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Introduction

Nowadays, solid state lighting (SSL) of organic chromophores has attracted a great deal of attention due to their potential applications in devices, such as light-emitting diodes,¹⁻³ photovoltaic devices,⁴⁻⁶ and sensors.⁷⁻⁹ Tuning and controlling the luminescent color of an organic material is crucial to meet the light-emission with an appropriate wavelength.^{10,11} It is well known that the optical properties of chromophores in the solid state strongly depend on the molecular structure and intermolecular interactions.¹²⁻¹⁴ Recent advances in organic fluorescent crystals have focused on material polymorphism and cocrystallisation, which are, generally, used to modulate the properties of organic molecules in crystals. Polymorphs can be defined as the existence of a particular compound in more than one crystal structure and cocrystals are molecular

Two polymorphs and cocrystal of styryl-pyridine derivatives with tuned emission induced by Co^{2+} and $Zn(phen)_3^{2+}$

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A styryl-pyridine derivative, 2,5-dibutoxy-1,4-bis[2-(4-pyridyl)ethenyl]benzene (L), has been designed and synthesised. Two polymorphs of L and crystals of $[Zn(phen)_3]_2L(ClO_4)_4$ were obtained by different crystallisation conditions. Polymorph- α was prepared by a solvent evaporation method. However, polymorph- β and a cocrystal of $[Zn(phen)_3]_2L(ClO_4)_4$ were obtained by different inducing reagents. It has been found that there are, in total, four independent conformations of the molecule L in the three kinds of crystals. We have calculated the standard molar enthalpy of formation (ΔH_m) of each conformation and demonstrated that the stabilisation energy of each conformation significantly relies on both the planarity of the molecules (L) and bond length of conjugated bridges. Furthermore, the photophysical properties of the three kinds of crystals also exhibit differences in the vibration and absorption spectroscopies, solid-state photoluminescence and time-resolved fluorescence, which may arise from the chromophore's stacking modes and the intermolecular electronic interactions in the crystals. These results revealed that the optical properties of functional organic materials could be tuned by controlling their crystallisation environment for a specific molecule.

solids composed of at least two types of neutral chemical species.^{10,15} As a large family of non-bonding interactions, hydrogen-bonding and π - π interactions play an important role in crystal formation as a driving force to stabilize the crystals.15-18 Adding appropriate inducing reagents is an available approach for polymorphs and cocrystals. Also, various effective additives have been reported in previous work, including polymers, organic compounds, metal ions and so on.15,19,20 For example, Wang reported that polymorphs of N,N-di(n-butyl) quinacridone (DBQA) can be obtained from a mixed solution of DBQA and 7,7,8,8-tetracyanoquinodimethane or perylene-3,4,9,10-tetracarboxydiimide. The most crucial reason is that the added reagents have π -conjugated systems similar to DBQA.¹⁵ In our previous work, two morphologies of 4'-(4-{2-[4-(N,Ndiphenylamino)-phenyl]ethenyl}phenyl)-2,2':6',2"-terpyridine appear as Eu³⁺/Ag⁺ induced features.²⁰

Herein, we report two polymorphs of 2,5-dibutoxy-1,4-bis[2-(4pyridyl) ethenyl]benzene (L) and a cocrystal, $[Zn(phen)_3]_2L(ClO_4)_4$ (phen = 1,10-phenanthroline), between L and $Zn(phen)_3(ClO_4)_2$ which were obtained by different inducing reagents. It is very interesting to find that the one chromophore molecule L could exist as four kinds of structures in different crystallisation environments and emit discriminate colors. The correlations between the conformation and standard molar enthalpy of formation (ΔH_m) have been interpreted, relying on both experimental data and theoretical calculations. Finally, the relationships



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[†] Electronic supplementary information (ESI) available: HRMS and NMR spectra, X-ray crystallography, powder XRD and IR characterisation, packing modes of the crystals and theoretical calculation results are described. CCDC 729228, 771894, and 737794. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3ce42069h

between their structures and photoluminescence properties have been investigated.

Experimental section

Materials and physical measurements

The reagents and solvents employed were commercially available and used as received without further purification. IR spectra were recorded with a Nicolet FT-IR Nexus 870 instrument (KBr disks) in the 400-4000 cm⁻¹ region. ¹H NMR spectra were performed on a Bruker 400 MHz Ultrashield spectrometer and are reported as parts per million (ppm) from TMS (δ). Mass spectra (MS) were obtained using an Agilent Q-TOF 6540 mass spectrometer. Elemental analyses were performed with a Perkin-Elmer 240C elemental analyzer. Absorption spectra were recorded on a UV-3600 spectrophotometer. The fluorescence spectra were determined with an F-4500 Spectro-fluorophotome. The powder X-ray diffraction (XRD) patterns were recorded using a 18 KW advance X-ray diffractometer with Cu K α radiation (λ = 1.54056 Å). For timeresolved fluorescence measurements, the fluorescence signals were collimated and focused onto the entrance slit of a monochromator with the output plane equipped with a photomultiplier tube (HORIBA HuoroMax-4P). The decays were analysed by "least-squares". The quality of the exponential fits was evaluated by the goodness of fit (χ^2). Fluorescence imaging of the crystals was taken on a Leica DMI6000 fluorescence microscope.

Synthesis of 2,5-dibutoxy-1,4-bis[2-(4-pyridyl)ethenyl] benzene (L)

The general synthetic scheme for the preparation of 2,5dibutoxy-1,4-bis[2-(4-pyridyl)ethenyl]benzene is outlined in Scheme 1.

Hydroquinone (11.13 g, 0.10 mol) and sodium hydroxide (8.35 g, 0.21 mol) were dissolved in ethanol. 1-Bromobutane (27.97 g, 0.20 mol) was added dropwise to the solution and refluxed for 8 h. The solution was then poured into water (1 L), and the precipitate was filtered off and recrystallised from ethanol to give compound 1 as a white solid in an 85% yield. ¹H NMR (400 MHz, d_6 -DMSO, δ) 6.624 (s, 4H, -ArH), 3.896-3.863 (m, 4H, -CH₂-), 1.692-1.622 (m, 4H, -CH₂-), 1.466-1.373 (m, 4H, -CH₂-), 0.942-0.905 (m, 6H, -CH₃); IR (KBr, cm⁻¹), 2958, 1869, 1639, 1510, 1237, 1043, 831, 767, 535.

Compound 2 was synthesised by the reported method.²¹ 20 mL dioxane and 50 mL concentrated hydrogen chloride



Scheme 1 Synthetic route for target compound L.

were added to a stirred solution of 1 (5.56 g, 0.025 mol), with three 50 mL portions of 40% formalin at 20 min intervals. During the period of addition, hydrogen chloride gas was passed through. Stirring and the introduction of hydrogen chloride gas were continued for a further 3 h. 150 mL concentrated hydrogen chloride was then added. After cooling, the solid material was filtered off, and recrystallised from ethanol to give compound 2 as white crystals in a 75% yield. ¹H NMR (400 MHz, d_6 -DMSO, δ) 6.935 (s, 4H, ArH), 4.653 (s, 4H, CH₃Cl), 4.029–3.997 (m, 4H, -CH₂–), 1.843–1.773 (m, 4H, -CH₂–), 1.595–1.513 (m, 4H, -CH₂–), 1.026–0.989 (m, 6H, -CH₃); IR (KBr, cm⁻¹) 2960, 1650, 1514, 1415, 1259, 1223, 1044, 867, 755, 608.

A solution of compound 2 (5.23 g, 0.016 mol) and triphenylphosphine (8.92 g, 0.034 mol) in 100 mL of anhydrous ethanol was stirred and refluxed for 8 h. After distilling the ethanol and washing with benzene three times, the white solid 3 was obtained in a 93% yield. The obtained product was used in the next step without characterisation.

Subsequently, t-BuOK (8.98 g, 0.080 mol) was placed into a dry mortar and milled. Then, 3 (8.45 g, 0.010 mol) and isonicotinaldehyde (4.28 g, 0.040 mol) were added and mixed. The mixture was milled vigorously for about 10 min. After the reaction was completed (monitored by TLC), the mixture was dispersed in 50 mL H₂O. The solution was extracted three times with 50 mL CH₂Cl₂. The dichloromethane solution was dried for 12 h and concentrated. The product was purified through a silica gel column eluted with petroleum ether-ethyl acetate (V:V = 8:1). A yellow solid was obtained in a 73% yield. ¹H NMR (400 MHz, d_6 -DMSO, δ): 8.570–8.556 (d, J = 5.6 Hz, 4H, -pyridine-H), 7.685-7.644 (d, J = 16.4 Hz, 2H, -CH=CH-), 7.510-7.496 (d, J = 5.6 Hz, 4H, -pyridine-H), 7.417-7.375 (d, J = 16.8 Hz, 2H, -CH=CH-), 7.394 (s, 2H, -ArH), 4.133-4.101 (t, 4H, -CH₂-), 1.853-1.784 (m, 4H, -CH₂-), 1.579–1.487 (m, 4H, $-CH_2$ -), 1.013–0.977 (t, 6H, $-CH_3$); ¹³C NMR (400 MHz, CDCl₃, $\delta_{\rm C}$): 150.12, 131.99, 131.49, 131.40, 128.78, 128.67, 127.05, 120.64, 68.52, 30.85, 18.93, 13.76. Anal. Calc. for C₂₈H₃₂N₂O₂: C, 78.47; H, 7.53; N, 6.54 (%). Found: C, 78.50; H, 7.49; N, 6.58 (%). HRMS (m/z, ES) Calculated for $C_{28}H_{33}N_2O_2$ m/z = 429.2542 [M +H]. Found m/z =429.2514.

Crystallisation of polymorph-α.

L, as a powder, was dissolved in a CHCl₃ solution at room temperature. Yellow needle crystals of polymorph- α suitable for single crystal X-ray diffraction analysis were obtained after five days.

Crystallisation of polymorph-β

First, the $CoL(NO_3)_2$ complex was prepared by mixing L and $Co(NO_3)_2$ (molar ratio = 1:1) in ethanol. Anal. Calc. for $CoC_{28}H_{32}N_4O_8$: C, 55.00; H, 5.27; N, 9.16 (%). Found: C, 55.12; H, 5.24; N, 9.22 (%).

Then, $CoL(NO_3)_2$ as a powder was dissolved in DMF at room temperature. Yellow block crystals of polymorph- β

suitable for single crystal X-ray analysis were obtained after two weeks.

Preparation of [Zn(phen)₃]₂L(ClO₄)₄

Zn(ClO₄)₂·6H₂O (0.37 g, 1.0 mmol), phen (0.18 g, 2.0 mmol) and L (0.42 g, 1.0 mmol) were dissolved in methanol (20 mL). The mixture was refluxed for 2 h, cooled to room temperature and filtered. Orange crystals were obtained in a 42% yield. IR (KBr, cm⁻¹), 3489, 3064, 2928, 1589, 1516, 1312, 1226, 1189, 724, 621. Anal. Calc. for $C_{100}H_{80}Cl_4N_{14}O_{18}Zn_2$: C, 58.92; H, 3.96; N, 9.62 (%). Found: C, 59.01; H, 3.91; N, 9.65 (%).

X-ray crystallography

Single-crystal X-ray diffraction measurements were carried out on a Bruker Smart 1000 CCD diffractometer equipped with a graphite crystal monochromator situated in the incident beam for data collection at room temperature. The determination of the unit cell parameters and data collections were performed with Mo K α radiation ($\lambda = 0.71073$ Å). The unit cell dimensions were obtained with least-squares refinements, and all the structures were solved by direct methods using SHELXL-97. The other non-hydrogen atoms were located in successive difference Fourier syntheses. The final refinement was performed by full-matrix least-squares methods with anisotropic thermal parameters for nonhydrogen atoms on F^2 . The hydrogen atoms were added theoretically and riding on the concerned atoms. The crystallographic data for the three crystals are shown in Table S1 in the ESI.† Additional crystallographic details and complete listings of the compounds have been deposited with the Cambridge Crystallographic Data Center as supplementary publications with reference number CCDC 729228 for polymorph- α , 771894 for polymorph- β , and 737794 for $[Zn(phen)_3]_2L(ClO_4)_4.$

Results and discussion

Preparation of the polymorphs and cocrystal

The two kinds of polymorph crystals were obtained from different crystallisation procedures. Polymorph- α was prepared by a solvent evaporation method and polymorph- β was generated from $CoL(NO_3)_2$. Infrared spectra (IR) provide unambiguous proof for the polymorphism. As shown in Fig. S3 in the ESI,[†] polymorph- α and polymorph- β exhibit different bands in the range from 1600 cm⁻¹ and 1000 cm⁻¹, which can be assigned to the vibrations of the benzene and pyridine moieties. XRD patterns provide further experimental evidence for the existence of polymorph- α and polymorph-β. Fig. S4 in the ESI[†] shows the experimental and simulated XRD patterns of polymorph- α and polymorph- β . Furthermore, the melting points of the two polymorphs were investigated. The melting point of polymorph- α (196.6 °C) is lower than that of polymorph- β (201.7 °C). Obviously, polymorph- β is more stable than polymorph- α because the melting point relies on the interactions between molecules (Van der Waals forces). However, polymorph- α was obtained instead of polymorph- β without inducing reagents. Therefore, Co²⁺ should decrease the activation energy for the formation of polymorph- β effectively. The third crystal, [Zn(phen)₃]₂L(ClO₄)₄, was obtained from a mixture of Zn(ClO₄)₂, phen and L due to strong interactions between L and the Zn(phen)₃(ClO₄)₂ complex. Detailed information on the differences will be further confirmed by single crystal X-ray diffraction analysis.

Crystal structures

All the chromophore (L) molecules with different conformations consist of two pyridine rings, a styryl unit and two butoxy chains in the three kinds of crystals.

The molecular structure of L in polymorph- α is displayed in Fig. 1a. In polymorph- α , the pyridine ring and the benzene ring are connected with C5–C6: 1.467 Å, C6=C7: 1.321 Å, C7–C8: 1.469 Å and the dihedral angle between the pyridine ring and the central benzene unit is 44.05°. C=C exists in a *trans*-isomer in molecule L. It is obvious that no π - π interactions exist in the polymorph. Meanwhile, there are C-H…N and C-H… π interactions between the neighboring molecules (see Fig. 2a). The distances of the C-H…N and C-H… π interactions are 2.733 Å and 2.832 Å, respectively.

As shown in Fig. 1b, there are two other conformations in the polymorph- β crystal of the chromophore molecule L. In conformation 2, the linkage connects the pyridine ring with the central benzene unit with bond lengths of C19–C20: 1.488 Å, C20=C21: 1.252 Å, C21–C22: 1.511 Å. In conformation 3, the linkage connects the pyridine ring with the central benzene unit with bond lengths of C5–C6: 1.500 Å, C6=C7: 1.154 Å, C7–C8: 1.480 Å. The dihedral angles between the pyridine ring and the central benzene unit are 8.00° in conformation 2 and 9.53° in conformation 3. These results indicate that the π -conjugated degree of the chromophore moiety in



Fig. 1 Crystal structures of polymorph- α (a), polymorph- β (b) and $[Zn(phen)_3]_2L(ClO_4)_4$ (c) with the H atoms omitted for clarity. (d) The comparative planarities of the four configurations of the chromophore molecule L with H atoms and butoxy chains omitted for clarity.



Fig. 2 The intermolecular interactions of polymorph- α (a), polymorph- β (b) and [Zn(phen)₃]₂L(ClO₄)₄ (c).

conformation 2 is higher than that in conformation 3. Fig. 2b illustrates that there are two types of C-H…N interactions between N2 and C-H in adjacent molecules. However, there are no interactions between N1 and the neighboring molecules.

The structure of the metal complex $[Zn(phen)_3]_2L(ClO_4)_4$ is shown in Fig. 1c. In molecule L, the pyridine rings and the benzene ring are linked with C5-C6: 1.452 Å, C6=C7: 1.320 Å and C7-C8: 1.452 Å, and the dihedral angle between the central benzene ring and the pyridine ring is 10.24°. These results suggest that there is a more highly conjugated system in molecule L existing in the crystal of the metal complex $[Zn(phen)_3]_2L(ClO_4)_4$. Therefore, there are strong $\pi - \pi$ interactions between phen and L in this crystal (Fig. 2c). The shortest distance between the benzene ring in chromophore L and phen in $Zn(phen)_3^{2+}$ is 3.288 Å, and between the pyridine and phen is 3.303 Å. On comparing the two polymorphs, it is interesting to note that there are no interactions between the chromophores. The chromophore L is isolated by $Zn(phen)_3^{2+}$ cations. As counter-ions, the ClO_4^{-} anions not only keep the charge balance, but connect the adjacent $Zn(phen)_3^{2+}$ cations through C-H···O interactions. However, there are no interactions between the ClO_4^- anions and L. Therefore, the cocrystal should be induced by $Zn(phen)_3^{2+}$ cations.

Correlations between the conformation and energy

To further understand the correlations between conformation and energy, DFT theoretical calculation was performed using the Gaussian 09 software package²² at the B3LYP, BLYP, B3P86/6-31G(d, p) level with the ground state geometries of the four conformations obtained from their crystal structures. Standard molar enthalpy of formation ($\Delta H_{\rm m}$) values for the four conformations are listed in Table S2 in the ESL† For molecule L in each conformation, the one with the lower $\Delta H_{\rm m}$ value is relatively stable, while that with a higher $\Delta H_{\rm m}$ value is unstable.

As described above, the conformations 1 and 4 have similar linkage lengths but the dihedral angles between the pyridine moiety and central benzene unit are 44.05° and 10.24°, respectively. The different dihedral angles cause the $\Delta H_{\rm m}$ value of conformation 4 to be much lower than that of conformation 1. Therefore, it can be inferred that the planarity of π -conjugated chromophore molecules is a crucial factor for their stabilisation as crystals.

From analysis of the crystals, conformations 2, 3 and 4 possess similar planarity and different linkage lengths (C=C bond lengths in the linking molecules are 1.252 Å, 1.154 Å and 1.320 Å in conformation 2, 3 and 4, respectively). However, the calculation results indicate that the $\Delta H_{\rm m}$ value of conformation 3 is the highest one and the $\Delta H_{\rm m}$ values of conformations 2 and 4 are almost the same. The C=C bond length is so short (1.154 Å) that the π -electron delocalisation has been handicapped to a certain extent in conformation 3. Accordingly, the energy of conformation 3 is the highest one, although it possesses good planarity. It can be explained that the bond length of the linkage connecting the pyridine ring with the central benzene unit is another crucial factor for their stabilisation as crystals.

Absorption and fluorescence spectra

The absorption and fluorescence properties of the three crystals were investigated at different determination conditions. The results indicate that the absorption and emission spectra of the three crystals exhibit almost the same behavior in dilute solution $(1 \times 10^{-5} \text{ mol L}^{-1})$. Therefore, we focused on their optical properties in the solid state.

Fig. 3 presents a comparison of the absorption spectra of polymorph-α, polymorph-β, $[Zn(phen)_3]_2L(ClO_4)_4$ and L in a dilute DMF solution $(1 \times 10^{-5} \text{ mol } L^{-1})$. Polymorph-α, polymorph-β and $[Zn(phen)_3]_2L(ClO_4)_4$ exhibit an absorption band at around 392 nm, 403 nm, and 412 nm, respectively, in the solid state. The π - π interactions between L and $Zn(phen)_3^{2+}$ can format oligomers, resulting in the lowest excitation energy of $[Zn(phen)_3]_2L(ClO_4)_4$.^{15,23} In addition, the absorption spectra of solid-state polymorph-β show a remarkable red shift compared to that of polymorph-α, which is caused by the different packing modes in the two crystals.



Fig. 3 Normalized absorption spectra of polymorph- α , polymorph- β and $[Zn(phen)_3]_2L(ClO_4)_4$ in the solid state.



Fig. 4 Normalized fluorescence spectra (λ_{ex} = 400 nm) of polymorph- α , polymorph- β and [Zn(phen)₃]₂L(ClO₄)₄ in the solid state.

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Fig. 5 Fluorescence decay curves for the three crystals. (Fluorescence lifetimes were monitored at 505 nm for polymorph- α , 525 nm for polymorph- β and 488 nm for [Zn(phen)₃]₂L(ClO₄)₄.)

The packing diagrams (Fig. S5 and S6, ESI[†]) show that the packing mode of polymorph- β is beneficial to the overlap between the chromophore molecules compared to that of polymorph- α . Enhancing the overlap degree of the chromophores can lead to an extended π -electronic system and enable the molecules to be excited more easily.²⁴

Fig. 4 shows the emission spectra of polymorph- α , polymorph- β , $[Zn(phen)_3]_2L(ClO_4)_4$ and L in dilute solution. The emission maximum band of the crystals of polymorph- α is located at a wavelength of 505 nm, which undergoes a red shift compared with that of L in dilute solution, due to the much stronger intermolecular interactions between the chromophore molecules.^{25–27} In contrast to the spectrum of polymorph- α , the emission band at 525 nm of polymorph- β is red-shifted by 20 nm, which is consistant with the absorption spectra above.

Interestingly, the emission band of $[Zn(phen)_3]_2L(ClO_4)_4$ shows an obvious blue-shift compared to those of polymorphs- α/β , which is similar to that in dilute solution. The spectral features can be explained by the fact that the chromophore molecules are isolated by $Zn(phen)_3^{2+}$ in the crystal of $[Zn(phen)_3]_2L(ClO_4)_4$ (Fig. 2c). The distance between them is as long as about 6.9 Å. The interaction between the chromophore molecules is so weak that it can be ignored. Therefore, $[Zn(phen)_3]_2L(ClO_4)_4$ exhibits monomer emission.

Solid-state fluorescence lifetimes

To obtain further insight into the photophysical properties, the fluorescence lifetimes (τ) were monitored at the maximum emission wavelength of the three crystals and the corresponding fluorescence decay curves are shown in Fig. 5.

 $Zn(phen)_3]_2L(ClO_4)_4$ has the shortest fluorescence lifetime and polymorph- β has the longest fluorescence lifetime (see Table S3, ESI[†]). The results provide further evidence that the fluorophore in $[Zn(phen)_3]_2L(ClO_4)_4$ favors monomer emission, similar to in dilute solution, due to there being no interactions between adjacent chromophore molecules. The fluorescence lifetime of polymorph- β is the longest, suggesting that the overlap degree within the chromophore molecule of polymorph- β is higher than that of polymorph- α .

Conclusions

In conclusion, in the present work, we found that the same molecule, L, exists in three kinds of single crystals, polymorph- α , polymorph- β and complex $[Zn(phen)_3]_2L(ClO_4)_4$, on tuning the crystallisation conditions. In addition, there are, in total, four independent conformations of molecule L in the three crystals. Relying on both experiments and theoretical calculations, it can be concluded that the C==C double bond length and the coplanarity between the pyridine and central benzene units can effectively reduce the stabilisation energy of the chromophore molecules. When the C==C double bond length is too short, the coplanarity becomes less important. Furthermore, an investigation of their optical properties shows that the three conformations display different colors (see Fig. 6) due to their different molecular configurations and interactions. These findings may have potential



Fig. 6 Photographs of the crystals of polymorph- α , polymorph- β and [Zn(phen)₃]₂L(ClO₄)₄ under UV excitation (λ_{ex} = 365 nm).

applications for crystal engineering to design different crystals and color-tuned optical materials.

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