Achieving amorphous ultralong room temperature phosphorescence by coassembling planar small organic molecules with polyvinyl alcohol

Wu, Hongwei; Chi, Weijie; Chen, Zhao; Liu, Guofeng; Gu, Long; Bindra, Anivind Kaur; Yang, Guangbao; Liu, Xiaogang; Zhao, Yanli

2019

Wu, H., Chi, W., Chen, Z., Liu, G., Gu, L., Bindra, A. K., Yang, G., Liu, X. & Zhao, Y. (2019). Achieving amorphous ultralong room temperature phosphorescence by coassembling planar small organic molecules with polyvinyl alcohol. *Advanced Functional Materials*, 29(10), 1807243-. <https://dx.doi.org/10.1002/adfm.201807243>

<https://hdl.handle.net/10356/137630>

<https://doi.org/10.1002/adfm.201807243>

This is the peer reviewed version of the following article: Wu, H., Chi, W., Chen, Z., Liu, G., Gu, L., Bindra, Anivind K., ... Zhao, Y. (2019). Achieving amorphous ultralong room temperature phosphorescence by coassembling planar small organic molecules with polyvinyl alcohol. *Advanced Functional Materials*, 29(10), 1807243. doi:10.1002/adfm.201807243, which has been published in final form at 10.1002/adfm.201807243. This article may be used for non-commercial purposes in accordance with Wiley Terms and Conditions for Use of Self-Archived Versions.

DOI: 10.1002/ ((please add manuscript number))

Article type: (Full Paper)

Achieving Amorphous Ultralong Room Temperature Phosphorescence by Coassembling Planar Small Organic Molecules with Polyvinyl Alcohol

*Hongwei Wu, Weijie Chi, Zhao Chen, Guofeng Liu, Long Gu, Anivind Kaur Bindra, Guangbao Yang, Xiaogang Liu, Yanli Zhao**

Dr. H. Wu, G. Liu, Dr. L. Gu, A. K. Bindra, Dr. G. Yang, Prof. Y. Zhao

Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, 21 Nanyang Link, 637371, Singapore

E-mail: zhaoyanli@ntu.edu.sg

W. Chi, Prof. X. Liu

Singapore University of Technology and Design, 8 Somapah Road, 487372, Singapore

Z. Chen

School of Computer Science and Technology, Donghua University, Shanghai 201620, China

Abstract: Development of novel strategies for achieving amorphous ultralong organic phosphorescence (UOP) at room temperature is highly desired. Herein, we report a simple approach by coassembling small organic molecules with polyvinyl alcohol (PVA) to afford amorphous UOP. These small organic molecules with planar conformation present quenched triplet state emission in excessive stacking solid state. When coassembling these molecules with PVA, their planar structures are well confined in coassembly films. Such confined environment leads to restricted molecular rotation and vibration, permitting these molecules to show stable triplet state and generate UOP. In control studies, corresponding structurally distorted molecules were also coassembled with PVA. However, they exhibit very weak or quenched UOP, since distorted structures with molecular rotation and vibration could easily dissipate the excitation energy in dilute film state. By employing this polymer confinement strategy, we further coassembled multicomponent luminescence dyes with PVA for multicolor luminescence displays, providing multicolor, uniform and flexible luminescence films. This work demonstrates a general strategy of employing small organic molecules to

coassemble with PVA to obtain amorphous UOP, which greatly expands the scope of organic molecules for developing simple but useful UOP films.

Keyword: coassembly, distorted molecules, flexible luminescence films, planar molecules, ultralong organic phosphorescence

1. Introduction

Ultralong organic phosphorescence (UOP) at room temperature is of great importance in emission events.^[1] Some artificial systems^[2-7] have been developed to realize UOP through the crystal engineering,^[8,9] host-guest interactions,^[10] polymer doping,^[11-14] and heavy atom effect.^[15] UOP is normally generated from crystal forms, since rigid crystal environment could protect the triple-state excitation and suppress the non-radiative relaxation pathways. For example, Tang *et al.* reported a series of organic molecules with crystallization-induced phosphorescence emission.^[16] Huang and co-workers developed an *H*-aggregation strategy in the crystal phase to achieve the crossing from single to triplet excited state for UOP.^[2] Liu *et al.* designed a red emission crystal with the UOP lifetime up to 0.748s for bioimaging.^[17] On the other hand, the crystal engineering is not applicable to all of the organic compounds capable of UOP, since (1) most of the organic compounds are difficult to grow stable crystals and (2) excessive intermolecular stacking in the solid state may weaken the emission, especially for molecules with aggregation-caused emission quenching (ACQ).^[18] The crystal engineering is more suitable for molecules with aggregation-induced emission or solid state emission to produce UOP. Consequently, it is still a challenge for developing molecules with non-aggregation-induced emission or solid state non-emission toward UOP.

Another way to develop the UOP systems is through doping or connecting organic molecules into rigid matrix that can increase intersystem crossing (ISC) effectiveness and suppress molecular motions for obtaining the UOP emission. For example, Fraser and co-workers coupled boron difluoride dibenzoylmethane with poly(lactic acid) to afford UOP materials.^[19] Recently, Ma *et al.* copolymerized acrylamide with different phosphors to acquire UOP polymers,^[20] whereas the cross-linked networks largely suppress the non-radiative transitions. Zhang *et al.* also developed an *N*-substituted naphthalimide polymer system with intramolecular charge transfer for emitting UOP under vacuum environment.^[12] Although these polymer systems could secure UOP, tedious synthesis is often required. Furthermore, the relationship between the doped molecules and polymer matrix is still

unclear. Therefore, it is necessary to conduct more extensive investigations using new strategies.

Since the coassembly strategy shows many advantages in developing advanced composite materials, it has been employed to prepare luminescent systems.^[21,22] Carbazole-based molecules as luminescent materials have been extensively studied.^[23,24] These compounds often show weak emission in the solid state due to their planar structures. When added with an electron acceptor to form the distorted donor-acceptor structure on the carbazole ring, the UOP could often be observed in the crystal state.^[2,25] Nevertheless, there is still no efficient way for planar carbazole molecules to emit UOP.

Figure 1. Schematic illustration of UOP processes by coassembling planar molecules with PVA. The coassembly could separate the planar molecules to avoid the excessive self-aggregation that often results in quenched emission. The PVA film also affords the rigid environment to protect the longtime T_1 to emit the UOP. As for the distorted molecules, the distorted conformation enhances the vibration and rotation as compared to corresponding planar molecules in the coassembly environment, showing weak or no UOP. Chemical structures of the planar and distorted molecules are exhibited. The symbol "<" is representative of less vibration and rotation of molecules on the left side than that on the right side in the coassembly environment.

Herein, coassembling planar carbazole molecules with polyvinyl alcohol (PVA) was developed to achieve amorphous UOP (Figure 1). Since PVA has a large amount of hydroxyl groups, it could form strong intermolecular hydrogen bonding interactions with compounds containing hydroxyl, amino and carboxyl groups.^[13] Hence, PVA could greatly suppress the vibration and rotation of these molecules than other polymers without active hydrogen bonding sites. A series of planar and distorted molecular structures were investigated, which have suitable energy gaps between the single and triplet states for ISC. Most of these molecules also contain O and N heteroatoms to trigger n- π transition for a large amount of triplet-excitation generation^[2] when they are in a rigid environment (Figure 1). In particular, when these planar carbazole molecules with PVA were coassembled, their planar structures were well protected in rigid coassembly films. The UOP was observed on account of weak molecular rotation and vibration in the confined environment with stable and long lifetime triplet state (Figure 1, UOP emission diagram). However, the UOP emission was quenched in the crystal state of these molecules due to the fact that planar conformation is easy to produce closed stacking with quenched emission.^[18] When adding a distorted group onto the carbazole structure or directly using corresponding distorted molecules, they showed weak or quenched UOP in the coassembly state, because the distorted structures could easily dissipate the excitation energy attributed to enhanced molecular rotation and vibration caused by distorted conformation in dilute state.

2. Results and Discussion

2.1. Luminescence properties of coassembly films

The photophysical properties of the coassembly films (PVA+**1**, PVA+**2**, and PVA+**3**) consisting of PVA and compounds **1**, **2** and **3** respectively were firstly investigated. The films with four ratios (0.1 mg, 0.3 mg, 0.5 mg, and 1 mg carbazole compounds mixed with 100 mg PVA) were prepared in order to obtain the best coassembly systems (Figures S1 and S2). These films showed the UOP after turning off the UV light under 254 nm (Figures 2a, S1, and S2). Since the films with 0.5 mg carbazole compounds exhibited the strongest emission, they were employed for subsequent studies.

Under the optimized conditions, these films could generate UOP for more than four seconds in the dark (Figures 2a and S2). Similar to some existing UOP molecules,^[1] these compounds also exhibited the fluorescence emission in a stable state (Figures 2b, S3, and S4). The phosphorescence spectra (Figure 2a) indicated that these three compounds showed different maximum emission wavelength (519 nm for **1**, 470 nm for **2**, and 525 nm for **3**).

These results proved the effect of different functional groups on the emission of carbazole compounds. Thus, different functional groups could influence the emission of carbazole compounds.^[15] More electron-donating hydroxyl group on compound **2** as compared to hydrogen on compound **1** and amino group on compound **3** would lead to the blueshift of the phosphorescence wavelength.

The excitation spectra were also recorded (Figures 2c and S5). Compounds **1** and **2** showed strong excitation intensity in the UV region reaching 450 nm. However, the intensity was weak in the visible region. Meanwhile, the compound **3** exhibited enhanced excitation in the visible region. To further study the UOP, the phosphorescent lifetime was determined (Figure 2d). Compound **2** showed the highest lifetime that was as high as 1.21 s (Figure 2d) under 460 nm emission wavelength. Then, the emission comparison between solid powder and coassembled films was carried out. The emission of **1**, **2** and **3** in the coassembled films exhibited obvious redshift as compared to that in the solid power state (Figures 2b, S3 and S4). The ultralong phosphorescent wavelength redshifts relative to the fluorescence wavelength in most of phosphorescent molecules.^[1] By combining with the lifetime study, the results suggest that the coassembly films could induce long phosphorescent emission.

As such, a series of planar carbazole molecules as UOP materials were achieved successfully. This UOP feature could be ascribed to noncovalent interactions between these organic molecules and PVA matrix in the coassembly, affording rigid environment for decreasing molecular rotation and vibration of the carbazole molecules and enhancing the ISC efficiency from S_1 to T_1 (Figure 1).^[13,14]

Figure 2. (a) Phosphorescent spectra of PVA+**1**, PVA+**2**, and PVA+**3** films at room temperature ($\lambda_{\text{ex}} = 320$ nm), respectively. Insets show the photographs of PVA+**1**, PVA+**2**, and PVA+**3** films (0.5 mg compounds **1**, **2** and **3** in 0.5 mL THF separately mixed with 100 mg/10 mL PVA) before and after turning off 254 nm UV lamp under ambient conditions. (b) Emission spectra of compound **2** in solid powder and coassembly film (0.5 mg PVA) under 280 nm excitation at room temperature. (c) Phosphorescent excitation spectrum of the PVA+**2** film under 470 nm emission. (d) Phosphorescent lifetime of PVA+**1**, PVA+**2**, and PVA+**3** films at room temperature, monitored at the emission wavelength of 500 nm, 460 nm and 525 nm, respectively ($\lambda_{\text{ex}} = 280$ nm).

2.2. Coassembly study

Transmission electronic microscopy (TEM) was employed to study the coassembly process. According to the literature reports,^[26,27] hydrophobic organic molecules with hydrophilic polymers could form the coassembled nano-aggregates through hydrophilic and hydrophobic interactions in water. The pure PVA showed regular sheet self-assembly (Figure 3a) when it was dried. Compound **2** was chosen as the study case because it has strong UOP emission. When adding 0.1 mg compound **2** in PVA solution, the surface of the coassembly aggregates showed a grid-like line distribution crossing the nanowires (Figure 3b), proving that the addition of compound **2** could partly destroy regular sheet assembly of PVA, and the assembled structures were more likely from the coassembly between compound **2** and PVA. The grid-like assembly became more obvious when adding 0.3 mg compound **2** with 0.5 mg PVA (Figure 3c,d), and showed some large aggregates at the intersection of nanowires. The coassembly nanoarchitectures turned out to be perfect in these two systems, as they showed strong emission (Figures S1 and S2). However, when adding 1 mg compound **2** in PVA, the grid-like structure became dim and many large block aggregates were formed (Figure 3e). Such excessive aggregation resulted in reduced phosphorescence emission (Figure S2). Compound **1** also showed similar coassembly trend (Figure S6).

Figure 3. TEM images of PVA films containing different concentrations of compound **2**: (a) PVA, (b) PVA+**2** (0.1 mg), (c) PVA+**2** (0.3 mg), (d) PVA+**2** (0.5 mg), and (e) PVA+**2** (1 mg). Scale: 500 nm. (f) ^1H NMR spectra of PVA (10 mg) in D_2O (1 mL), **2** (1 mg) in MeOD (0.5 mL), and PVA (5 mg) + **2** (1 mg) in a mixture of MeOD (0.5 mL) and D_2O (0.5 mL). (g) FTIR spectra of PVA, **2**, and PVA+**2** film. The PVA concentration is 1 mg/mL, the concentration of PVA+**2** is 5 mg of **2** mixed with 10 mL PVA solution.

The coassembly process was also demonstrated by ^1H NMR spectra in MeOD and D_2O (Figure 3f). The proton peaks appeared at 4.25–4.69 ppm derived from hydroxyl groups of PVA showed 0.15 ppm shift to low field after complexing with compound **2**. At the same time, the protons D and E of compound **2** also had a shift of 0.15 ppm. On the other hand, the protons B and C of compound **2** only showed 0.06 ppm shift, implying that the aromatic hydrogens near the hydroxyl group are more affected, and the hydroxyl group of compound **2** could form strong intermolecular hydrogen bonds with PVA after the complexation.^[28] The difference in the proton shifts proves the existence of the coassembly.

Additional evidence from FTIR spectra further confirmed the formation of coassembly between compound **2** and PVA in the film state. In FT-IR spectra, the peak of hydroxyl group at $3000\text{--}3700\text{ cm}^{-1}$ and C-N characteristic vibration peak of the carbazole ring at $1500\text{--}1600\text{ cm}^{-1}$ in coassembled film largely shifted as compared to respective compound **2** and PVA (Figure 3g). The C-H vibration peak around 3000 cm^{-1} exhibited a small shift. These results prove that hydrogen bonding interactions induce strong coassembly. Based on the TEM, NMR

and FTIR studies, a coassembly mechanism for obtaining organic UOP materials could be proposed. When coassembling a small amount of planar aromatic molecules with a large amount of PVA polymer, rigid nano-aggregates could be formed due to some intermolecular noncovalent interactions such as hydrophobic, hydrophilic, and hydrogen bonding interactions. The coassembly environment could isolate these organic planar molecules to avoid the unfavorable aggregation in solid or crystalline state. Moreover, the coassembly could effectively suppress the vibration and rotation of these organic molecules to promote the ISC process of S_1 to T_1 .^[12]

2.3 Systematic study of carbazole molecules for UOP

Three carbazole molecules (**1-3**) showed UOP emission. For profoundly revealing the luminescence mechanism, the conformational research is greatly needed. It is well known that carbazole molecules have planar conformation that prevents them to generate brightness emission in the solid state, while such planar molecules are easy to give strong emission in the solution state.^[18] The single crystal structures of compounds **2**, **3**, and **8** were determined by us, and the crystal data of other compounds were adopted from literature^[29-38] for the conformation analysis.

Figure 4. (a) Chemical structures, single crystal structures, and photographs (on and off under 254 nm UV light) of the carbazole molecules. Some single crystal structures were drawn based on literature data. Calculated S_1 - T_1 energy gap (ΔE_{ST}) of compounds (**1-6**) by TD-DFT. The unit is eV. (b) Emission spectra of compound **2** ($\lambda_{ex} = 270$ nm) in THF and THF/H₂O (10:90). The concentration is 100 μ M. (c) Emission spectra of compound **6** ($\lambda_{ex} = 270$ nm) in THF and THF/H₂O (10:90). The concentration is 100 μ M. (d) AIE emission spectra of compound **10** ($\lambda_{ex} = 270$ nm) in THF and THF/H₂O (10:90). The concentration is 100 μ M. The insets in (b-d) show the photographs of compounds **2**, **6**, and **10** in pure THF and THF/H₂O (10:90) under 254 nm UV light.

It could be seen from crystal structures that compounds **1**,^[29] **2** and **3** all showed planar conformation (Figure 4a). The emission of compound **2** in single molecule and aggregation states obviously reflects the nature of its planar structure (Figure 4b). The weak emission was observed in the aggregation state (in 90% water and 10% THF) on account of the planar conformation.^[18] These results show that the planar structure is a very important factor for UOP emission of these molecules. For proving our hypothesis, adding twisted groups on the carbazole skeleton for UOP was investigated in the coassembly state with PVA. Firstly, a benzene ring was introduced as the side arm to get compound **4**.^[30] The C-N bond between the benzene ring and carbazole ring is still in a common plane with the carbazole ring (Figure 4a). The benzene ring is perpendicular to the carbazole ring, making the molecule a certain degree of distortion. Although the compound **4** showed UOP emission (Figures 4a and S7), its emission intensity was weaker as compared to the film of compound **2** (Figures 4a and Movie S1), the difference could be confirmed by naked eye, and a small redshift of emission between film and solid states was also observed (Figure S8). Then, the quantum yields of these four compounds in the coassembly and solid powder states were tested (Table S1), and the quantum yield of compound **4** (12.0 %) was lower than that of compounds **1** (27.0 %), **2** (16.0 %), and **3** (23.7 %). It is also important to note that most of the coassembly films showed higher quantum yields as compared to the powder samples, suggesting that the coassembly films could provide enhanced emission efficiency. Then, compound **5** was obtained by adding a double bond as the side chain. It was hard for the double bond to freely rotate, resulting in twisted conformation^[31] for compound **5** (Figure 4a). As observed from its crystal structure, the double bond had a distorted angle with the carbazole ring, and this enhanced distortion was also proven by the decreased ACQ effect (Figure S9). When

coassembling it with PVA, the resulted film did not show UOP emission, although its powder emission was obvious (Figure S10).

Lastly, we investigated the influence of long alkyl side chains for UOP. Long alkyl chains can normally increase the flexibility of entire molecules and lead to a degree of distortion. Thus, we introduced six carbon alkyl chain to carbazole to afford compound **6** (Figure 4a). Since the single crystal structure of this compound was unable to achieve, the crystal structure of a very similar compound was employed for the analysis.^[32] Large distortion between the alkyl chain and the carbazole core was observed from the single crystal structure (Figure S11),^[32] showing the decreased ACQ effect (Figure 4c). As a result, the UOP was not observed for compound **6** (Figures 4a and S12).

It is well known that the phosphorescent emission is largely related to the singlet-triplet energy gap (ΔE_{ST}), and the ΔE_{ST} could be used to assess the trend of inter-system crossing process. Therefore, we investigated the S_1 - T_1 energy gap by the time-dependent density functional theory (TD-DFT) calculation (Figure 4a and Table S2). Compound **2** exhibited the smallest energy gap (0.54 eV), agreeing well with its bright emission as compared to other carbazole compounds. Compounds **1** (0.85 eV) and **3** (1.12 eV) showed larger energy gap than that of compounds **4** (0.79 eV), **5** (0.77 eV), and **6** (0.75 eV). Although these compounds showed large S_1 - T_1 energy gaps that often prevent the molecules to emit the phosphorescence, they still presented the UOP emission in the coassembly state, reflecting that the rigidity effect of the coassembly system could enable the molecules to conquer large bandgap to emit UOP in the film state. Therefore, it is believed that the distortion is the dominant factor in the UOP emission rather than the singlet-triplet energy gap (ΔE_{ST}) in these six compounds. These results manifest that the planar molecules are easy to generate the UOP when they are coassembled with PVA, while the corresponding distorted molecules are hard to acquire the UOP or only show weak UOP. The benzene ring in compound **4** has larger steric hindrance than the alkyl chain in compound **6**, restricting its free rotation unlike the alkyl chain. Therefore, the compound **4** could still emit UOP. According to the aggregation-induced emission (AIE) mechanism,^[18] distorted molecules tend to rotate and vibrate in dilute solution and induce strong non-radiation energy consumption, eventually leading to weak emission. On the other hand, restricted intermolecular rotation and vibration can reduce non-radiation energy consumption and enhance the emission intensity in aggregated or crystal state. Therefore, dilute supramolecular coassembly systems actually enhance the rotation and vibration of the distorted molecules as compared to their aggregated or crystal state, which is not conducive to the generation of a stable and long lifetime triple state. But for planar

molecules, the coassembly reduces non-radiation energy consumption as excessive intermolecular aggregation is suppressed. In this scenario, planar molecules are easy to generate stable and long lifetime triple state (see schematic mechanism in Figure 1).

Figure 5. Phosphorescent spectra of (a) PVA+7 film, (b) PVA+8 film, and (c) PVA+9 film at room temperature ($\lambda_{\text{ex}} = 320$ nm). Insets show singlet-triplet energy gap, single crystal, and photographs of compounds 7-9, respectively. (d) Single crystal, singlet-triplet energy gap and photographs (on and off under UV light) of compound 10. (e) Phosphorescent spectrum of PVA+11 film at room temperature ($\lambda_{\text{ex}} = 320$ nm). Insets show single crystal and photographs of compound 11. (f) Single crystal and photographs (on and off under UV light) of compound 12.

2.4 Extended systems for UOP

To confirm that luminescent planar molecules could easily coassemble with PVA for UOP, we investigated various organic molecules. Compound 7 showed planar conformation^[33] in its crystal state (Figure 5a). It emitted obvious blue UOP (Figures 5a, S13 and S14) with a lifetime of 0.24 s and quantum yield of 2.6%. We then synthesized compound 8, which had a similar structure (Figure 5b) to 7 but with longer alkyl chain. Although it has a long alkyl chain, to our surprise, it still exhibited planar conformation based on its crystal structure, emitting very weak UOP (Figures 5b and S15, Table S1). The reason behind the planar conformation might be that the benzene ring in compound 8 has smaller steric resistance to the alkyl chain as compared to the carbazole ring in compound 6. Therefore, it can be derived

that the long alkyl chain is able to freely rotate while weakening or quenching the UOP emission in dilute solid state. Compounds **7** (1.58 eV) and **8** (1.59 eV) with similar singlet-triplet energy gap (ΔE_{ST}) indicate that the alkyl chain is the dominant factor for their UOP emission (Figure 5a,b).

We also investigated other systems including planar biphenyl ring compounds **9** and **10**, molecule **11** with fused four benzene rings, and classic AIE molecule **12** having four benzene rings (Figure 5c-f).^[18] The planar conformation was found from the single crystal of compound **9**,^[34] and bright cyan UOP was observed (Figures 5c, S16 and S17) with a lifetime as long as 0.90 s and quantum yield of 9.4 %. However, when adding a double bond on the biphenyl ring to obtain compound **10**,^[35] the UOP from this distorted molecule (see its single crystal structure in Figure 5d) was not observed and it showed blueshift emission from powder to film states (Figure S18). Aromatic compounds containing such double bond often exhibit AIE property, which was confirmed by observing the emission spectra (Figure 4d) in single molecule and aggregated states of compound **10**. The AIE property suggests that the molecule is easy to consume the excitation energy through the vibration and rotation of the molecule in dilute film system, which is not conducive to produce the stable triplet state. For the large π conjugated planar molecule **11**,^[36] it exhibited obvious green UOP emission (Figures 5e and S19) with the quantum yield of 0.5 %. For classic AIE molecule **12** also having four benzene rings,^[37] it did not emit any UOP from the coassembly state (Figures 5f and S20), because its distorted conformation inevitably dissipated the triplet excitation energy in dilute state.

In terms of the ΔE_{ST} evaluation, the ΔE_{ST} value (Figure 5c,d) of compound **10** (0.35 eV) is much smaller than that of compound **9** (1.59 eV), indicating that the distortion is the dominant factor for UOP emission in this case. From these results, it was again confirmed that these compounds with planar conformation are easy to acquire the UOP emission when coassembled with PVA, while the corresponding distorted molecules are prone to show weak or quenched UOP emission.

2.5 Luminescence mechanism

Having investigated the extended systems for UOP, we verified the mechanism of suppressing vibration and rotation for UOP emission in the coassembly film, and used compounds **9** and **10** as representatives. Since increasing the temperature can enhance the vibration and rotation of molecules, the test temperature at 373K was employed for making a suitable vibration environment for these compounds. Indeed, the coassembly film of PVA+**9** showed a decrease

in the UOP emission intensity upon increasing the temperature to induce strong vibration and rotation (Figure 6a). Meanwhile, there was almost no change at the long wavelength region of the PVA+**10** film, which might be related to triplet emission that was difficult to detect (Figure 6b). These results suggest that the restriction of vibration and rotation could indeed induce the planar molecules to emit UOP in the coassembly film state even at room temperature, as PVA film could well protect the triplet state of the planar molecules. However, the protective effect was not obvious for distorted molecules, because the distorted molecules having more vibration and rotation at the dilute film state could hardly emit UOP at room temperature (Figure 6b). As a reference, the emission spectra of compounds **9** and **10** at 373K and room temperature in the powder state were also investigated. Quite weak reinforcement effect in the fluorescent region and no change at the phosphorescent area were observed (Figure 6c,d), indicating that the excessive aggregation was not conducive to the triplet emission for these molecules. Thus, these observations further support that coassembling the planar molecules with PVA is an efficient way to induce UOP at room temperature. Next, the UV-Vis spectra of compound **9** in dilute solution, coassembly film, and powder state were investigated (Figure 6e). As compared with the spectrum in dilute solution, a short redshift (11 nm) on the absorbance maximum and smooth curve indicate that compound **9** in the coassembly film is still in a weak stacking state, while the powder with dense molecular stacking presents rougher curve and larger redshift. Thus, the restriction effect of vibration and rotation occurs in the dilute solid state (*i.e.*, coassembly film) by coassembling the planar molecules with PVA.

Based on these photophysical studies, we proposed a mechanism for the UOP emission (Figure 6f) as follows. First, a large number of PVA could dilute a small amount of planar organic molecule and suppress their excessive stacking in the solid form. Next, multiple intermolecular interactions between them provide a regular environment to restrict the vibration and rotation of these small organic molecules even at room temperature. Effective ISC occurs when the small organic molecules have a suitable ΔE_{ST} . In particular, planar organic molecules containing O and N heteroatoms are easy to trigger the n- π transition for triplet-excitation generation.

Figure 6. Verifying the mechanism of the UOP emission. Emission spectra of (a) PVA+**9** film and (b) PVA+**10** film at different temperatures ($\lambda_{\text{ex}} = 320$ nm). Emission spectra of (c) **9** and (d) **10** powders at 298k and 373k ($\lambda_{\text{ex}} = 320$ nm). (e) Absorbance spectra of **9** in THF solution (10 μM), coassembly film state, and powder state. (f) Schematic representation to describe the UOP emission in dilute film state at room temperature by restricting the vibration and rotation. The “HT” represents high temperature, and “RT” represents room temperature.

2.6. Coassembled multiple components for multicolor luminescence

Compared to the crystalline materials for UOP, the coassembly systems showed more flexibility and processability. Especially, the coassembly systems could be mixed with a variety of dyes, so that multicolor display technology could be expected. Therefore, we coassembled multicomponent dyes for developing flexible multicolor display materials.^[38,39] We chose compound **9** and a yellow emission dye (**13**) with a short lifetime (< 0.5 ms) for the coassembly.^[40] The detailed fabrication procedure is outlined in Figure 7. First, the luminescence molecules were added into PVA aqueous solution (100 mg/10 mL), and homogeneous solution was obtained after ultrasonication for 20 min. Then, the film was obtained by pouring the solution into a petri dish followed by drying at 80 °C for 3 h.

Blue emission from the film was clearly observed upon exposure to 254 nm UV lamp (Figure 7b-d). Subsequently, the green emission was visible after turning off the UV light due to the existence of UOP emission. Next, we changed the excitation light source to 365 nm UV light for generating strong emission from the molecule **13**. In this case, blue and yellow mixed

emission was observed under 365 nm UV light (Figure 7b-d), making the luminescence color close to white light (Figure 7d) with the CIE coordinate of (0.26, 0.30). After turning off the UV light, no persistent emission was observed, because the 365 nm UV light with lower energy could not excite the UOP from compound **9** with short emission wavelength (Figures 7c and S17). Overall, three luminescence colors were achieved by simply coassembling these two compounds with PVA and adjusting the UV light wavelength. The obtained film showed good flexibility, exhibiting a great potential for the device fabrication.

Figure 7. Multicolor display fabrication. (a) Mixing compounds **9** (2 mg/2 mL in THF), **13** (1 mg/1 mL in THF) and PVA (100 mg/10 mL in water) followed by ultrasonication for 20 min. The solution was then poured into a petri dish. Finally, the flexible film was torn out from the petri dish. (b) Emission spectra of the film at excitation of 254 nm and 365 nm as well as phosphorescent spectrum after turning off the 254 nm UV light. (c) Photographs of the obtained films for multicolor display. The film displayed blue color under 254 UV lamp, and green color after the removal of the excitation source. The film showed blue and yellow mixed color under 365 UV lamp. (d) CIE 1931 chromaticity diagram at these different states.

3. Conclusion

In summary, a general strategy by coassembling planar organic molecules with water soluble PVA has been developed for amorphous ultralong room temperature phosphorescence. Planar molecules are prone to emit long lifetime phosphorescence through the formation of rigid coassembly environment, where the stacking between organic molecules is restricted in the polymer matrix. Since the molecular rotation and vibration are largely limited in the coassembly, stable triple state emission is permitted. For corresponding distorted molecules, the coassembly environment would increase the molecular rotation and vibration, thus weakening or preventing the emission of UOP. This study has provided a general guideline that what kinds of small organic molecules are suitable to coassemble with PVA to realize the UOP. Moreover, a multicomponent coassembly has been applied to develop multicolor luminescence displays. The flexible nature of the multicolor-tunable films has demonstrated a great application potential for the device fabrication. The present research might open up an avenue for developing coassembled systems toward the UOP emission capable of being applied in the areas of luminous sensing, display devices, and data security.

4. Experimental Section

Experimental procedures, fluorescence spectra and photographs, TEM images, calculated energy levels, and phosphorescent lifetime. CIF files for compounds **2**, **3**, and **8**.

Supporting Information

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

Acknowledgements

This research is supported by the Singapore Academic Research Fund (No. RG11/17 and RG114/17), the Singapore Agency for Science, Technology and Research (A*STAR) AME IRG grant (No. A1883c0005), and the Singapore National Research Foundation Investigatorship (No. NRF-NRFI2018-03).

Received: ((will be filled in by the editorial staff))

Revised: ((will be filled in by the editorial staff))

Published online: ((will be filled in by the editorial staff))

REFERENCES

- [1] S. Xu, R. Chen, C. Zheng, W. Huang, *Adv. Mater.* **2016**, *28*, 9920.

- [2] Z. F. An, C. Zheng, Y. Tao, R. F. Chen, H. F. Shi, T. Chen, Z. X. Wang, H. H. Li, R. R. Deng, X. G. Liu, W. Huang, *Nat. Mater.* **2015**, *14*, 685.
- [3] J. Yang, Z. C. Ren, Z. L. Xie, Y. J. Liu, C. Wang, Y. J. Xie, Q. Peng, B. Xu, W. J. Tian, F. Zhang, Z. G. Chi, Q. Q. Li, Z. Li, *Angew. Chem. Int. Ed.* **2017**, *56*, 880.
- [4] Y. Shoji, Y. Iwabata, Q. Wang, D. Nemoto, A. Sakamoto, N. Tanaka, J. Seino, H. Nakai, T. Fukushima, *J. Am. Chem. Soc.* **2017**, *139*, 2728.
- [5] Z. Y. Yang, Z. Mao, X. P. Zhang, D. P. Ou, Y. X. Mu, Y. Zhang, C. Y. Zhao, S. W. Liu, Z. G. Chi, J. R. Xu, C. Wu, P. Y. Lu, A. Lien, M. R. Bryce, *Angew. Chem. Int. Ed.* **2016**, *55*, 2181.
- [6] W. J. Zhao, Z. K. He, J. W. Y. Lam, Q. Peng, H. L. Ma, Z. G. Shuai, G. X. Bai, G. X. Hao, B. Z. Tang, *Chem* **2016**, *1*, 592.
- [7] S. Hirata, K. Totani, J. Zhang, T. Yamashita, H. Kaji, S. R. Marder, T. Watanabe, C. Adachi, *Adv. Funct. Mater.* **2013**, *23*, 3386.
- [8] Y. Y. Gong, G. Chen, Q. Peng, W. Z. Yuan, Y. J. Xie, S. H. Li, Y. M. Zhang, B. Z. Tang, *Adv. Mater.* **2015**, *27*, 6195.
- [9] Y. Y. Gong, L. F. Zhao, Q. Peng, D. Fan, W. Z. Yuan, Y. M. Zhang, B. Z. Tang, *Chem. Sci.* **2015**, *6*, 4438.
- [10] H. Chen, X. Ma, S. Wu, H. Tian, *Angew. Chem. Int. Ed.* **2014**, *53*, 14149.
- [11] Y. Su, S. Z. F. Phua, Y. Li, X. Zhou, D. Jana, W. Q. Lim, W. K. Ong, C. L. Yang, Y. L. Zhao, *Sci. Adv.* **2018**, *4*, eaas9732.
- [12] X. F. Chen, C. Xu, T. Wang, C. Zhou, J. J. Du, Z. P. Wang, H. X. Xu, T. Q. Xie, G. Q. Bi, J. Jiang, X. P. Zhang, J. N. Demas, C. O. Trindle, Y. Luo, G. Q. Zhang, *Angew. Chem. Int. Ed.* **2016**, *55*, 9872.
- [13] K. Jiang, L. Zhang, J. F. Lu, C. X. Xu, C. Z. Cai, H. W. Lin, *Angew. Chem. Int. Ed.* **2016**, *55*, 7231.
- [14] K. Jiang, Y. H. Wang, C. Z. Cai, H. W. Lin, *Chem. Mater.* **2017**, *29*, 4866.
- [15] S. Z. Cai, H. F. Shi, J. W. Li, L. Gu, Y. Ni, Z. C. Cheng, S. Wang, W. W. Xiong, L. Li, Z. F. An, W. Huang, *Adv. Mater.* **2017**, *29*, 1701244.
- [16] W. Z. Yuan, X. Y. Shen, H. Zhao, J. W. Lam, L. Tang, P. Lu, C. L. Wang, Y. Liu, Z. Wang, Q. Zheng, J. Z. Sun, Y. G. Ma, B. Z. Tang, *J. Phys. Chem. C* **2010**, *114*, 6090.
- [17] S. M. A. Fatemina, Z. Mao, S. D. Xu, Z. Y. Yang, Z. G. Chi, B. Liu, *Angew. Chem. Int. Ed.* **2017**, *56*, 12160.
- [18] Y. Hong, J. W. Lam, B. Z. Tang, *Chem. Soc. Rev.* **2011**, *40*, 5361.

- [19] G. Zhang, J. Chen, S. J. Payne, S. E. Kooi, J. N. Demas, C. L. Fraser, *J. Am. Chem. Soc.* **2007**, *129*, 8942.
- [20] X. Ma, C. Xu, J. Wang, H. Tian, *Angew. Chem. Int. Ed.* **2018**, *57*, 10854.
- [21] P. Xing, H. Chen, H. Xiang, Y. Zhao, *Adv. Mater.* **2018**, *30*, 1705633.
- [22] M. Zhang, M. L. Saha, M. Wang, Z. Zhou, B. Song, C. Lu, X. Yan, X. Li, F. Huang, S. Yin, P. J. Stang, *J. Am. Chem. Soc.* **2017**, *139*, 5067.
- [23] F. De Schryver, J. Vandendriessche, S. Toppet, K. Demeyer, N. Boens, *Macromolecules* **1982**, *15*, 406.
- [24] K. R. Justin Thomas, J. T. Lin, Y. T. Tao, C. W. Ko, *J. Am. Chem. Soc.* **2001**, *123*, 9404.
- [25] L. Gu, H. Shi, C. Miao, Q. Wu, Z. Cheng, S. Cai, M. Gu, C. Ma, W. Yao, R. Gao, Z. An, W. Huang, *J. Mater. Chem. C* **2018**, *6*, 226.
- [26] Q. Miao, C. Xie, X. Zhen, Y. Lyu, H. Duan, X. Liu, K. Pu, *Nat. Biotechnol.* **2017**, *35*, 1102.
- [27] H. Wu, Y. Zhou, L. Yin, C. Hang, X. Li, H. Ågren, T. Yi, Q. Zhang, L. Zhu, *J. Am. Chem. Soc.* **2017**, *139*, 785.
- [28] M. S. Kwon, D. Lee, S. Seo, J. Jung, J. Kim, *Angew. Chem. Int. Ed.* **2014**, *53*, 11177.
- [29] M. T. Reetz, S. Hütte, R. Goddard, U. Minet, *J. Chem. Soc. Chem. Commun.* **1995**, *2*, 275.
- [30] C. Avendaño, M. Espada, B. Ocaña, S. García-Granda, M. Díaz, B. Tejerina, F. Gómez-Beltrán, A. Martínez, J. Elguero, *J. Chem. Soc. Perkin I* **1993**, *2*, 1547.
- [31] X. Tian, W. Shi, K. Shen, C. Li, J. Lin, Y. Che, *J. Organomet. Chem.* **2006**, *691*, 994.
- [32] W. Q. Geng, G. Y. Xu, H. P. Zhou, *Acta Crystallogr. E* **2010**, *66*, 230.
- [33] R. Fausto, A. Matos-Beja, J. A. Paixao, *J. Mol. Struct.* **1997**, *435*, 207.
- [34] M. A. Jackisch, F. R. Fronczek, C. C. Geiger, P. S. Hale, W. H. Daly, L. G. Butler, *Acta Crystallogr. C* **1990**, *46*, 919.
- [35] Z. B. Yu, J. Sun, Z. T. Huang, Q. Y. Zheng, *CrystEngComm* **2011**, *13*, 1287.
- [36] F. Thébault, L. Öhrström, M. Haukka, *Acta Crystallogr. C* **2011**, *67*, 143.
- [37] A. Hoekstra, A. Vos, *Acta Crystallogr. B.* **1975**, *31*, 1716.
- [38] D. Li, F. Lu, J. Wang, W. Hu, X. M. Cao, X. Ma, H. Tian, *J. Am. Chem. Soc.* **2018**, *140*, 1916.
- [39] X. Wang, Y. Xu, X. Ma, H. Tian, *Ind. Eng. Chem. Res.* **2018**, *57*, 2866.
- [40] H. Wu, C. Hang, X. Li, L. Yin, M. Zhu, J. Zhang, L. Zhu, *Chem. Commun.* **2017**, *53*, 2661.

A general approach by coassembling planar small organic molecules with polyvinyl alcohol (PVA) to afford amorphous ultralong organic phosphorescence (UOP) is developed. When coassembling these molecules with PVA, their planar structures are well confined in rigid coassembly films, permitting these molecules to show stable triplet state and generate UOP. Further coassembling multicomponent luminescence dyes with PVA leads to multicolor, uniform and flexible luminescence films.

Keyword: coassembly, distorted molecules, flexible luminescence films, planar molecules, ultralong organic phosphorescence

Achieving Amorphous Ultralong Room Temperature Phosphorescence by Coassembling Planar Small Organic Molecules with Polyvinyl Alcohol

Hongwei Wu, Weijie Chi, Zhao Chen, Guofeng Liu, Long Gu, Anivind Kaur Bindra, Guangbao Yang, Xiaogang Liu, Yanli Zhao*

TOC Figure