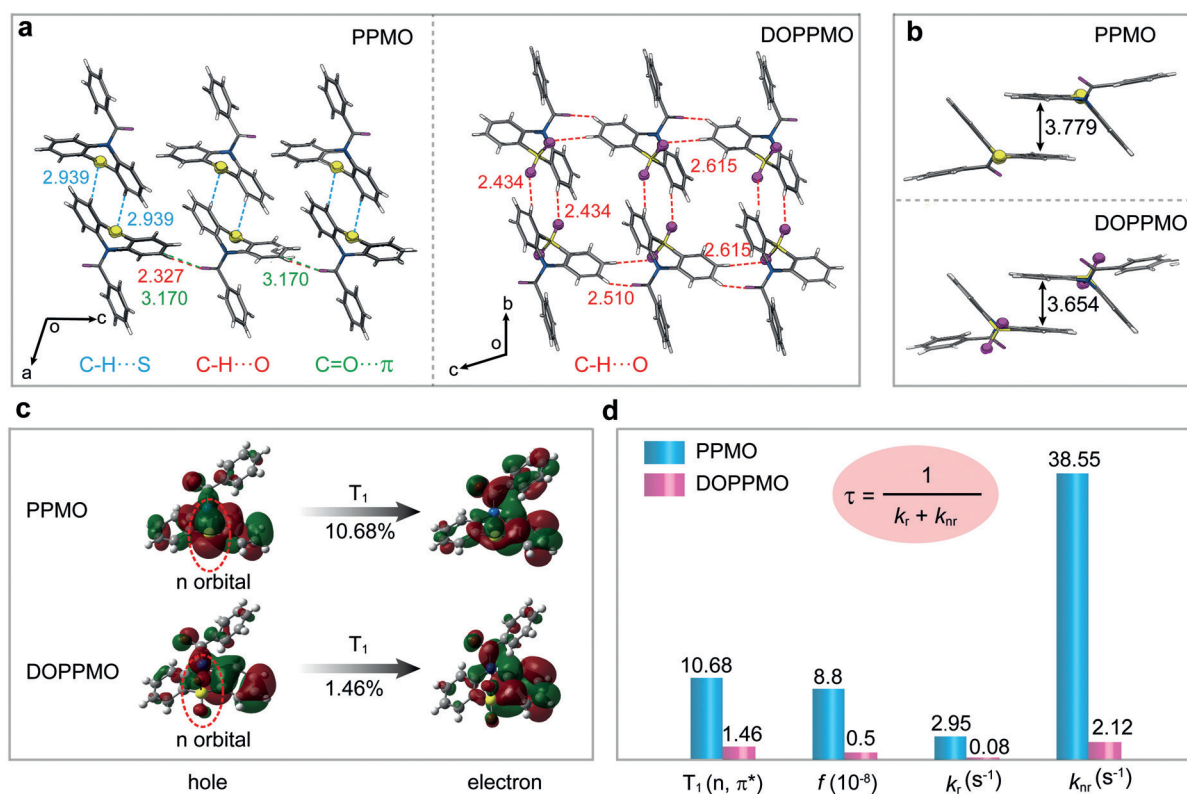
phosphorescence intensity reaches maximum when excited at 352 nm (Figure 2c).

To elucidate the relationship between the molecular structure and the phosphorescence properties, single crystals were cultivated by slow evaporation from a mixture of acetone and petroleum ether. Compounds PPMO and DOPPMO crystallize in the monoclinic system and they have similar layered packing (Figure S19). As shown in Figure 3a, abundant intermolecular hydrogen bonds could be observed in the crystal structures. However, additional C–H $\cdots$ O (2.510 Å, 2.615 Å) hydrogen bonds were found in the DOPPMO crystal. A rigid 2D network structure is established via molecular interlocking connected by C–H $\cdots$ O interactions in the same layer and  $\pi$ – $\pi$  stacking in different layers. It is worth noting that the distance of the intermolecular  $\pi$ – $\pi$  stacking is shortened (3.779 Å for PPMO vs. 3.654 Å for DOPPMO, Figure 3b). This can be explained by a reduction of the electron density on the benzene rings on both sides of phenothiazine upon the oxidation of sulfur (electron-donating group) to sulfonyl (electron-withdrawing group). As a result, the repulsive  $\pi$ – $\pi$  force is reduced. The denser packing with highly more rigid molecular conformations may greatly suppress the non-radiative pathways of the excited molecules, leading to pronounced UOP. The denser packing is further verified by densities of 1.3707 and 1.3975 g cm $^{-3}$  for the PPMO and DOPPMO crystals, respectively. Compounds PEO and DOPEO also crystallize to the monoclinic system. Compared to PEO, DOPEO has abundant intermolecular C–H $\cdots$  $\pi$  and C–H $\cdots$ O interactions in the crystal (Figure S20). The multiple intermolecular interactions

are helping to suppress molecular motions and thereby reduce the possible energy loss via non-radiative relaxation channels. On the basis of the measured fluorescence and phosphorescence efficiencies and the lifetimes of the molecules, the radiative and non-radiative decay rates were calculated following the standard methods.<sup>[20]</sup> We found that the fluorescence radiation rate of DOPPMO is increased compared to PPMO (from  $1.6 \times 10^7$  to  $2.7 \times 10^7$  s $^{-1}$ ) and the fluorescence emission is blue-shifted, indicating that the intermolecular conjugation decreases and the S $_1$  energy level rises. Among the four examined compounds, the values of  $k_{\text{ISC}}$  are relatively low, but they are still good enough to guarantee sufficient ISC.<sup>[21]</sup> As shown in Table S4, both radiative and non-radiative decay rates of DOPPMO are lower than those of PPMO (from 2.95 to 0.08 s $^{-1}$  for  $k_r$ , from 38.55 to 2.12 s $^{-1}$  for  $k_{\text{nr}}$ ). According to the equation  $\tau = 1/(k_r + k_{\text{nr}})$ , the low  $k_r$  and  $k_{\text{nr}}$  values of DOPPMO are essentially accountable for its remarkable phosphorescence lifetime (Figure 3c).

To gain deeper insight into the origin of the ultralong phosphorescence lifetime of DOPPMO and DOPEO, time-dependent density functional theory (TDDFT) calculations were carried out. The calculated energy gap and SOC constants ( $\xi$ ) between the involved singlet and triplet states of PPMO and DOPPMO are shown in Figure S21. According to El-Sayed's rule, a small energy gap  $\Delta E_{\text{ST}}$  and large SOC are favorable for the ISC process. For DOPPMO, there is a large  $\Delta E_{\text{ST}}$  (0.07 eV) and a small SOC between S $_1$  and T $_n$ , so the ISC of DOPPMO is not as efficient as in PPMO. On the contrary, natural transition orbitals (NTOs) of T $_1$  were also





**Figure 3.** a) Single-crystal structure and molecular packing of PPMO and DOPPMO. b)  $\pi$ - $\pi$  interaction distances in PPMO and DOPPMO crystals. c) Natural transition orbitals of T<sub>1</sub> for PPMO and DOPPMO molecules in the crystals. d) (n,  $\pi^*$ ) configuration proportions (in %), oscillator strength  $f$ ,  $k_r$ , and  $k_{nr}$  of T<sub>1</sub> for PPMO and DOPPMO.

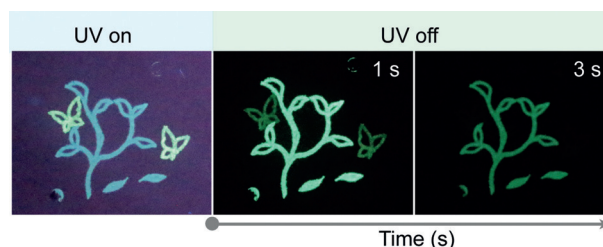
calculated to qualitatively describe the electronic configuration (Figure 3c). Notably, the (n,  $\pi^*$ ) components of T<sub>1</sub> drop from 10.68% in PPMO to 1.46% in DOPPMO, indicating that DOPPMO has a slower radiative decay rate ( $k_r$ ) than PPMO, since T<sub>1</sub> with a pure ( $\pi$ ,  $\pi^*$ ) configuration can show an extremely slow decay rate ( $10^0 \text{ s}^{-1}$ ). This was further confirmed by the hugely reduced oscillator strength  $f$  (factor 15) from PPMO to DOPPMO crystals, owing to the fact that  $k_r$  is proportional to  $f$ . It is thus speculated that the introduction of d- $\pi$  bonds to the phenothiazine system may significantly suppress radiative decay in the crystals, leading to a significant increase in the phosphorescence lifetime. To summarize, the introduction of d- $\pi$  bonds leads to a nearly pure ( $\pi$ ,  $\pi^*$ ) configuration of T<sub>1</sub> with an extremely slow decay rate, which may contribute to the UOP. The theoretical calculations and the experimental data agree well with the assumptions.

To explore the versatility of the d- $\pi$  bond introduction strategy, we investigated other types of phenothiazine derivatives, *N*-ethylphenothiazine (CzS-Et) and 10-ethyl-10*H*-phenothiazine-*S,S*-dioxide (DOP). It was found that DOP ( $\tau = 72 \text{ ms}$ ) shows a lifetime enhancement compared to CzS-Et ( $\tau = 4.56 \text{ ms}$ ) (Figures S25 and S26).<sup>[19a]</sup> This further demonstrates that the introduction of d- $\pi$  bonds plays a vital role in regulating the phosphorescence lifetime.

Given the remarkably different afterglow-time features, a primary application for data encryption was demonstrated. A pattern with two butterflies and one small sapling was fabricated, as shown in Figure 4. A blue sapling (made of DOPEO) and two green butterflies (made of PEO) are

clearly visible under 365 nm UV-lamp irradiation. When switching off the UV lamp, the complete pattern can be seen in the first 1 s. With passing time, only the small sapling remains visible. A persistent sapling shape was observed lasting for around 3 s, thus providing means to identify fraud.

In summary, a d- $\pi$  strategy was proposed to prolong the phosphorescence lifetimes of organic phosphorescent substances. The protocol was very simple and easy to realize by chemical modification. Among the compounds, the ultralong lifetime of DOPPMO increases by a factor of 19 to 455 ms with the introduction of d- $\pi$  bonds. DOPEO, with a record phosphorescent lifetime of up to 876 ms and a phosphorescence efficiency of 8.2%, was obtained under ambient conditions. Combining single-crystal analysis with theoretical simulations, we concluded that the d- $\pi$  bond not only reduces the (n,  $\pi^*$ ) contribution to the T<sub>1</sub> state, but also produces closer  $\pi$ - $\pi$  stacking and stronger intra- and inter-



**Figure 4.** Demonstration of the security protection application of PEO and DOPEO: Photographs taken under 365 nm UV light (left) and after ceasing the UV irradiation (right).

molecular interactions, leading to reduced radiative and non-radiative decay rates for ultralong phosphorescence. This result not only demonstrates the potential of d- $\pi$  bonds for prolonging organic phosphorescence lifetimes, but also extends the scope of metal-free organic phosphorescent substances.

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### Conflict of interest

The authors declare no conflict of interest.

**Keywords:** crystal engineering · d- $\pi$  bonds · excited states · organic phosphorescence · phenothiazines

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