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The endeavor of vibration-induced emission (VIE) for dynamic emissions

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Organic chromophores with large Stokes shifts and dual emissions are fascinating because of their fundamental and applied interest. Vibration-induced emission (VIE) refers to a tunable multiple fluorescence exhibited by saddle-shaped *N,N'*-disubstituted-dihydrobenzo[*a,c*]phenazines (DHPs), which involves photo-induced configuration vibrations from bent to planar form along the N–N axis. VIE-active molecules show intrinsic long-wavelength emissions in the unconstrained state (planar state) but bright short-wavelength emissions in the constrained state (bent state). The emission response for VIE-active luminogens is highly sensitive to steric hindrance encountered during the planarization process such that a tiny structural variation can induce an evident change in fluorescence. This can often be achieved by tuning the intensity ratio of short- and long-wavelength bands. In some special cases, the alterations in the emission wavelength of VIE fluorophores can be achieved step by step by harnessing the degree of bending angle motion in the excited state. In this perspective, we summarize the latest progress in the field of VIE research. New bent heterocyclic structures, as novel types of VIE molecules, are being developed, and the general features of the chemical structures are also being proposed. Technologically, novel emission color-tuning approaches and VIE-based probes for visualizing biological activity are presented to demonstrate how the dynamic VIE effect can be exploited for cutting-edge applications.

1. Introduction

Shedding light on the fluorescent mechanisms of chromophores with large Stokes-shifted and dual emissions is of great significance, as it could provide reliable guidance for the development of high-performance multi-colour emission materials.^{1–10} As shown in the Jablonski diagram in Fig. 1a, the dual bands of an individual fluorophore can generally be divided into small (normal) and large (abnormal) Stokes-shifted emissions.^{11–13} The overlap of the normal short-wavelength emission with the lowest-lying absorption band originates from the initial emissive state near the Franck–Condon excited state, while the red-shifted emission far from the absorption band arises from the structurally transformed emissive state formed by additional excited-state transformations, such as enhanced charge transfer,^{14–19} energy transfer,^{20–25} complex formation,^{26–31} and structural and/or conformational changes.^{32–55} Due to the significant configurational and/or structural changes in the excited state, the ratio of short- and long-wavelength bands can be manipulated in a controllable and dynamic manner, activating unprecedented multi-colour luminescence.^{9,56–61}

Regarding the specific π -conjugated structures and luminescent mechanisms, scientists have made notable achievements with intriguing systems and concepts, such as the excimer/exciple,^{26–28,30,31} fluorescence resonance energy transfer (FRET),^{20–25} twisted intramolecular charge transfer (TICT),^{48–55} and excited-state intramolecular proton transfer (ESIPT).^{36–42} Most of the mechanisms originate from the accidental discovery of a specific fluorescence phenomenon,^{62–73} after which the excited-state dynamics and the structure–property relationships were extensively studied and well established. These discoveries have been regarded as guidelines for exploring a range of applications. A self-contained luminescence system/concept can be constructed (Fig. 1b)^{50,65} that includes: (1) basic building blocks with common characteristics, (2) unique excited-state processes, and (3) amazing properties and functions that have not been achieved by other luminescence systems. A well-known example of a dual-emission system based on a unimolecular reaction is the TICT concept,⁵⁰ for which Grabowski and co-workers formulated a structural hypothesis based on the molecule *N,N*-dimethylaminobenzonitrile (DMABN) in 1973.⁷⁴ Donor and acceptor moieties linked by single bonds build typical TICT molecules. Upon photoexcitation, the TICT molecules are involved in rapid electron transfer from the donor to acceptor units, accompanied by mutually perpendicular donor and acceptor round the single bond. The TICT process is highly dependent on the polarity and viscosity of the solvent, so TICT fluorophores hold

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Fig. 2 (a) Chemical and crystal structure of *N,N'*-diphenyl-dihydrobenzo[*a,c*]phenazines (DPAC), together with their structural characteristics. (b) Diagrammatic sketch illustrating the vibration-induced emission (VIE) involving a photo-induced configuration vibration from bent to planar form along the flexible N–N axis, driven by excited-state aromaticity reversal. (c) Steady-state emission spectra at room temperature in solvents with different polarities. (d) Temperature/viscosity dependent emission spectra of DPAC in *n*-butanol from 233 K to 133 K. (e) Chemically-locked structures with tunable excited states. (f) *ortho*-Methyl effect induced tunable ground states. Reproduced from ref. 79 (c and d) and ref. 95 (e) with permission from the American Chemical Society, Copyright 2015 and 2017. Reproduced from ref. 97 (f) with permission from the Wiley-VCH, Copyright 2018.

regulate the ground-state geometry of DPAC from a bent to a planar configuration step by step (Fig. 2f).⁹⁷

This accidental discovery is turning into a sustainable achievement. In this perspective, we aim to highlight the noticeable progress in VIE-active luminogens over the past year, including (1) novel bending heterocyclic cores for the molecular library of the VIE system, (2) new strategies for dynamic emission colour changes and real-time functions, (3) applications as biological probes, and (4) excimer formation of a VIE-active luminogen in a crystal. We also discuss the present pros and cons of the VIE system and look forward to its further development.

2. Designing new bending heterocyclic cores for the VIE molecular family

DPAC, acting as the most typical DHP core, has been widely utilized in VIE research (Fig. 3a).⁸⁴ However, such a monotonous structure greatly restricts the development of VIE research both fundamentally and in applications. Therefore, there is an urgent need to exploit new VIE cores. To meet this requirement, replacing the *N*-phenyl groups by other heteroatoms with lone electron pairs has been the primary consideration, for which

the aim has been to retain the central core as a flexible 8 π -electron ring (Fig. 3a). Additionally, according to our previous research on DHPs, the steric hindrance between the phenanthrene moiety and *N*-substituted aryl groups plays a key role in the VIE process (Fig. 3a). Based on this perspective, a series of



Fig. 3 (a) General characteristics of VIE-active molecules. (b) Chemical structures of PNO, PNS and PNSe as novel kinds of VIE-active molecules and reference compound PNC. (c) Absorption and emission spectra in various solvents at room temperature. Reproduced from ref. 98 with permission from Wiley-VCH, Copyright 2019.



DHP derivatives were designed and synthesized, in which one of the *N*-aryl groups was replaced by an O (PNO), S (PNS), or Se (PNSe) atom and dimethyl-methanediyl (PNC) (Fig. 3b).⁹⁸ As a result, these three compounds exhibited ultraviolet lowest-lying absorption bands located at 330–400 nm and strongly bathochromic shifted emissions at 465, 555, and 570 nm, with corresponding large Stokes shifts of 7906, 11 480, and 11 955 cm⁻¹ (PNO < PNS < PNSe, see Fig. 3c), respectively. The order of the Stokes shifts resulted mainly from the better polarization of the S and Se atoms than that of the O atom, which could extend the π -conjugation of the global minimum state (*i.e.* planarization state) and thus narrow the energy gap. Notably, there was a negligible emission band at 429 nm in PNSe, which was very similar to that in DPAC, indicating a pronounced VIE characteristic. In contrast, PNC only exhibited a normal emission band at 417 nm with a Stokes shift of 5313 cm⁻¹ since the elongated π -conjugation of PNC was interrupted by the non-conjugated bridge CMe₂. The steady-state results combined with further time-resolved and computational data proved the ubiquity of VIE in DHP derivatives and provided a sufficient theoretical basis for the development of new VIE cores.

By further exploring the relationship between the photoinduced structural planarization and steric hindrance, phenothiazine derivatives were chosen for further study due to their similar structures to those of DHPs and potential applications in bioimaging. Therefore, we developed a series of new compounds NAS, NAS-1, and NAS-2 (Fig. 4a).⁹⁹ According to X-ray analysis of the three compounds, the order of the bending angles (Θ_a) in the phenothiazine moiety was NAS (152.08°) > NAS-1 (147.89°) > NAS-2 (131.12°). Notably, the *N*-phenyl showed a perpendicular orientation to the phenothiazine core in NAS and NAS-1 but a parallel orientation in NAS-2. These results could safely demonstrate that the bent angle Θ_a in NAS-2 was derived from the hindrance between the naphthalene ring and *N*-phenyl. Further proof could also be obtained from the steady-state spectra (Fig. 4b). NAS and NAS-1 showed coincident onset (purple circles), which was consistent with the

characteristics of normal emission. However, NAS-2 showed a distinct separated onset (blue and red circles), which was the same as the absorption and emission of DPAC. This separation indicated that NAS-2 possessed different configurations from the initial ground state to the final S₁ state. Accordingly, it was concluded that there was indeed a VIE phenomenon, similar to that of DHPs, in NAS-2, which was further demonstrated by the time-resolved data and computational approaches. This work established a clearer relationship between the VIE and steric hindrance and facilitated the design of VIE cores, which greatly extended the application of the VIE mechanism.

The two studies mentioned above indicated that steric hindrance plays an important role in the dual emission in the VIE cores. However, what is the real driving force behind the photoinduced structural planarization process?⁸² Such a structural relaxation was reported for the conjugated 8 π system dibenz[*b,f*]oxepin in 1992 (Fig. 3a).³³ Its preferential bent configuration in the ground state can be explained by Hückel's rule,¹⁰⁰ in which the planar structure possessed unfavourable antiaromatic properties due to the 8 π electron array in the middle ring. Upon excitation, however, the equilibrium configuration tended to be planar, driven by excited-state aromaticity reversal, which can be explained by Baird's aromaticity rule.^{80–82} Such a structural planarization allowed for the global conjugation of the whole molecule and led to a large Stokes shift. Therefore, it can be speculated that the 8 π electron array is another important factor in the photoinduced structural planarization process. Recently, Naka *et al.* reported a class of 8 π system dibenzo[*b,f*]arsperins,¹⁰¹ which also exhibited severely bent boat-like configurations in the ground state (Fig. 5a). Both 3-Me and 3-Ph exhibited intrinsic emission bands (~370 nm) and longer-wavelength emission broad bands (500–700 nm), with large Stokes shifts of 7249 and 6830 cm⁻¹ (Fig. 3b), respectively. The longer-wavelength emission intensity ratio was solvent dependent. It decreased with increasing solvent polarity due to the lower polarity of the planar structure in the excited state (Fig. 3b and c). Moreover, a high viscosity

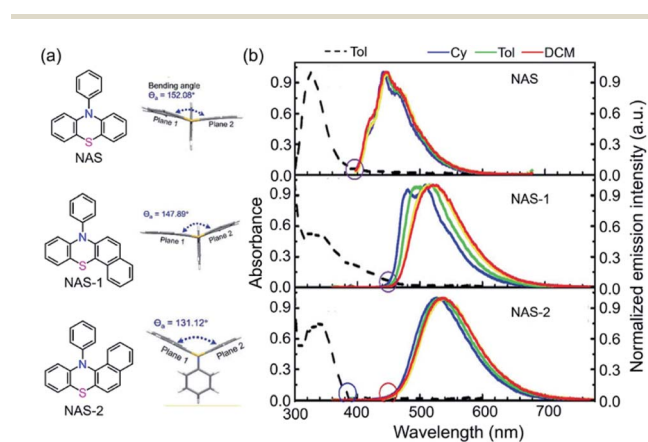


Fig. 4 (a) Chemical and single-crystal structures for NAS, NAS-1 and NAS-2. (b) Absorption and photoluminescence spectra in various solvents at room temperature. Reproduced from ref. 99 with permission from the Wiley-VCH, Copyright 2019.



Fig. 5 (a) Chemical structures of dibenzo[*b,f*]oxepine and dibenzo[*b,f*]arsperin derivatives 3-Me and 3-Ph. (b) Single-crystal structure of 3-Ph. (c) Photoluminescence spectra of 3-Ph in various solvents. (d) Calculated potential energy surface of 3-Ph with the variation in the torsion angle in the S₀ and S₁ states. Reproduced from ref. 101 with permission from the Wiley-VCH, Copyright 2019.





Fig. 7 Schematic representation of the supramolecular assembly and disassembly processes of DPAC-[B15C5]₂. Reproduced from ref. 105 with permission from the American Chemical Society, Copyright 2020.

the DPAC moiety at the para site of 9,14-phenyl through ester groups to form a potassium ion (K⁺) responsive molecule DPAC-[B15C5]₂ (Fig. 7),¹⁰⁵ in which DPAC was the fluorescent signaller and benzo-15-crown-5 was the K⁺ recognition site. 15-crown-5 could form a 2 : 1 sandwich-like supramolecular assembly with K⁺. Meanwhile, the diameter of K⁺ (2.66 Å) was so much smaller than the distance of the centres of the two 15-crown-5 moieties in DPAC-[B15C5]₂ (23.18 Å) that only an intermolecular supramolecular assembly could be formed, thus causing aggregation of the system and constraining the planarization of the DPAC moiety. By fine tuning the degree of aggregation, the emission colour changed from orange-red *via* white to blue with the gradual titration of K⁺. Conversely, a reversible process could clearly be seen in which the emission colour recovered from blue *via* white and orange-red with the titration of 18-crown-6, because 18-crown-6 possessed a higher complexing ability with K⁺ and thus caused disaggregation of the system. Moreover, water was found to have a similar effect on 18-crown-6. Even trace amounts could generate evident emission colour changes in the system. In the utilization of this supramolecular assembly, the detection limit of water in toluene was calculated to be as low as 0.035 wt%. This work provided sufficient proof for and a deep understanding of the relationship among supramolecular interactions, aggregation, and the VIE process.

Temperature is another important factor that influences the molecular vibrations, which makes DHPs an ideal candidate for the construction of thermometers.^{85,86} To be specific, on the one hand, a lower temperature provides less energy for the thermal motion of DHPs, and may keep them in bent excited states even if they are in the form of a single molecular state. On the other hand, a low temperature tends to reduce the solubility of DHPs in solution and cause aggregation, thus restricting their excited state planarization process. However, only ultra-low temperatures (below ~233 K) can suppress the vibration of DHPs in normal solutions, which severely limits their application in the field of daily temperature detection. Therefore, the dilemma between daily temperature requirements and the vibration restriction of DHPs must be overcome. In this regard, we developed an ultra-sensitive and range-tunable ratiometric thermometer DPC (Fig. 8a).¹⁰⁶ Its excited bent-to-planar process could be tuned *via* temperature-induced aggregation and disaggregation. Based on the different solubilities of DPC in ethanol/glycerol mixed solvents at different temperatures and glycerol fractions, the degree of aggregation could be

controlled. An increasing temperature would dissociate the aggregates and enhance the orange-red emission, while a decreasing temperature would re-aggregate the dissociated DPC molecules and enhance the blue emission, thereby achieving a significant ratiometric response to temperature (Fig. 3b). Moreover, the range-tunable property could be realized by simply tuning the fraction of each component of the mixed solvent, since ethanol is a good solvent for DPC while glycerol is a poor one. As a result, it was realized for the first time that this fluorescent ratiometric thermometer possessed an ultra-high sensitivity at ~2000% °C⁻¹ and a broad overall linear response region from -11.4 °C to 37.7 °C. More interestingly, the fluorescent signal at various temperatures exhibited a good linear relationship on the CIE chromaticity diagram (Fig. 8c and d). In this manner, temperature information could be invaluable read with only a smartphone instead of a professional spectrometer. This work perfectly resolved the conflict between high sensitivity and broad response range and provided a novel perspective for developing thermometry schemes.



Fig. 8 (a) Chemical structure of DPC and an illustration of the VIE process. (b) Mechanism of ratiometric thermometers established by the aggregation and disaggregation of VIE-active molecules. (c) CIE chromaticity diagram, where the symbols are the measured values and the line segments are the calculated analogous values. (d) The fitted curves of the CIE coordinates corresponding to the FL spectra of DPC in an ethanol/glycerol mixture with $f_g = 40\%$ at different temperatures. Reproduced from ref. 106 with permission from the Royal Society of Chemistry, Copyright 2020.



In addition to using solvents as the media, DHPs incorporated into polyurethanes (PUs) can be applied not only for temperature detection but also for exploring the microphase separation of PUs.¹⁰⁷ PUs possess particular properties due to the thermodynamic incompatibility between the soft and hard segments, thus making it possible to tune the excited intramolecular vibrations of the DHPs. An alternative strategy is to introduce DHPs into PUs through physical blending or chemical bonding. Therefore, we used DPAC doped in PUs (**PU-4701-1**) and its derivatives grafted to PUs in different forms (**PU-4701-2**, **3**, **4**). As shown in Fig. 9a, the DPAC moieties were external to the **PU-4701-1** chain and subjected to little restriction in the planarization process. Consequently, they exhibited pink emission colours at room temperature. In the case of **PU-4701-3**, however, DPAC was grafted to PUs *via* bilateral chemical bonds, which greatly suppressed the excited bent-to-planar process and emitted strong blue fluorescence. As for **PU-4701-2** and **PU-4701-4**, the unilateral chemical bonds between DPAC and PUs imposed weaker restrictions than **PU-4701-3**, but stronger than

PU-4701-1, thus emitting pink-purple fluorescence. Temperature is an important factor in the change in the microphase structures of PUs. For example, **PU-4701-2** exhibited a cross-regional emission colour change from blue to orange-red in the region of $-30\text{ }^{\circ}\text{C}$ to $90\text{ }^{\circ}\text{C}$ (Fig. 8b). The high consistency between the continuous temperature cycles and the small-angle X-ray scattering experiments provided an alternative scheme for measuring the degree of microphase separation in the PUs as a “fluorescent ruler” (Fig. 8c). This work opens up a new path for polymer investigation through fluorescence techniques.

4. Biological probes

VIE-active compounds can act as ideal signal moieties because of their unique dual emission properties, which is beneficial for achieving ratiometric detection.^{108–111} Hence, developing VIE-based probes for visualizing biological activity is extraordinarily fascinating.^{87,91,92} The enzymatic fluorescent probe **Q1** based on the VIE mechanism was designed and synthesized for



Fig. 9 (a) Diagrammatic sketch illustrating the DPAC-doped polyurethanes **PU-4701-1**–**PU-4701-4**. (b) PL spectra of **PU-4701-2** at various temperatures (-30 to $90\text{ }^{\circ}\text{C}$). (c) Scattering curves of **PU-4701-1** achieved by small-angle X-ray scattering at various temperatures (10 – $90\text{ }^{\circ}\text{C}$). Reproduced from ref. 107 with permission from the American Chemical Society, Copyright 2019.





Fig. 10 (a) Synthesis of VIE-based sensor **Q1**. (b) Diagrammatic sketch illustrating the working principle of **Q1**, showing VIE properties before and after reacting with phosphatase in living cells. (c)–(e) Fluorescence images of LO2 and HeLa cells. Reproduced from ref. 112 with permission of the Royal Society of Chemistry, Copyright 2020.

detecting and imaging the protein tyrosine phosphatase 1B (PTP1B) in living cells (Fig. 10a).¹¹² **Q1** was composed of the DPAC moiety and a phosphate radical and dissolved well in solvent, thereby exhibiting a free emissive state. When **Q1** reacted with PTP1B, hydroxyl-substituted DPAC was acquired and showed poor solubility, thereby exhibiting a fixed emissive state and enhanced blue emission (Fig. 10b). Unlike the conventional VIE phenomenon, this probe showed almost constant orange-red emissions at ~ 600 nm during the enzymatic reaction process with PTP1B, which could act as an “internal standard”. However, the increasing blue emission intensity could be applied for detecting PTP1B as the reaction

proceeded. Through this mechanism, **Q1** was determined to have a detection limit of $5.7 \text{ ng } \mu\text{L}^{-1}$ for PTP1B, and it showed a rapid response, and good selectivity and stability. Furthermore, **Q1** could be used to detect PTP1B in living cells (Fig. 10c–e). Under the conditions of constant emissions in the red channels, **Q1** emitted brighter emissions in the green channel in HeLa cells, indicating that HeLa cells contained more PTP1B. This work provided an idea for the construction of VIE-based biological probes.

Hydrophobic DHPs are a series of ideal molecules for developing core-shell structures in the field of biosensors. Based on this viewpoint, He and co-workers developed

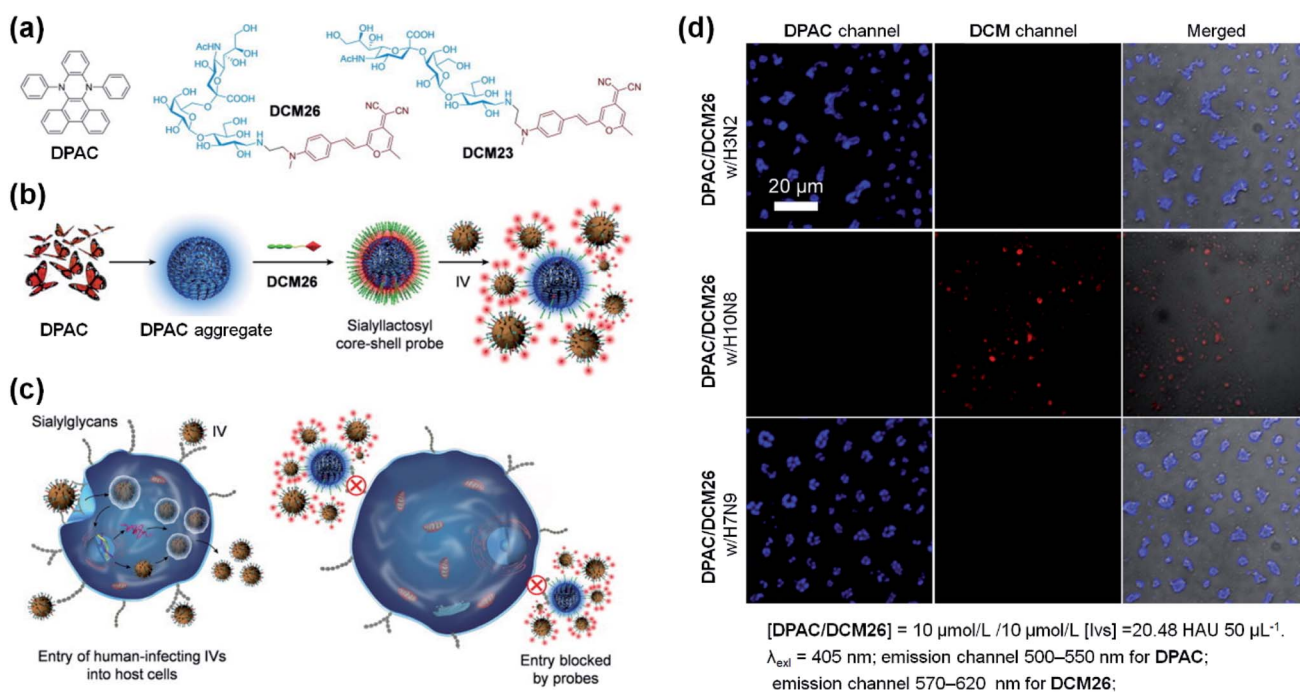


Fig. 11 (a) Molecular structures of DPAC, DCM26 and DCM23. (b) Scheme for the stepwise self-assembly to prepare a core-shell sialyllactosyl sensor for the ratiometric fluorescence sensing of influenza viruses. (c) Illustration of the sensor utilized for blocking the entry of human-infecting influenza viruses (IVs) into host cells. (d) Fluorescence images of DPAC/DCM26 sensor in the presence of IV with different HA specificities. Reproduced from ref. 113 with the permission of Elsevier, Copyright 2019.



a sialyllactosyl probe for influenza virus (IV) detection and blocking.¹¹³ DPAC acted as the core structure and the aggregation-enhanced blue fluorophore due to its poor solubility and restricted configuration in aqueous solutions. DCM-based sialyllactosides were applied to assemble with DPAC to form a sialyllactosyl probe, emitting a red fluorescence *via* Förster resonance energy transfer (FRET) from DPAC to DCM (Fig. 11a and b). Since the specific binding blocked the FRET process, a strong DPAC channel (blue) could be observed while the DCM channel (red) was nearly absent when the probe was treated with H3N2 or H7N9. However, the non-specific collisions between H10N8 and the probe particles had little influence on the dual emissions, thus exhibiting only a strong DCM channel (Fig. 10d). Apart from the sensing ability, the probe could also suppress the IVs entering human cells by antagonizing the interactions between the viruses' surface-bound hemagglutinin and cell-surface sialylglycans (Fig. 11c). This study provided further understanding of the construction of biological probes through the smart design of DHPs by utilizing their aggregation-enhanced fluorescence property.

5. Excimer formation of VIE-active luminogen in a crystal

Excimer emission^{26–28,30,31} and emission mechanochromism^{114–117} have been found in the crystalline solids of the VIE-active compound 12-phenyl-12H-benzo[*a*]phenothiazine (NAS-2, see Fig. 4a and 12).⁹⁹ Normally, NAS-2 crystals are expected to emit normal Stokes-shifted emissions due to the lattice energy, which could prohibit the planarization process. However, the NAS-2 crystal exhibited dual emissions in the crystal state, located at 390 and 520 nm (Fig. 12a). Compared to the emission of the DPAC crystal located at \sim 386 nm, it is believed that the

short-wavelength emission originated from the monomer bent configuration of NAS-2. Since the planarization process resulting in the long-wavelength emission was excluded due to the lattice energy, intermolecular interactions can be considered to be the main factor, most likely as an excimer. This speculation was first proven by molecular packing in the crystal (Fig. 12b and c). The different bending angles of NAS-2 and NAS-1 lead to different orientations of *N*-phenyl due to the steric hindrance. As a result, NAS-2 is more suitable for forming proximal π - π interactions for the naphthalene unit, while NAS-1 avoids any possible π - π stacking. By investigating the emission behaviour of the NAS-2 crystal based on the depth from its surface, there was mainly a 390 nm emission (purple-blue) at the surface, and dual emission (pale blue) at the kernel of the crystal (Fig. 12a and d). Hence, it was concluded that excimer formation was preferred as the depth increased, while π - π stacking ruptured at the surface due to the dangling molecules. Furthermore, the existence of the excimer was also proven by the transient photoluminescence (Fig. 12e). The decay component of 20.8 ps monitored at the normal emission of 400 nm was well matched with the rising component of 21.3 ps monitored at the excimer emission of 500 nm. The discovery of the excimer in NAS-2 is significant, opening up an avenue for the study of the π - π interactions of VIE-active luminogens.

Broadly speaking, the role of excimer or dimer is one of the most important issues for organic luminogens in the solid state, which has been explored in the field of room-temperature phosphorescence (RTP).^{118–120} Utilizing VIE design principles to achieve tunable RTP may be feasible. To achieve this, it is very important to understand the actual role of the π - π interactions. In this regard, Tang, Li, and co-workers provided a clear direction by exploring the effect of the dimer in persistent RTP in detail.¹²¹ By adopting the phenothiazine 5,5-dioxide group as



Fig. 12 (a) Photoluminescent spectra of NAS-2: black solid line for the ground powder, and coloured solid lines for the red square in (d) of the crystal with different depths from the surface to the kernel. Packing of (b) NAS-2 and (c) NAS-1 in the crystal lattice. (e) Transient photoluminescence characteristics of NAS-2 in the crystal as monitored at various wavelengths. Reproduced from ref. 99 with permission of the Wiley-VCH, Copyright 2019.



two parameters simultaneously in biomembranes, providing a correlation between the membrane viscosity and the efficiency of cellular respiration or photosynthesis. It is inevitable that systematically studying the excited state process of complex systems will be of great significance both in terms of scientific value and in practical applications in the future. The final goal of 'dynamic living molecular emitting probes for living cells' would be realized based on this VIE-concept molecular design.

As an expanding field, VIE research simultaneously provides us with opportunities and challenges. We hope this perspective will provide guidance for the innovation of smart VIE-active light-emitting materials and facilitating applications in the field of bio-sensors and bio-imaging.

Conflicts of interest

There are no conflicts to declare.

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