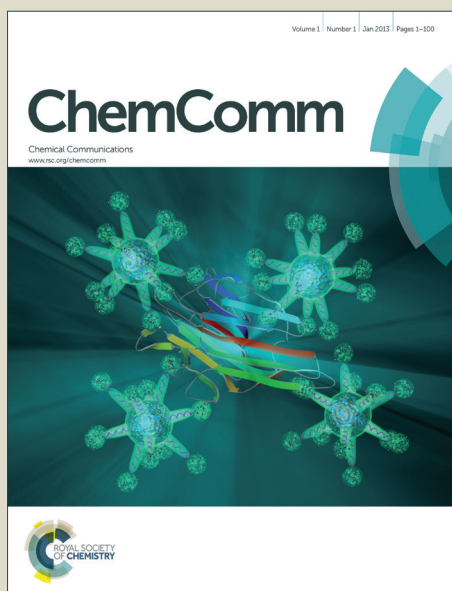


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COMMUNICATION

Colour-tunable Fluorescence of Single Molecules based on the Vibration Induced Emission of Phenazine

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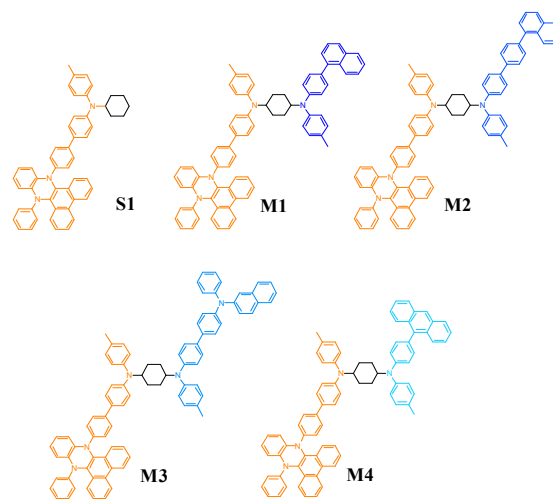
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Due to the vibration of phenazine unit, compound S1 exhibits dual fluorescence in solution but one peak in solid. Based on this novel phenomenon and combine with the intramolecular energy transfer (IET) effect, a colour-tunable luminescence, even near white emission from single molecule could be achieved in two different ways: controlling the polarity of solvent and the aggregation index.

In recent years, the multi-colour luminescent materials have drawn much attention due to their potential applications in flexible full-colour displays and next-generation lighting sources. Furthermore, white fluorescent molecules are clearly of interest and importance, because they will bring a revolution in the applications to new classes of displays. A key point for the mission to obtain tunable fluorescence is that the emission spectra could be influenced by external factors, including the crystal form of molecules,¹ energy transfer process,² temperature³ etc. Amongst the above variants, the energy transfer provides a convenient means for colour tuning over a spectral range bounded by the isolated donor and acceptor spectra. The methods to utilize energy transfer including conjugated polymer nanoparticles⁴, silica nanoparticles.⁵ Compared to the multi-component molecular emitters for getting white emission, using single molecule would give perfect colour reproducibility and better stability.^{6,7} Nonetheless it remains a challenge to achieve a white emission from a single molecule by means of a precise molecular design.

Compound **S1** shown in Scheme 1 gives two fluorescent peaks in solution, while one peak in the solid state (461 nm) (Figure S1). This phenomenon is quite different from the normal fluorophors. Attributed to the TICT⁸ (twisted intramolecular charge transfer) effect for the common D-A structure (diphenylamine as donor and 9,14-diphenyl-9,14-dihydrodibenzo[a,c]phenazine as the acceptor), the blue emission display a bathochromic shift with the increase of solvent polarity and merges the red emission into one

peak in polar solvent. Consequently, the colour of fluorescence turned from orange to yellow (Figure S2c). Further evidence for the TICT process in the excited state surface comes from the temperature effect. When the temperature of THF solution decreases from 313 K to 243 K, the blue emission spectra shows a gradual red-shifted emission maximum accompanied by a continuous increase in the intensity (Figure S2d).⁹ However, the red emission change a little both with solvent polarity and temperature, so it is barely explained by TICT effect only.

Scheme 1. The structures of the target molecules **S1**, **M1** - **M4**.

We believe the vibration of phenazine unit (**S0**) (Scheme S1) plays a significant role to induce the red emission. In order to prove the vibration process, **S0** has been synthesized (the single crystal Figure S13 and Table S3) and some quantum mechanical calculations were carried out (Figure S3). When the phenazine reference **S0** in the lowest energy state for solid, the fluorescence peak is observed at 390 nm. When it vibrated to co-plane in solution, the emission peak reaches 589 nm (Table S1).

All calculative results are in line with the experimental data (Figure S4). Moreover, we use THF as good solvent, water as poor solvent. The vibration of phenazine will be restricted when increase the ratio of water. As shown in Figure S5, **S0** has a red peak in 598 nm when water fraction (f_w) = 0%. However, the red peak intensity decreases with the increase of water fraction. When f_w = 99% the vibration has been restricted, and only has a peak in 460 nm. It indicates that the vibration of the phenazine unit induced a new red emission for **S1**. And we named it as Vibration Induced Emission (VIE) phenomenon where does not mean enhanced emission. In fact, VIE would be one of intrinsic emission of the molecules induced just by the vibration of phenazine unit.

If the intensity of red and blue emissions could be controlled for a suitable proportion, a white emission would be achieved. Intramolecular energy transfer is a tractable way for controlling the fluorescence intensity. So **M1** – **M4** (Scheme 1) have been synthesized by introducing different blue emitters linked with **S1** via cyclohexane. The blue fluorophore molecules **S2** – **S4** were also examined as reference compounds (Scheme S1, SI). Detailed synthetic, purification procedures and identify methods (^1H NMR, ^{13}C NMR and MS) of the compounds were described in the Supporting Information (SI). To achieve effective intramolecular energy transfer (IET), two conditions need to be satisfied: 1) the efficient overlap between the donor emission and acceptor absorption spectra; 2) the donor-acceptor distance is small. Both above factors have an important effect on energy transfer efficiency.¹⁰ The distance between the donor and acceptor is 5.78 Å (Figure S6), which is much smaller than Förster radius 33.7 Å. So the overlap integrals between donor (emission) and acceptor (absorption) can be regulated for controlling the energy transfer. The emission wavelength has a bathochromic-shift for **S2** – **S4** (Figure S7a). As a result, the overlap integrals decrease from **S2** to **S4** (Figure S7b). Such as **M1** and **M4**, there is an efficient overlap between the donor emission (**S2**) and the acceptor absorption (**S1**) in UV region for compound **M1**. In contrast, little overlap between the donor and acceptor can be observed for compound **M4** (Figure S8a-b). Moreover, to gain insight of the intramolecular energy transfer process, time-resolved fluorescence life time measurements were performed (Figure S8c-d). The donor emission decay time of **M1** is short for **S2**, while the donor emission decay time of **M4** is markedly enhanced like **S4** as no overlap between the donor and acceptor. Such observations clearly indicate that there exists effective intramolecular energy transfer in **M1** and no intramolecular energy transfer in **M4**.

The absorption of **S1** is similar in different solvents, while reference donors **S2** – **S4** show obvious bathochromic-shift emission (Figure S9) with the increase of solvent polarity. This phenomenon gives us enlightenment that we can control the energy transfer by increasing solvent polarity. For **M1** and **M2**, Figure S10 shows the absorption spectra of acceptor (**S1**) versus the emission spectra of donor (**S2** and **S3**). The overlap integrals reduce when increase the polarity of solvent, as well as the energy transfer efficiency. So a colour-tunable emission process could be achieved. As shown in Figure 1, because the

overlapping area reduced with the increase of solvent polarity, the IET efficiency reduce and make the blue emission intensity enhanced while the red emission intensity weaken, combine the solvent effect of donor the two peaks of **M2** merge into a broad peak in DMF. The fluorescence colour of **M2** turned from orange to blue with the increasing polarity of the solvent. When dissolved in EtOH, compound **M2** gave a close white emission (CIE 0.28, 0.27) (Figure 1a). Due to the different intramolecular energy transfer efficiency, the other compounds show different fluorescence. For example, the higher energy transfer efficiency makes **M1** having weak blue emission, so the colours turn from orange to light yellow and a near-white emission can be achieved (CIE 0.34, 0.36) in MeCN (Figure 1b). The fluorescent colour of **M3** turns from pink to yellow and gives a close white emission (CIE 0.27, 0.28) in THF. The absorption spectra of **M1** – **M4** are shown in Figure S11 and the emission spectra and chromaticity coordinates of other compounds could be seen in Figure S12 in Supporting Information. The PL quantum yield Φ_F is listed in Table S2.

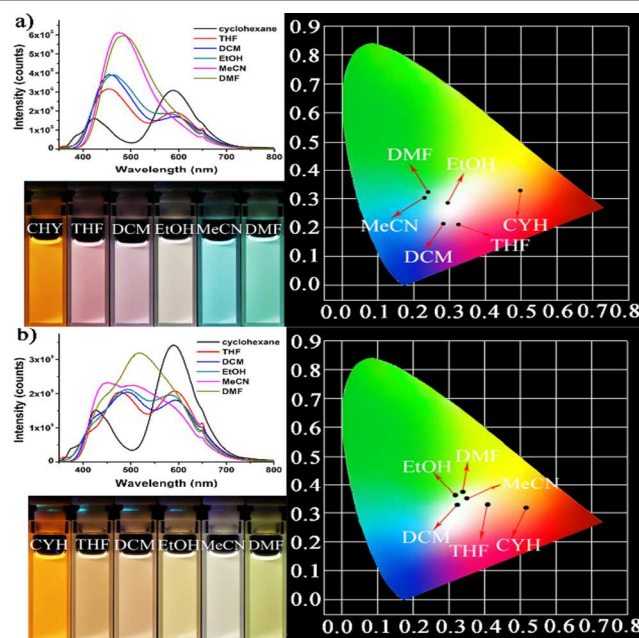


Fig. 1 (a) The fluorescence spectra of **M2** in different solvents (1×10^{-5} M) excited at 325 nm (left top). The chromaticity coordinates (CIE) of **M2** in different solvents at a concentration of 1×10^{-5} M (right). The fluorescence images of **M2** in different solvents at a concentration of 1×10^{-5} M under 365 nm UV-light (left bottom). (b) The fluorescence spectra of **M1** in different solvents (1×10^{-5} M) excited at 325 nm (left top). The chromaticity coordinates (CIE) of **M1** in different solvents at a concentration of 1×10^{-5} M (right). The fluorescence images of **M1** in different solvents at a concentration of 1×10^{-5} M under 365 nm UV-light (left bottom).

Moreover, based on the vibration induce emission the obvious emission colour-tunable could be achieved by controlling vibration of phenazine unit. The method is just simple using THF as a good solvent and water as a poor solvent. The vibration of phenazine unit would be restricted when molecules aggregate in high water fraction. Figure 2a shows the normalized fluorescence spectra of compound **M1** in THF/H₂O of different water ratios. Compound **M1** exhibits two emission peaks located at 456 nm

and 601 nm in pure THF. However, the long wavelength (λ_{em} = 601 nm) emission receded with the increase of water fraction (f_w). When f_w = 90 % the solution gives a close white emission (Figure 2b, CIE 0.28, 0.27). Due to the vibration of phenazine unit was restricted, it only has one blue emission (λ_{em} = 450 nm) when the f_w = 99 %. So the emission gives an orange – white – blue process for **M1**.

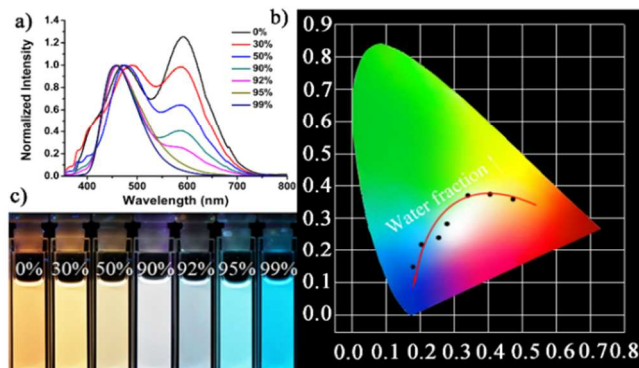


Fig. 2 (a) The normalized fluorescence spectra of **M1** in different water ratios of THF/H₂O excited at 335 nm at 1×10^{-5} M. (b) The chromaticity coordinates (CIE) for **M1** in different ratios of THF/H₂O. (c) The fluorescence images of **M1** in different ratios of THF/H₂O under 365 nm UV-light.

For better describing the dynamic scene of state transformational process, we dropped the solution of compound **M1** on silica gel plate for getting a state transform process from solution to solid (Figure 3). This dynamic process could be explained by vibration effect. The vibration of the phenazine unit would be restricted when the solvent was volatilized. So a similar phenomenon was observed, i. e. the emission give an orange – white – blue process when the DCM was volatilized in 10 seconds. The whole process could be seen in the video in Support Information. This phenomenon make the compound have potential application in detection of organic vapour.

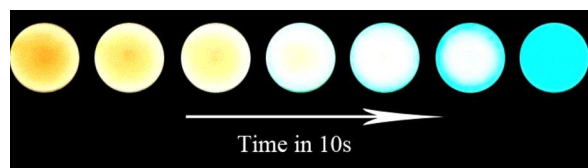


Fig. 3 The solution-to-solid transform fluorescence images when **M1** (1mg/0.5ml, DCM) dropped on silica gel plate in 10 seconds under 365 nm UV-light.

Conclusions

In summary, a novel phenazine core structure **S1** exhibits an interesting phenomenon: Vibration Induced Emission (VIE), i. e. two fluorescence peaks in solution but one peak in solid. Based on this core unit, some novel compounds (**M1** – **M4**) were prepared. Such Vibration Induced Emission (VIE) provides novel approach to obtain near white emission from single organic molecule (**M1** and **M2**) in two ways: 1) control the intramolecular energy transfer efficiency; 2) control the vibration ability of phenazine-unit by increasing the water fraction in the solvent. VIE would be one of intrinsic emission of the molecules and the

detailed investigation of vibration mechanism is underway by means of ultrafast spectroscopies. This successful molecular design principle-proof is unprecedented and promises potential implementation to prepare white-light emitting single molecule in future applications.

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Notes and references

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