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ARTICLE TYPE

Polymorphic Crystals and their Luminescence Switching of Triphenylacrylonitrile Derivatives upon Solvent Vapour, Mechanical, and Thermal Stimuli

Yujian Zhang,[ξ, ab] Qingbao Song,[ξ,a] Kai Wang,[d] Wengang Mao,[a] Feng Cao,[b] Jingwei Sun,[a] Lingling Zhan,[a]
5 **Yaokang Lv, [a] Yuguang Ma,[c] Bo Zou,*[d] and Cheng Zhang*[a]**

For piezo-, vapo-, and thermochromic materials, it remains a challenge to figure out underlying reason for fluorescence color changes upon external stimulation and determine why only some fluorophores reveal
10 emission switching. A novel triphenylacrylonitrile derivative (TPAN-MeO) with remarkably twisted conformations has been carefully prepared via the Suzuki coupling reaction. The fluorescence of TPAN-MeO in aggregate state depends on the polymorphism forms: three crystalline forms BCrys, SCrys and YCrys are brightly blue, sky-blue and yellow emission, respectively; meanwhile the amorphous powders are also strong fluorescent with green emission. The crystals BCrys and SCrys indicate the mechano- and
15 piezochromism in that grinding and high pressure could alter emission colour, respectively. In addition, the amorphous film reveals vapo- and thermochromic behaviour in that organic vapour and heating could change the green colour into sky-blue. Interestingly, the solvent vapour and heating stimuli can trigger a crystal-to-crystal transformation between SCrys form and YCrys form.

Introduction

20 The switchable and altering fluorescence of organic molecules in the aggregated state were of great interest due to their potential applications such as display devices, sensor and security inks.[1] As a result, the preparation of variable organic solids exhibiting a dynamic fluorescence response upon external stimulation
25 (heating, light and pressure etc.) has obtained considerable attention. Generally, optical properties of organic molecules in aggregated state were strongly affected by the intramolecular conformation and packing modes. For instance, H-type packing existing widely in π-conjugated dye obviously decreased its
30 emission quantum yield (Φ_f) due to the strong excitonic coupling.[1d,2] In sharp contrast, such excitonic coupling was dramatically weakened in the *J*-aggregate and the X-aggregate, which contributed to a high emission efficiency.[3] In addition, the supra-molecular interaction including C-H/π and C-H/N(O)
35 induced the rigid molecules and restricted intramolecular motions without the H-type stacking, also making the organic powders reveal the rather high emission efficiency.[4] Clearly, the fine-tuning of intermolecular packing and intramolecular conformation could availably alter the optical properties of small
40 organic molecules. However, the largest number of reported dyes revealed the various optical properties accompanied with simultaneous change in molecular arrangement and conformation.[1, 5] Thus, it was not clear which factor dominated the effect on optical properties. Importantly, it was still lack of an
45 appropriate model system to separately understand the influence of molecular conformation and arrangement on fluorescence.

Polymorphism with the same constitutional formula, in which molecules stacked in more than one crystalline phase, showed the evident difference in optical properties.[5,6] Moreover, polymorphic
50 crystals could be interconverted under external-stimuli as a result of the conformational flexibility and the subtleties of weak intermolecular interactions.[7] For example, Fraser's and Park's group reported mechanochromic fluorescence (MCF) and polymorphic modulation for the difluoroboron avobenzone[7a] and dicyano-
55 distyrylbenzene derivatives[7b], respectively. The thermal stimuli was also employed to vary solid-state luminescence between the polycrystalline powders.[7c-7e] In addition, the polycrystalline organometallic complex revealed a remarkable difference in its luminescence under organic vapour stimuli.[7f-7j] Although a large
60 number of organic fluorophores exhibiting the efficient reversible emission switching behaviours have been reported, it was still a great challenge to develop the polycrystalline fluorophores with responsive emission switching under multi-stimuli. [8]
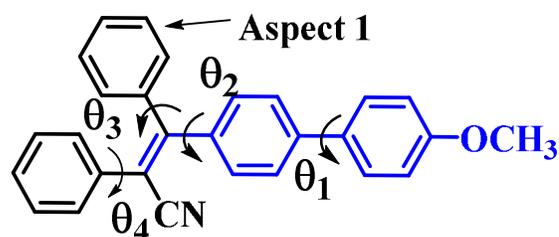
65 **Fig. 1** Structures and dihedral angle of **TPAN-MeO**, the dihedral angle (θ_1) between anisole and its neighbouring benzene, the dihedral angle (θ_2-θ_4) between acrylonitrile and its adjacent benzene.

Herein, we have prepared a polycrystalline fluorophore (**TPAN-MeO**, **Fig. 1**) containing the twisted **TPAN** and anisole. Three crystal polymorphs (**BCrys**, **SCrys** and **YCrys**) of **TPAN-MeO** exhibited the bright luminescence of different colors (deep blue, sky-blue and yellow, respectively). The crystals **BCrys** and **SCrys** revealed an obvious MCF behaviour. Additionally, upon vapour treatment, the sky-blue emission of **SCrys** were changed into a weak yellow emission, with the resulting crystals in line with **YCrys**. Interestingly, the melted crystals cooled down at the room temperature were transformed into amorphous powders (**GAm**), interestingly, which may became the crystalline solids (**YCrys** or **SCrys**) during other annealing conditions. Clearly, the switchable fluorescence of **TPAN-MeO** in the aggregated state was achieved under solvent vapour, mechanical grinding, and heating stimuli. Furthermore, the three polymorphs with different luminescence offered us an excellent way to understand the conformational effects on optical properties.
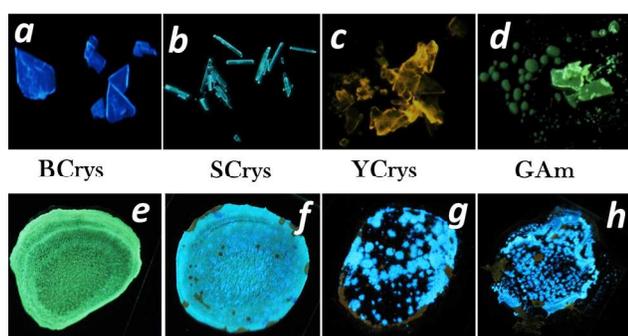
Fig.2 Photographs of TPAN-MeO under the illumination at 365 nm: (*a*) BCrys, deep blue crystal, (*b*) SCrys, sky-blue crystal, (*c*) YCrys, yellow crystal and (*d*) GAm, green amorphous powders; (*e*) Amorphous film prepared by the drop-casting, (*f*) the as-prepared film placed at the room temperature for 24 h, (*g*) the as-prepared film heated at 70 °C for 30 min, (*h*) the original film upon exposure to n-hexane vapour.

Results and discussion

As depicted in **Fig.S1**, the absorption spectra of **TPAN-MeO** in THF exhibited an evident peak at 334 nm, which was attributed to the π-π* transition. Whereas it emitted almost no fluorescence (Φ_f< 1%) in the solution state. In aggregated state, the flaky crystals of **TPAN-MeO** with yellow emission (**YCrys**, **Fig.2c**) can be obtained readily by slow evaporation of an ethyl acetate solution. The desired crystal revealed a weak luminescence (Φ_f= 9%) with fluorescence lifetime (τ) of 1.14 ns. Upon evaporation of an ethanol/CH_2Cl_2 mixture at the room temperature, needle-like single crystals of **TPAN-MeO** with sky-blue emission (**SCrys**, **Fig. 2b**) were formed at the bottom of the beaker. While evaporating the above mixtures at -10 °C, two different types of polymorphs, nubby crystals (**Fig.2a**) and needle-like crystal were reaped simultaneously. The former was colourless with the blue emission (referred to as **BCrys**), and the latter was also colourless with sky-blue emission, which was the same as that of **SCrys**. Compared to the emission peak of **YCrys** with λ_{max} = 540 nm, the fluorescence spectra of **BCrys** and **SCrys** were blue-shifted to 458 nm and 474 nm (**Fig. S2**), respectively. The Φ_f of corresponding crystals were increased to be 0.73 and 0.60, respectively, which were obviously larger than that of **YCrys**. Interestingly, the amorphous powders obtained by heat

treatment showed the green emission (**Fig.2d**, 511 nm) with a high Φ_f of 0.26. These results demonstrated the uniqueness of **TPAN-MeO** as a luminophores that could reveal the four-colour luminescence only by altering solid environments. Generally, the twisted luminophore exhibited the bluer emission with higher efficiency in crystalline phase than that in amorphous phase due to the weak intermolecular interaction.[9] However, in our case, **YCrys** indicated an obvious redshift and a lower emission efficiency relative to GAm. What was the reason for the opposite effects? **YCrys** exhibited the weak luminescence, which could be in principle ascribed to a small radiative or a large nonradiative rate constant. As shown in **Table1**, the radiative rate constant (k_r= Φ_f/τ) of **YCrys** was 8.2×10^7 s^{-1}, which was very close to that of GAm (k_r=9.0×10^7 s^{-1}). However, the non-radiative rate constant [k_{nr}= (1-Φ_f)/τ] in crystal **YCrys** (k_{nr} = 8.3×10^8 s^{-1}) was evidently larger than that in amorphous phase (**GAm** k_{nr}=2.6×10^8 s^{-1}). Clearly, the lager non-radiative decay channel of **YCrys** closely related to the especial intramolecular conformation, results in fluorescence quenching, which are further discussed below.[7b,10]

Table 1 The photophysical properties of **TPAN-MeO** in the different aggregated state, the dynamic parameters determined from the Function $I \propto \Sigma_i A_i \exp(-t/\tau_i)$ (A_i and τ_i are the relative weights and lifetimes respectively, i =1, 2).

	Φ_f^a	$<\tau>^b$ [ns]	λ_{max} [nm]	χ^2	k_f[s^{-1}]^b	k_{nr} [s^{-1}]^b
BCrys	0.73	3.02	458	1.041	2.4×10^8	8.9×10^7
SCrys	0.60	2.51	474	1.060	2.4×10^8	1.6×10^8
YCrys	0.09	1.14	539	0.998	8.2×10^7	8.3×10^8
GAM	0.26	2.88	511	1.001	9.0×10^7	2.6×10^8

^{a} Φ_f measured by calibrated integrating sphere; ^{b} An apparent decay time constant $<\tau>$ was determined by using the relation $<\tau> = \sum_{i=1}^n A_i \times \tau_i$ ($n = 1\sim2$); ^{t} the radiative rate constant $k_r = \phi_f/<\tau>$; The non-radiative rate constant $k_{nr} = (1-\phi_f)/<\tau>$;
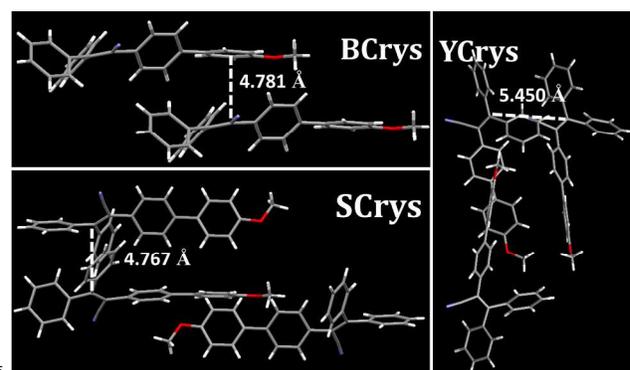
Fig.3 Molecular stacking structure in the polymorphic crystals (BCrys, SCrys and YCrys) of **TPAN-MeO**

Polymorphic crystal structure of **TPAN-MeO** were determined, and the respective crystallographic data were depicted in supporting information (SI). The unit cell of **SCrys** was triclinic, space group *P*-1, consisting of one discrete molecule. And the single crystal BCrys and YCrys belonged to a crystal system of monoclinic space group Cc and P2 (1)/*n*, respectively. As shown in **Figs. S4-6**, the aromatic C-H/π hydrogen bonds existed in all three polymorphs. Two other types of hydrogen bonds (C-H/O, C-H/N) were observed in single crystal **BCrys** and **SCrys**. However, No π–π overlap was formed

in three polymorphs due to the twisted conformation. Clearly, these secondary bonding interactions played an important role in the crystal formation as a key force to stabilize the crystals. In addition, these intermolecular weak interactions could hinder the rotation of phenyl rings and block nonradiative pathway, which contributed to activate the strong fluorescence.[4a-b,11] Thus, the TPAN-MeO molecules in the aggregated state revealed the drastically enhanced fluorescence compared with those of isolated state in solution. As depicted in **Fig.3**, the polymorph **BCrys** adopted a stacking mode of *J*-type aggregation along molecular long axis. For **SCrys** and **YCrys**, two types of edge-to-face molecular packing were formed. Moreover, the inter-plane distance of polymorphic crystals were more than 4.7 Å, and there was little overlap between adjacent π conjugations (**Figs.S4-S6**). The results revealed that almost no intermolecular π-π interactions existed in the crystalline state. Thus, the emission properties of crystals mainly depended on the individual molecule. In other words, the molecular conformation played a crucial role in determining the emission of polymorphic crystals.

Table 2 the dihedral angle in the polymorphic crystals (**BCrys**, **SCrys** and **YCrys**) of TPAN-MeO

Polymorphism	$\theta_1{}^a$	$\theta_2{}^b$	$<\theta_r>^c$	$\theta_3{}^b$	$\theta_4{}^b$
BCrys	46.9	42.0	44.5	43.5	60.8
SCrys [d]	34.6	36.1	35.4	58.8	48.2
	19.0	44.4	31.7	39.0	61.2
OCrys [d]	26.3	40.5	33.4	48.3	65.4
	29.6	29.8	29.7	59.2	53.5

[a] The dihedral angle between anisole and its neighbouring benzene; [b] the dihedral angle between acrylonitrile and its adjacent benzene; [c] $<\theta_r> = (\theta_1 + \theta_2)/2$; [d] Two crystallographically independent conformational molecules

In **BCrys**, the dihedral angle ($\theta_1{}^{BCrys}$) between the anisole and its adjacent benzene is 46.9° as depicted in **Table 2**. There were two crystallographically independent conformational molecules in the crystal of **SCrys**. The dihedral angle ($\theta_2{}^{SCrys}$, 36.1°, 44.4°) of **SCrys** got very close to that of **BCrys** (42.0°). However, the θ_1 was obviously decreased to 34.6° and 19.0°, respectively. Clearly, the smaller average dihedral angle ($<\theta_r>$) along the molecular long axis in **SCrys** (35.4° and 31.7°, see **Table 2**) meant that the effective π-electron conjugation degree was higher than that in **BCrys** (44.5°). Hence, the red shift of the emission peak of **SCrys** relative to that of **BCrys** should be ascribed to the intramolecular conformational planarizartion. As depicted in **Fig.3**, polymorph **YCrys** also exhibited an edge-to-face packing with two the different conformational molecules in the unit. The main difference between two polymorphs (**SCrys** and **YCrys**) was the coplanar extent ($<\theta_r>$), the former was 35.4° and 31.7° and the latter was 33.4° and 29.7°, respectively (**Table 2**). The results indicated the effective conjugation length of **YCrys** was further extended along the molecular long axis. As a result, the emission maximum of **YCrys** (λ_{max} = 540 nm) red shifted by 64 nm with respect to **SCrys** (λ_{max} = 474 nm). Clearly, **YCrys** and **SCrys** had the similar molecular stacking modes, but the different molecular conformation, which resulted in the change in fluorescent colours.
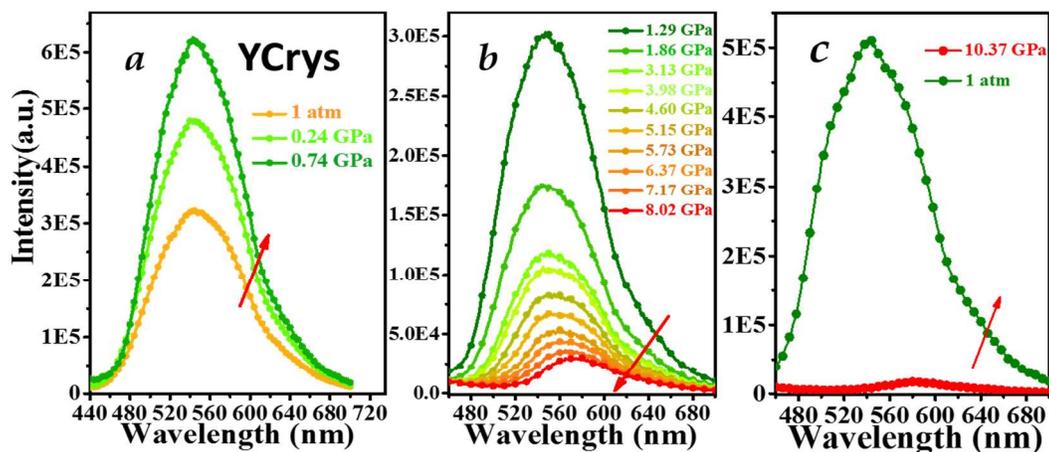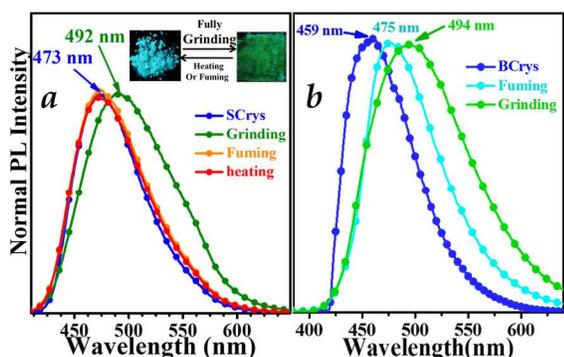

Fig. 4 Fluorescence spectra of the crystal YCrys under the hydrostatic pressure from compression (a, b) to decompression (c).

As mentioned above, **TPAN-MeO** formed three different kinds of crystals: **BCrys** (blue emitting, Φ_f = 0.67), **SCrys** (sky-blue emitting, Φ_f = 0.63) and **YCrys** (yellow emitting, Φ_f = 0.09). Obviously, **YCrys** revealed rather low luminous efficiency relative to others. Regardless of the intermolecular interactions, a twisted conformation generally contributed to form a nonradiative excited state, which resulted in a low Φ_f. However, **YCrys** showed the relatively more coplanarity along the 4-methoxy-1,1'-biphenyl (highlighted in blue in the **Fig. 1**) than that of **SCrys** and **BCrys**. Remarkably, the dihedral angles ($\theta_3{}^{BCrys}$) between acrylonitrile and aspect *α* in **BCrys** was 43.5° as shown in **Table 2**. The **SCrys** had two conformationally different molecules in the unit, the dihedral angles ($\theta_3{}^{SCrys}$) were changed into 58.8° and 39.0°. The $\theta_3{}^{SCrys}$ in one of the conformations was obviously larger than that of **BCrys.** In **YCrys**, the dihedral angles ($\theta_3{}^{YCrys}$) were further increased to 59.21° and 48.34°. Obviously, the aspect *α* of TPAN was relatively more twisted with the acrylonitrile. As a result, the highly twisted structure greatly turned on the nonradiative activation pathways. With Φ_f = 0.09 and τ=1.14 ns (see **Table 1**), the nonradiative rate constant of **YCrys** was $k_{nr}{}^{YCrys}$ =8.3×10^8 s^{-1}, thus approximately 1 order of magnitude larger than that of **BCrys** ($k_{nr}{}^{BCrys}$ =8.9×10^7 s^{-1}, Table 1) which resulted in the weak fluorescence. Clearly, the cause of the complicated fluorescence behaviours could fall into two parts: the

increase in coplanar extent along molecular long axis gave rise to the continuous spectra redshift; meanwhile, the various fluorescent efficiency were mainly attributed to the distortion between aspect α and acrylonitrile. **Fig.S7** revealed that the PL intensity of **YCrys** crystals were remarkably enhanced as decreasing the temperature. These results indicated the slight intramolecular motions including the rotations and the vibrations of phenyl rings still existed in aggregated state, which dissipated the excited energy, and thus inducing luminescence quenching processes. To further approve the proposal, the *in-situ* steady-state PL experiments of **YCrys** were performed under high pressure. As depicted in **Fig.4a**, with slight increasing hydrostatic pressure, the PL intensity was clearly enhanced until the pressure up to 0.74 GPa. After further compression, the emission intensity was gradually weakened, and the fluorescence spectra were concomitantly red-shifted (**Fig.4b**), which coincided with the previous results.[5a-c,12] Interestingly, when the hydrostatic pressure was gradually released, the emission spectra returned to initial state (**Fig.4c**). The similar PL behaviour was also observed in samples **SCrys** and **BCrys** as shown in **Figs.S8-S9**. In low pressure region, the intermolecular interaction was slight increased, which availably restricted the intramolecular motions and boosted up the PL efficiency. And the intermolecular distances had no clear change.[13] Upon the further compression, the π-π interaction was activated and dominant, hence the decrease in the PL intensity and redshifts of the crystal were observed at high pressures ($\geq$ 1.29 GPa). Clearly, the intramolecular motions still existed even in aggregate state, which quenched its luminescence.


Fig.5 Fluorescence spectra of the SCrys (*a*) and BCrys (*b*) upon multi-stimuli.
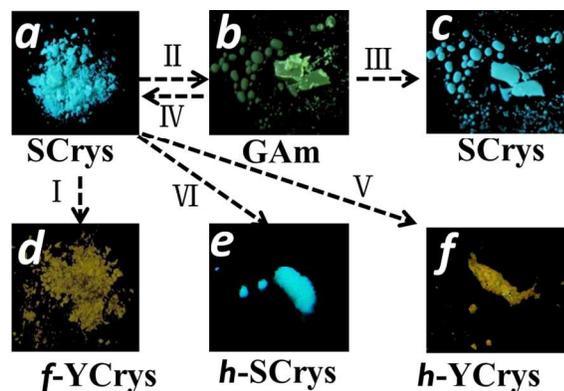
Fig.6 Digital images of samples **TPAN-MeO** in different states recorded under UV light. Ⅰ）Fuming with CH_2Cl_2 vapour; Ⅱ）heated to the melted state and cooled down at room temperature; Ⅲ）heating process at 70 ℃ for 1h；Ⅳ）Fuming with n-hexane vapour; Heated to the melted and then slightly contacted with a glass capillary at 168 ℃ (Ⅴ) and at 101 ℃ (Ⅵ).

By grinding of crystals **SCrys** and **BCrys** in an agate mortar, all of their fluorescence colour were changed into the similar green colour as depicted in **Fig.5**. The powders of two samples revealed the similar emission spectra (~493 nm). The results indicated that the two crystals might become an amorphous state upon grinding, which were further confirmed by the identical PXRD (see **Fig. S11**). Unusually, the ground powders of the **BCrys** could not be recovered to its initial state upon exposure to organic vapour (n-hexane, ethanol) or heating process. After the heating and organic solvent stimuli, the amorphous powders had a similar PXRD pattern and emission spectrum as that of **SCrys** as shown in **Fig. 5**. The results meant that the packing pattern of **SCrys** may be a more stable state than that of **BCrys**. **Fig.2e** showed that the drop-casting film of **TPAN-MeO** was amorphous with the bright green luminescence (λ_{max}= 508 nm, see **Fig.S13**), which resembled that of the sample **GAm**. And the amorphous film was not a steady state at the room temperature. As depicted in **Fig.2f**, the as-prepared film placed at room temperature for 24 h became the crystalline state with the sky-blue emission (λ_{max}=471 nm; see **Fig.S13**). The transition rate of fluorescence could be accelerated by increasing in the temperature. For instance, its luminescence colour became completely sky-blue after heating above 70 ℃ for 30 min (see **Fig.2g**). In addition, the green-emitting film was also transformed into crystalline powders upon exposure to n-hexane vapour, showing the sky-blue luminescence. PXRD experiments exhibited that the packing arrangement of the sky-blue emitting film was consistent with that of the **SCrys** (see **Fig.S14**).
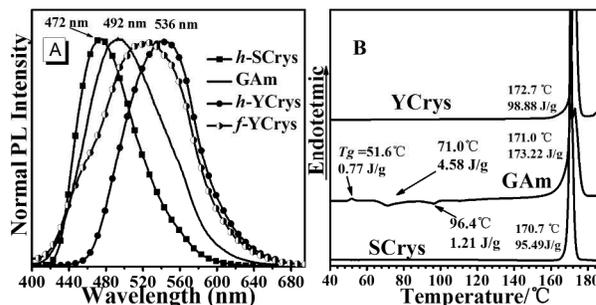
Fig.7 Normalized photoluminescence spectra (*a*) and DSC thermograms (*b*) of samples **TPAN-MeO** in the different states

The Crystals of **SCrys** were initially colourless in appearance, but appeared to become yellow in colour upon exposure to CH_2Cl_2 vapour for one minute at room temperature as depicted in **Fig.6d**. The emission spectra of the yellow powders (**f-YCrys**) revealed a broad emission spectra ranging from 440 nm to 560 nm (**Fig. 7a**). As shown in **Fig. 8a**, the diffraction patterns of sample **f-YCrys** exhibited sharp and intense reflections at 2θ = 8.2°, 12.3°, 16.4°, 18.5°, 20.5° and 20.8°, which were similar to that of **YCrys**. Moreover, a weak, broad, and diffused peak ranging from 16° to 25° also existed. Clearly, the **SCrys** revealed the vapor-induced the crystal-to-crystal conversion behaviour. Interestingly, the **TPAN-MeO** powders showed the thermally induced reversible phase transition properties. When the crystalline powders of **SCrys** were heated to the melted state and cooled down at room temperature, the amorphous powders (**GAm**) was formed as shown in **Fig.6b**. And the green-emitting phase could revert back to initial **SCrys** upon

n-hexane vapour (**Fig. 6a**). The DSC curves of GAm powders indicated two cold-crystallization transition peaks (71.0 °C, ΔH =4.58 J/g; 96.4 °C, ΔH =4.58 J/g) ahead of the melting (171.0 °C, ΔH = 173.22 J/g), however, which was not observed in crystals **YCrys** and **SCrys** (**Fig.7b**). The result showed that the **GAm** was a meta-stable amorphous phase and changed into a more stable crystalline phase via an exothermal recrystallization process. As expected, heating **GAm** powder at 70 ° C for 1 h also recovered the original state showed in **Fig.6c**, which was associated with the first-order endothermic peak. If the **SCrys** crystals were thermally melted and then slightly contacted with a glass capillary at about 168 °C, which was a little smaller than the melting temperature (171 °C). The yellow-emitting powders (**h-YCrys**) was produced at once, which revealed the luminescence properties similar to that of the **YCrys**. Interestingly, when the temperature was decreased to 101 °C, the obtained powders (**h-SCrys**) became colourless with the sky-blue emission. This observation revealed that the second cold-crystallization peak could be ascribed to a transition from **GAm** to the more stable **h-SCrys**. The powder X-ray diffraction analysis was performed after the heating stimulus-triggered phase transition. As depicted in **Fig.8b**, The crystal structure of **h-YCrys** and **h-SCrys** obtained via heating treatment was rather similar to that of **YCrys** and **SCrys** crystallized from the solution phase, respectively. The experimental results exhibited that the crystal-to-crystal transformations was also achieved upon heating process.
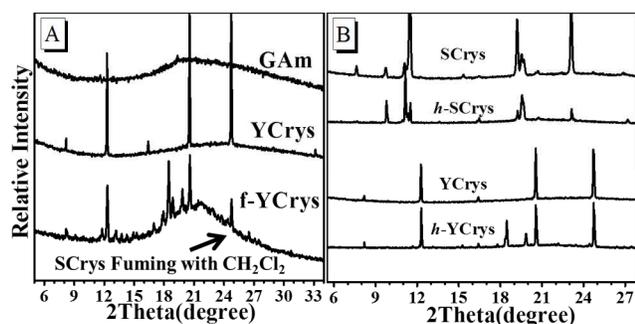

Fig.8 Powder X-ray diffraction patterns of samples **TPAN-MeO** in the different states

Conclusions

In conclusion, organic crystals (**BCrys**, **SCrys** and **YCrys**) with blue, sky-blue, and yellow fluorescence have been prepared under altered growing conditions. On the basis of single-crystal structural and photophysical analysis, we found that the various fluorescence of the polymorphs could be attributed to the conformational change rather than the intermolecular interaction. In addition, it was confirmed that the intramolecular motions still existing in crystalline state quenched the fluorescence via *in-situ* steady-state PL experiments. The PL spectra indicated that changes in the molecular aggregate state of **BCrys** and **SCrys** crystals upon grinding or under high pressure resulted in the altering molecular conformation, and thus induced the mechano(piezo)chomic fluorescence. Interestingly, the crystal-to-crystal molecular conversion between the **BCrys** and **YCrys** was readily achieved under heating and solvent vapour stimulation. Clearly, employing "polymorphs" with the multiple mutable interactions to prepare stimuli-responsive materials and understand its formation mechanisms was rational and successful.

Notes and references

*a*Department of Materials chemistry, Huzhou University, xueshi Road No.1 313000 Huzhou, P. R. China;
*b*College of Chemical Engineering, Zhejiang University of Technology, Caowang Road No.18 Hangzhou 310000, P. R. China; Tel:+86-571-88320508; E-mail: czhang@zjut.edu.cn
*c*State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou, P. R. China
*d*State Key Laboratory of superhard materials, Jilin University, Changchun, P. R. China E-mail: zoubo@jlu.edu.cn

*§*Y. J. Zhang and Q. B. Song contributed equally to this work.

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Table of Contents (TOC)
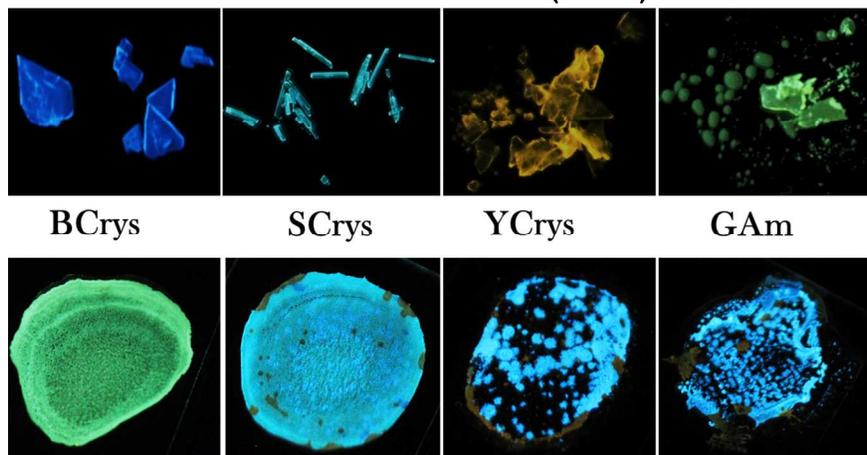
The organic crystals BCrys, SCrys and YCrys exhibits blue, sky-blue, and yellow fluorescence, respectively. Their various fluorescence of the polymorphs can be attributed to the conformational change. In addition, the responsive fluorescence switching of polymorphs are readily achieved under grinding, heating and solvent vapour stimulation