



Robust single molecular white fluorescence facilitated by blocking aggregate growth in Densely-Woven solid polymeric network

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ABSTRACT

Single molecular white emissions are difficult to achieve owing to the challenges in delicately manipulating the intensity of complimentary emissions. Many emissive dyes display complimentary emissions in monomer and aggregated states, but the aggregate growth in solution or in solvent evaporating process always results in unstable white emission due to the formation of macrophases of the aggregates. Herein we report that by blocking the growth of the aggregate in the densely-woven solid polymeric network, the complementary monomer and aggregate emission can be firmly locked, so that ultra-stable single molecular white emission display excellence tolerance to humidity, water, organic vapors and extreme temperatures can be achieved.

1. Introduction

White-light emissive materials have attracted widespread attention due to their potential applications in next-generation displays and light devices [1–5]. To realize white-light emission, a popular and effective strategy is to combine several emissive components with complementary emission colors (blue/yellow or blue/green/red) [6–8]. However, such a multicomponent system often suffers from inevitable phase separation, and the components may display different color aging rates, which result in inhomogeneous and unstable luminescence [9].

To tackle these problems, single molecule white light emitters (SMWLE) have attracted intensive interests owing to the advantage of no phase separation, stable color preserving, and simple device fabrication procedure [4,5,10]. However, it is difficult to realize dual- or multi-emission bands in a single organic molecular emitter according to Kasha's rule [11,12]. Therefore, constructing organic SMWLE still remains challenging. Even so, scientists have successfully developed some smart alternative ways to realize SMWLE, such as creating two complementary emission parts in one molecule [13], designing molecules with two stable conformations displaying complementary emissions [14], or molecules with complementary monomer and multimers emissions [15–17]. Besides molecules with partial intramolecular energy/charge transfer [18–20], excited-state intramolecular proton transfer (ESIPT) [21,22], fluorescence and phosphorescence dual emission and dual phosphorescence are also designed as SMWLE materials.

Although the aforementioned strategies seem very promising, one may encounter a practical problem of matching the intensity of the

complementary emissions to obtain white emissions. This might be achieved with a tremendous energy and economic input through molecular design [10]. Actually, with the flourishing of aggregation induced emission (AIE), a vast number of dye molecules are found to display aggregation state dependent emissions [23–25]. Blue emission in monomer or twisted conformations whereas yellow ones in aggregates or planar conformations are often encountered [26,27]. This means that there exists a vast molecular library for white emissions. However, few of them have been reported to display white emission [28,29], either in solution or in solid states. The main reason is the difficulties to generate homogeneously distributed blue and yellow emission with comparable intensities but without phase separations at macroscopic level. In case of bad solvent triggered monomer to aggregate and twist to planar conformation transition in solution, the continuous growth of the aggregate would result in precipitates [30,31], which makes it impossible to generate stable homogeneous white emission. Similarly, if the dye molecule may have polymorphs in crystalline state that display complementary emissions, it is hard to obtain homogeneous white emissions due to the large size of the crystals [27]. Clearly, the bottleneck that prevents creating white emission by combining the complementary monomer and aggregate emission is to prevent the development of the aggregates into macroscopic ones. However, so far no such attempt has been reported.

Herein, we report the first example of creating white fluorescence by confining the initial aggregates displaying complementary emissions in the densely-woven polymeric network obtained with the strategy of solid phase molecular self-assembly (SPMSA) [32–37]. Water is the bad

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solvent for most AIE dyes. As the dye in good solvent is added into the aqueous solution of a polyelectrolyte (PE), its initial aggregates can be quickly sequestered in the process of precipitates triggered by mixing with an oppositely charged polyelectrolytes. Because molecules or small particles cannot migrate freely in solid phases, and the densely-woven PE networks have strong space confinement effect to the dye, the initial aggregates would not grow further, which thus prohibit the small particles from growing into macroscopic phases. As a result, the complementary emission would remain stable with time. In this way, by controlling the dye doping amount to manipulate the molar ratio between the dye molecules in the monomer and aggregates, white emission can be achieved facilely. We show that this is a general strategy leading to finely controlled emissions. In addition, the densely-woven polymeric network also acts as a shield to endow the white emission with superb tolerance to humidity, water, temperature and organic vapors, making it possible to offer stable white light in various severe environment.

2. Materials and experiments

2.1. Preparation of the densely-woven solid polymeric film

Anionic polyacrylamide (PAM, Mw ~ 12,000,000) was purchased from Sangon Biotech. polyhexamethylene biguanidine hydrochloride (PHMB) was purchased from Bide Pharmatech Ltd. The experimental water was ultra-pure water (Milli-Q water) with a resistivity of 18.2 MΩ · cm obtained by a Millipore ultra-pure water machine. An aqueous solution of PHMB and an aqueous solution of PAM was added, reaching final concentrations of 50 mM for the ammonium positive charges of PHMB and 50 mM for the carboxylate negative charges of PAM. White precipitates were immediately formed after mixing. The collected precipitates were then treated in two parallel ways: subjected to a pressure imposed by finger pressing and noodle machine manufacturing under ambient environment.

2.2. Dye doping into the polymeric film

Y5 is a commercial dye from Bodagelin Chemicals, Beijing, with the purity being 99.9 %. Doping of Y5 into the PAM-PHMB film is carried out by injecting the 2 mM Y5 NMP solution into the PAM aqueous solution, then mixed with the aqueous solution of PHMB. The precipitates is pressed and thoroughly dried in a desiccator before fluorescence measurements.

2.3. Stored under different conditions

The dried PAM-PHMB@Y5 film is stored in the required atmosphere (different volatile organic compound) or different relative humidity until the fluorescence spectrum is measured.

2.4. Fluorescence measurement

The fluorescence spectrum, fluorescence lifetime, and quantum yield were all given by the Edinburgh Instruments Limited FLS980 steady-state transient fluorescence/phosphorescence spectrometer (77–500 K).

2.5. Theoretical calculation

The internal stored 6-311G** basis set of Gaussian 16 program at the pbe0 level functional was used to optimize and calculate the frequencies of the stable configurations of Y5. S₀, S₁ and T₁ states were calculated at pbe0/6-311 g* level with TD method within and without water.

2.6. CIE coordinates calculation

The corresponding Commission Internationale de l'Éclairage (CIE)

chromaticity coordinates are calculated and plotted using normalized fluorescence spectrum.

2.7. SEM observation

Add one drop of Y5 solution with different NMP/water ratio on the silicon surface and observe it through scanning electron microscope (SEM) after drying. Experimental parameters: The voltage is 1.0 kV and the current is 5uA.

2.8. IR measurement

PAM-PHMB@Y5 is pressed on the diamond surface to obtain the corresponding infrared vibration information through Fourier transform attenuated total reflection infrared spectroscopy (FT-ATR-IR).

3. Results and discussions

3.1. The luminescence properties of Y5 molecule

We choose a commercially available yellow fluorescence molecule with sulfonamide bond and ester group, Y5, as a SMWLE candidate (Fig. 1a, S1). Y5 displays blue emission in its good solvent NMP. Upon addition of poor solvent water into the NMP solution of Y5, Y5 precipitates quickly as the fraction of water exceeds 50 % with the blue fluorescence of Y5 decreases gradually, and a yellow emission occurs after increasing the water fraction (Fig. 1b). Spectra measurements reveal that Y5 gives merely blue emission at the water fraction below 30 %, and this emission was completely replaced by the yellow emission at 555 nm at the water content of 90 % (Fig. 1c, S2). SEM observation reveals that the particle size increases significantly and finally becomes precipitates, which is in line with the AIE behavior of Y5. (Figure S3) Control experiments indicate that the blue emission is from the B1 part of the Y5 molecule, whereas the yellow emission is from the Y1 part (Fig. 1d and Fig. S4a-b). The CIE coordinates of the two-luminescence of Y5 is just on the opposite side of the pure white emission, indicating the possibility of generating white emission with the single molecule of Y5 (Fig. 1e). However, it is difficult to obtain stable white emission through adjusting the volume ratio of the mixed solvent since Y5 will precipitate slowly (Fig. S4c). Similarly, doping Y5 into polymer films by solvent evaporating will result in separated blue and yellow emission spots instead of homogeneous white emission (Table S1 and Figure S5). This inspires that the key leading to homogeneous white emission is to inhibit the unlimited growth of the Y5 aggregates. Obviously, both the solution and slow solvent evaporation process could not achieve this goal.

3.2. The realization of white fluorescence of Y5 in the densely-woven solid network of PAM-PHMB

Considering solid phase is much effective in preventing molecular migration, next we decide to quench the growth of the initial Y5 aggregates utilizing the solid-phase molecular self-assembly (SPMSA) strategy recently developed in our lab [32–37]. Since SPMSA starts from the aqueous precipitates of oppositely charged molecules, target molecules can be deposited into the SPMSA facilely through coprecipitation. Herein, the precipitates were generated by mixing the aqueous solutions of cationic polyelectrolyte polyhexamethylene biguanide hydrochloride (PHMB) and anionic polyacrylamide (PAM). Since the Y5 in NMP had been pre-injected into the PAM solution just before mixing the two polymer solutions, a fluorescent film was obtained by condensing the precipitates under a mild mechanical pressure of 5 MPa (Fig. 2a). The film was dried in a desiccator overnight before fluorescence measurement.

It is happy to find that the film displays homogeneous fluorescence at various Y5 doping (Fig. 2b), and the overall fluorescence color changes from blue to yellow with increasing the doping amount of Y5. No

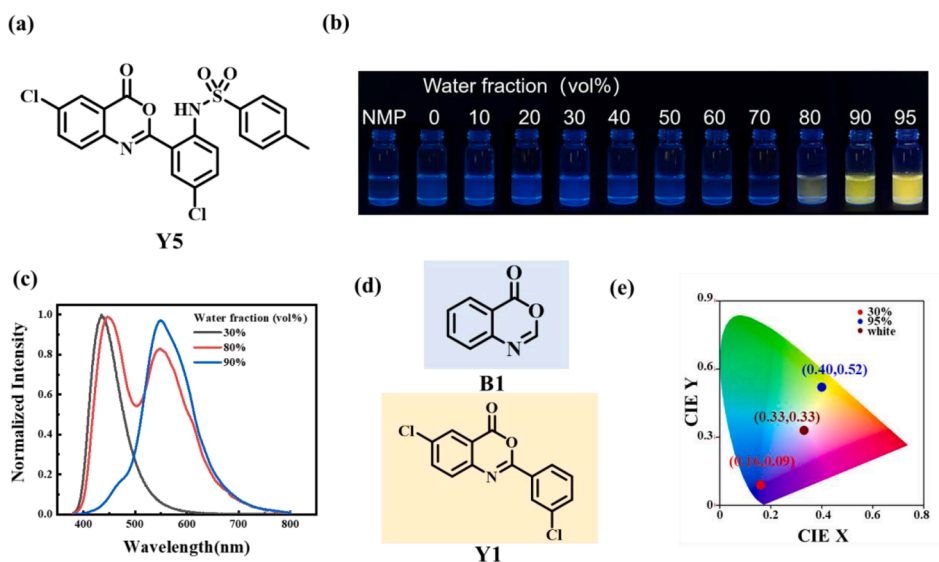


Fig. 1. (a) Molecular structure of Y5. Photos (b) and normalized fluorescence spectrum (c) of Y5 in mixed solvent of NMP and water with different ratio. (d) Molecular structure of blue emission part, B1 and yellow emission part, Y1. (e) CIE coordinate of blue and yellow emission of Y5 and its possibility for single molecular white emission.

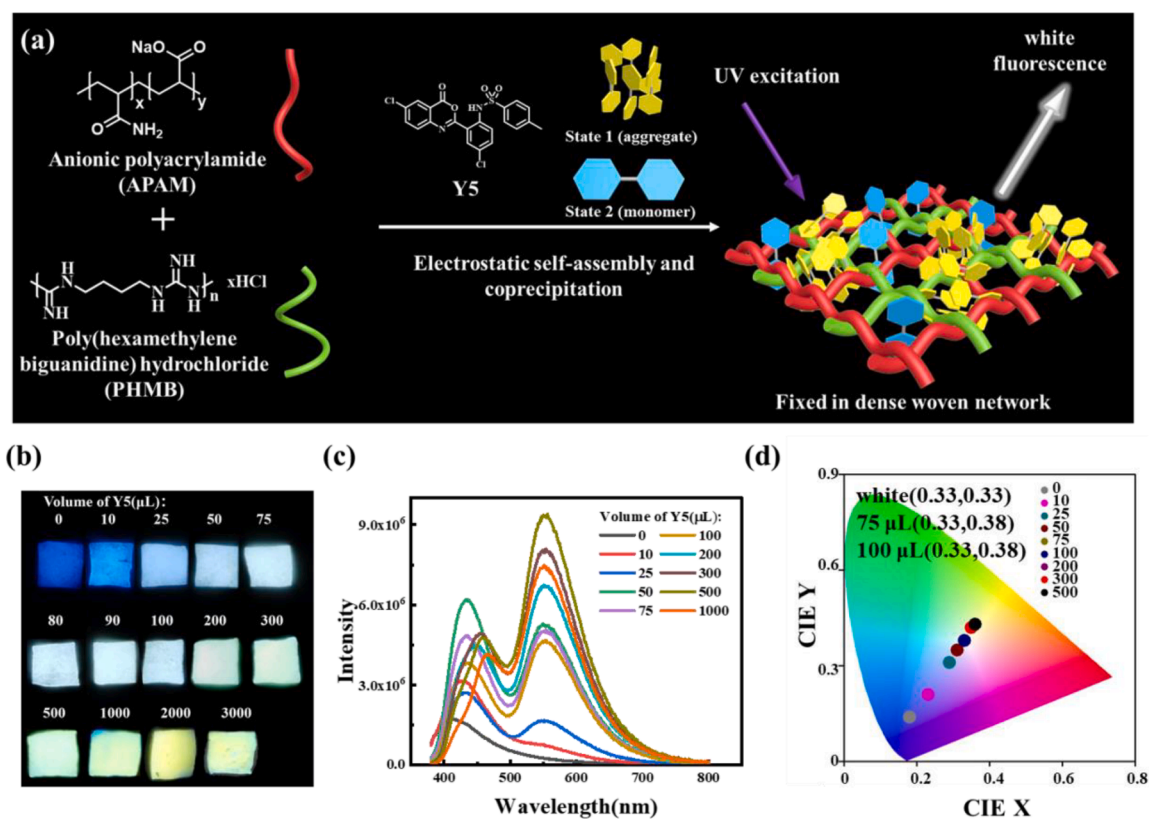


Fig. 2. (a) Preparation method for PAM-PHMB@Y5 with the principle for realizing different luminous colors. Fluorescent photos (b), fluorescence spectrum (c) and CIE coordinates (d) of PAM-PHMB@Y5 with different doping amount.

separated yellow or blue emission dots are observed, indicating the growth of the Y5 aggregates has been successfully prohibited. It is noticed that white emissions can be obtained by simply controlling the amount of doped Y5 in the film. Spectra measurements revealed that at low Y5 doping rate, the film gives blue emission at 430 nm, while the yellow emission appears gradually with increasing the Y5 doping. This indicates that the fraction of aggregated Y5 molecules are increasing

with increasing concentration. At the Y5 volume of 50 ~ 100 μl, the intensity of the blue and yellow emissions is comparable (Fig. 2c). The CIE coordinates for the white fluorescence is (0.31, 0.35), (0.33, 0.38), and (0.33, 0.38) obtained at 50, 75, and 100 μl Y5 solution, respectively (Fig. 2d), which are all in the close vicinity of pure white emission of (0.33, 0.33). The fluorescence quantum yield for the white-emitting film is 26.64 %, which is significantly higher than the $\phi_f = 1.28\%$ for Y5 in

NMP solution. Clearly, the Y5 molecules have been immobilized in the PHMB-PAM film, which have restricted the nonradiative pathways resulted from thermal motion.

3.3. Mechanism of electrostatic densely-woven network in regulating dual conformation white fluorescence

To unravel the origin of the 430 and 550 nm emission in the film, (TD)-pbe0/6-311G* calculations were implemented to study the conformation and energy level structure of Y5. The calculation (Fig. 3a) shows that Y5 has two stable molecular conformations. When the hydrogen atom in sulfonamide bond forms intramolecular hydrogen bond with ester bond, Y5 molecule stay in a planar state with dihedral angle of $1-1'-2'-2''=5.97^\circ$. On the contrary, when no intramolecular hydrogen bond possesses in Y5, the molecular structure becomes more distorted with dihedral angle 33.75° .

Fig. 3b showed that the frontier molecular orbits of Y5 in different states are all concentrated on the red highlighted part, which indicates that the toluene group on the other side of the sulfonamide bond does not participate in the emission behavior. Further analysis of the electron cloud density distribution in HOMO and LUMO shows that when Y5 exists in dispersed state, such as in good solvent NMP, intramolecular hydrogen bond is formed with shorter blue fluorescence emission. With the addition of poor solvent, Y5 gradually aggregate, and the intramolecular hydrogen bond breaks. Frontier orbital calculation and the corresponding maximum fluorescence emission obtained through theoretical calculations confirm that the delocalization degree of the electron cloud gradually expands in this process, causing the red shift of the emission color. (Table S2).

Based on the above analysis, we infer that in the dense network of PAM-PHMB, Y5 shows a similar performance. At low concentrations, Y5

mainly exists in the form of single molecules with intramolecular hydrogen bonds, which displays bright blue emission. However, with increasing the doping amount, Y5 starts to aggregate, and the intermolecular interactions becomes dominant, which yields yellow fluorescence.

The existence of the two conformations can also be confirmed by IR spectra. Shown in Figure S6, the peak of 1665 cm^{-1} corresponds to the vibrating absorption of N—H in sulfonamide bond, while the peak at 1775 cm^{-1} corresponds to the ester bond. In Y5 powder, Y5 exists in aggregate form with strong intermolecular force, thus Y5 mainly maintain in the form with intermolecular hydrogen bond. In this situation, the N—H in sulfonamide bond will form hydrogen bonds with multiple nearby molecules at the same time, causing the decrease of the dipole moment and the absorption intensity. Meanwhile, the ester bond has higher relative intensity because of the conjugation effect. On the contrary, when doped in the polymer network, Y5 exists in the dispersion form. N—H of sulfonamide bond forming intramolecular hydrogen bond with carbonyl group of ester bond. The number of hydrogen bonds for each N—H in sulfonamide bond decreases, causing the increase of the dipole moment and the vibration frequency. As a result, the characteristic absorption increases while moving to a lower wavenumber. For carbonyl group in ester bond, the conjugation effect is weakened, dipole moment is reduced, and characteristic absorption intensity is weakened, because of the participating in hydrogen bond. With the increase of the doping amount, the Y5 aggregate and its characteristics shown in infrared spectrum are gradually close to that of Y5 powder. TEM observation also reveals that the PAM-PHMB densely-woven solid network has tiny meshes about 1 nm, which is smaller than the size of Y5 molecule (Figure S7). Therefore, as Y5 is doped in the network via coprecipitation, it will be entrapped by the network firmly. The above effect cooperatively prevents the aggregation of Y5 in the PAM-PHMB

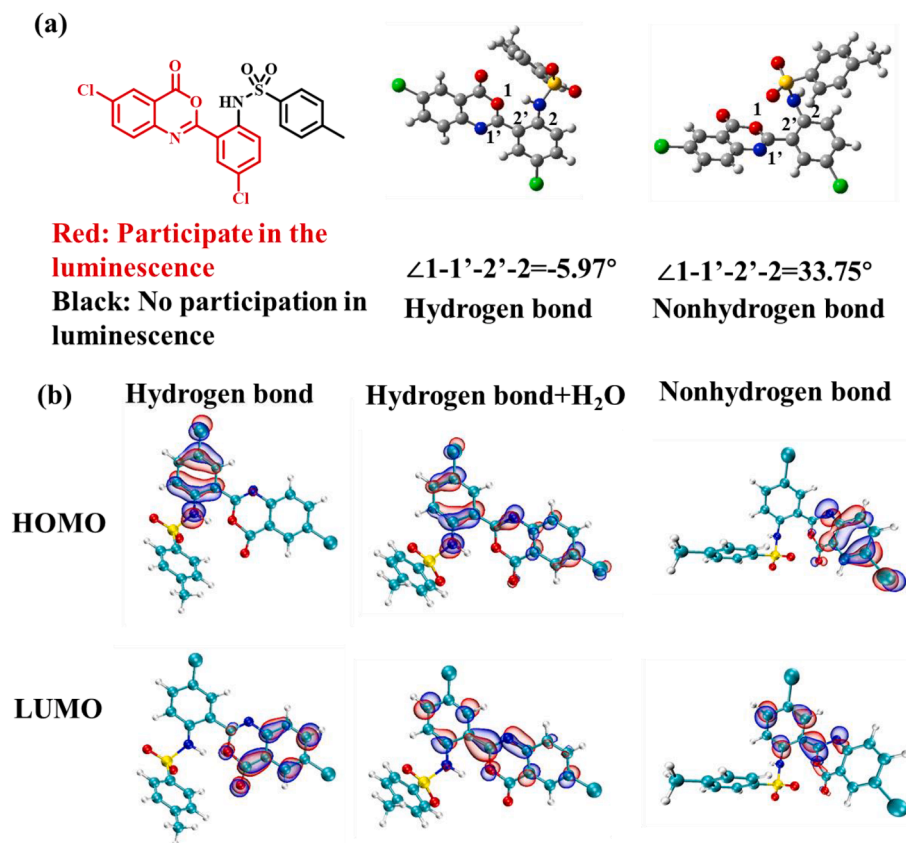


Fig. 3. (a) Two different conformations of Y5 with corresponding dihedral angles. (b) Calculated HOMO and LUMO for Y5 with intramolecular hydrogen bond, additional H₂O as surroundings and without intramolecular hydrogen bond.

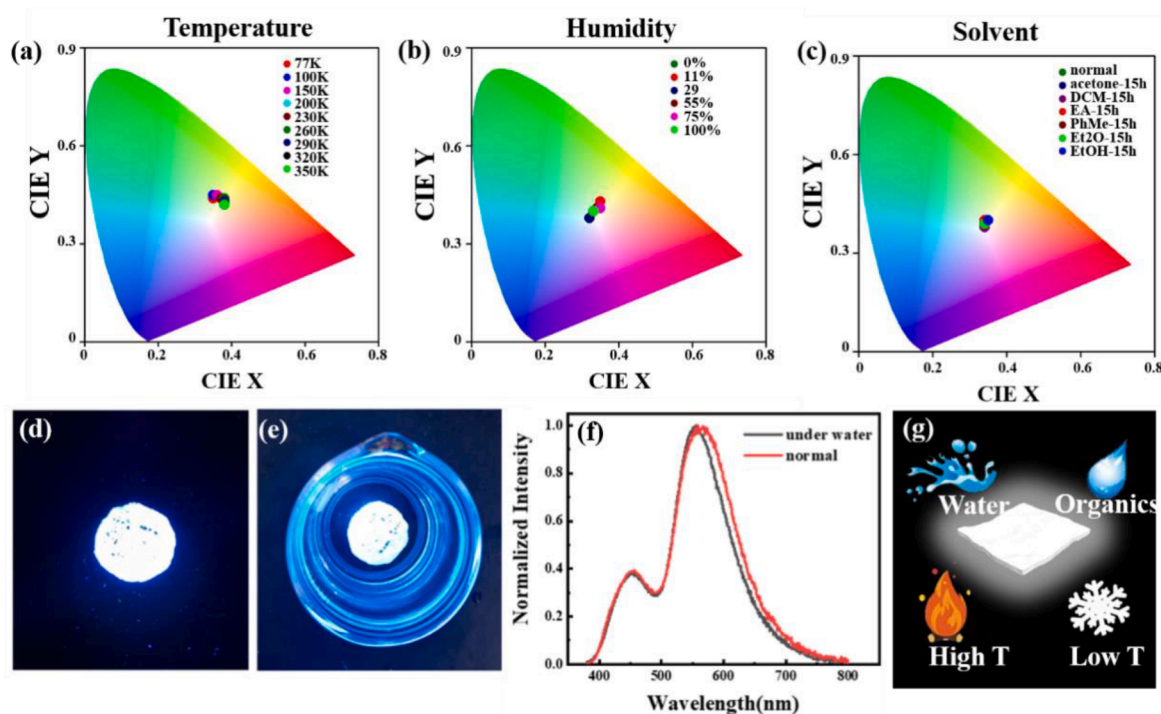


Fig. 4. CIE coordinates for PAM-PHMB@Y5 under different temperature (a), humidity (b) and organic solvent atmosphere (c) shows excellent stability. (d-e) photos of the white light emitting film of PAM-PHMB@Y5 under normal storage condition (d) and underwater (e), and (f) is the corresponding fluorescence spectrum. (g) Possible application of PAM-PHMB@Y5 as a high tolerant emitting material suitable for the usage under extreme conditions.

network and realizes single molecule white fluorescence.

3.4. Stability and application of white emitting solid material

The solid PAM-PHMB films not only restricts the growth of the initial Y5 aggregates, but also offers robust long-term emission stability. Usually, the emission of organic dyes can be easily influenced when exposed to organic solvent, increased temperature, and increased environmental humidity. However, the white emission is so stable that no detectable luminous color change has been observed as the film is placed in those environments (Fig. 4a-c and Table S3-S5).

Based on the super stability, environmental tolerance, and high quantum efficiency, PAM-PHMB@Y5 can be used as the next generation of white emitting materials, especially in special environments, such as underwater (Fig. 4d-f), extreme temperature, organic volatiles and humidity environment (Fig. 4g, S8).

4. Conclusion

In summary, we successfully obtained robust SMWLE using the strategy of solid-phase molecular self-assembly to block the aggregate growth of potent single molecular white emissive dye. The dye monomer displays blue emission while its aggregates display yellow emission. Under solution or solvent evaporating conditions, the aggregates would grow continuously so that the system displays inhomogeneous yellow and blue emission. Upon blocking the molecular migration in solid phase, the dye aggregate would not grow and the ratio between the monomer and aggregate can be accurately controlled, which finally leads to white emission. Since the solid phase is composed of the densely-woven polymeric network formed by strongly interacted polyelectrolyte chains, it not only serves as a platform for white fluorescence regulation by firmly confine the molecular states of the dye, but also serves as a protective shield to offer robust emissions against fluorescence quenching from volatile vapors, water, humidity, and severe temperature conditions. We anticipate the current strategy allows to obtain

a series of SMWLE with high-efficiency and high environmental tolerance.

CRediT authorship contribution statement

Tongyue Wu: Writing – original draft, Methodology, Investigation. **Jiachen Guo:** Writing – original draft, Investigation, Methodology. **Jianbin Huang:** Investigation, Methodology. **Yun Yan:** Writing – review & editing, Supervision, Conceptualization.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Yun Yan reports financial support was provided by Peking University.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cej.2022.140974>.

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