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论文题目：Preparation of a new crystal form and exploration
mechanochromic property of an organic fluorescent
material

Preparation of a new crystal form and exploration of mechanochromic property of an organic fluorescent material

Qing Wen Lin

ABSTRACT:

The organic optoelectronic materials have been extensively used in the field of dye-sensitized solar cells, light emitting diodes, light sensors and organic field-effect transistors. Triphenylamine derivatives have displayed promising properties in the development of organic optoelectronic materials. This research stems from the author's involvement in a popular science experiment focused on the preparation of triphenylamine derivatives as organic luminescent crystal materials through the Knoevenagel condensation name reaction. Curiosity sparked the investigation into the relationship between the physical color and molecular crystal structure of organic materials. The Knoevenagel condensation between 4-diphenylaminobenzaldehyde and malononitrile yielded 2-(4-diphenylaminobenzylidene) malononitrile (abbreviated as DPAM), which produced two different colors of organic luminescent crystals when different methods of recrystallization were used. The yellow needle-shaped crystal A-1 has been confirmed as a previously unreported new crystal form with an orthorhombic crystal system, while the orange red block-shaped crystal A-2 is a known crystal form with a monoclinic crystal system by single crystal X-ray crystallographic analysis. Notably, the red crystal A-2 was found to undergo crystalline transition through grinding or pressing, resulting in the formation of the yellow crystal A-1, demonstrating a significant mechanochromic phenomenon. The relationship between crystal structure, crystal morphology, and mechanochromic luminescence of compound DPAM is discussed, along with the impact of solvent polarity on its photophysical properties. This study presents a promising crystalline material for applications in pressure sensing, anti-counterfeiting, and information encryption.

Keywords: fluorescent material, crystal form, mechanochromism, Knoevenagel condensation, triphenylamine

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1. Introduction

Organic optoelectronic materials and devices represent a crucial area of research in materials science and organic photonics, garnering significant attention due to their extensive potential applications in imaging, displays, detection, optical communication, and photodetection [1-3]. These materials possess unique flexibility and processability, offering limitless possibilities for the development of flexible electronics, wearable devices, and smart textiles. Through molecular design, synthesis, and the exploration of their crystal forms, the optical properties of organic materials can be precisely tuned, thereby enhancing the efficiency and versatility of applications in light emission, absorption, and photoconversion.

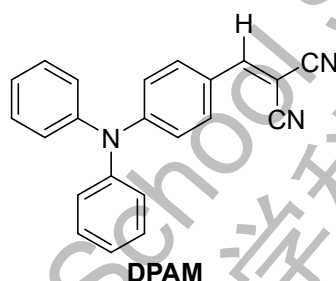


Figure 1. Molecular structure of DPAM

Triphenylamine derivatives are ideal intramolecular charge-transfer (ICT) compounds, characterized by the presence of an electron-donating (D) group and an electron-accepting (A) group linked through π -conjugation [4]. Consequently, they have demonstrated promising properties for applications in organic field-effect transistors (OFETs), light-emitting devices, dye-sensitized solar cells, and photovoltaic devices. In the molecule 2-(4-(diphenylamino)benzylidene) malononitrile (DPAM), the triphenylamine group acts as the electron-donating unit, while the dicyano group serves as the electron-accepting unit, connected by a vinyl bond [5]. Wang reported an efficient synthesis of DPAM by the Knoevenagel condensation reaction [6], and Son identified the one crystal form of DPAM [7]. However, the relationship between the crystal structure, morphology, and mechanochromic luminescence of DPAM has not been thoroughly investigated, let alone the exploration of new crystal forms. Therefore, this study focuses on the preparation of a new crystal form of DPAM and its mechanochromic response. We discuss the relationship between crystal structure, crystal morphology, and mechanochromic luminescence, along

with the impact of solvent polarity on its photophysical properties.

2. Experimental section

a) Materials and methods

All chemicals were purchased from commercial sources, and all solvents were purchased in HPLC-grade-quality. ^1H NMR and ^{13}C NMR spectra were recorded at 25 °C on a Bruker AVANCE 400M superconducting NMR spectrometer, with deuterated chloroform as the lock solvent. The working solution concentration for NMR was 20 mg/mL. All chemical shifts are given in the ppm-scale and refer to the nondeuterized proportion of the solvent. IR was recorded from a Nicolet iS10 FT-IR spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) with the wavenumber range of 400 - 4000 cm^{-1} . HRMS were obtained using an Agilent 6230 TOF mass spectrometer (Agilent, Waldbronn, Germany) with Electron Spray Ionization (ESI). The thermogravimetric analysis (TGA) of compounds was conducted using a DSC Q100 thermal analysis system (TA Instruments, New Castle, DE, USA). The TGA test was performed under a nitrogen atmosphere, heating from 25 °C to 400 °C at a rate of 10 °C·min $^{-1}$, with weight-temperature curves recorded. The differential scanning calorimetry (DSC) test was performed in the temperature range of 20 - 200 °C, at a heating rate of 10 °C·min $^{-1}$, with heat flow-temperature curves recorded. The single crystal structure of compounds was determined using a Bruker D8 Venture Ims3.0 X-ray single-crystal diffractometer (Bruker, Berlin, Germany). Fluorescence analysis was performed using Shimadzu RF-5301 at room temperature. Measurement of UV visible absorption was performed by UH5300 UV visible spectrophotometer.

b) Preparation of DPAM

To a solution of 4-(diphenylamino) benzaldehyde (2.74 g, 10 mmol) and malonanitrile (1.48 mL, 10 mmol) in ethanol (40 mL) was added 4 drops of piperidine. The solution was stirred at room temperature for 3 h, and water (40 mL) was added to the reaction mixture. The product 2-(4-(diphenylamino) phenylmethylene) malonanitrile (DPAM) was precipitated as an amount of orange red crystal (A-2), and obtained in 95% yield (3.04 g) by filtering and drying at 110 °C for 3 h.

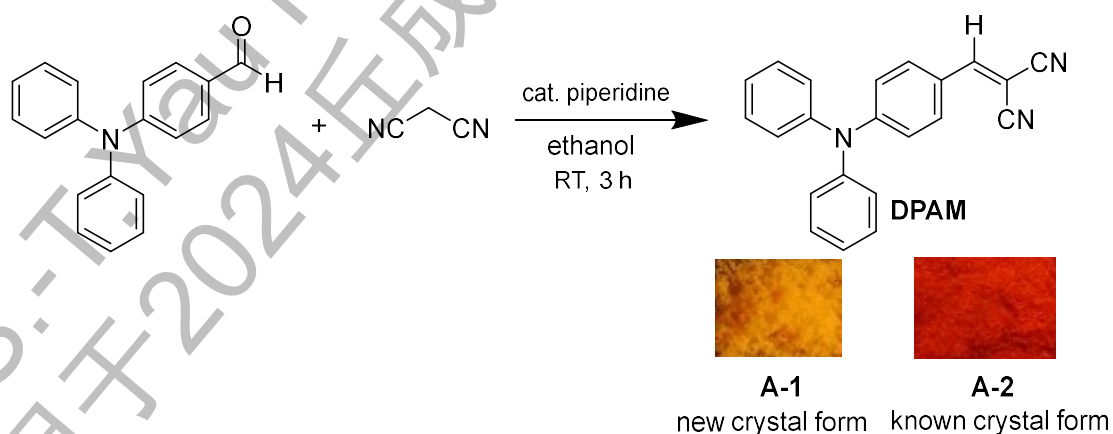
The above DPAP product (1.52 g) was completely dissolved in ethanol (30 mL) under

reflux, and the water (8 mL) was added. Then the mixture solution was poured into ice water (100 mL) to precipitate yellow crystal (A-1), which was obtained in 90% yield (1.37 g) by filtering and drying at 110 °C for 3 h.

3. Results and discussion

a) Synthesis and characterization of DPAM

2-(4-Diphenylamino-benzylidene)-malononitrile (DPAM) was synthesized by piperidine-catalyzed Knoevenagel condensation reaction between 4-diphenylaminobenzaldehyde and malononitrile. The reaction was carried out in ethanol at room temperature for 3 hours with piperidine as a catalyst and produced DPAM in 95% yield, as shown in Scheme 1. The yellow needle-shaped crystal A-1 was obtained from a mixed solvent of ethanol and water, and the orange red block-shaped crystal A-2 was obtained from pure ethanol. The spectroscopic data are in line with the desired molecular structure of DPAM, and confirmed with NMR (Figures 2 and 3) and mass spectrometry (Figure 4). The characterization data of DPAM are as follows: ^1H NMR (CDCl_3 , 400 MHz) $\delta = 7.78 - 7.66$ (m, 2H), 7.51 (s, 1H), 7.38 (dd, $J = 10.8, 4.9$ Hz, 4H), 7.27 - 7.14 (m, 7H), 7.00 - 6.87 (m, 2H); ^{13}C NMR (CDCl_3 , 101 MHz) $\delta = 157.88, 153.49, 145.16, 132.98, 129.96, 126.72, 126.13, 122.80, 118.49, 115.18, 114.07, 75.59$; HRMS (ESI): calcd. for $\text{C}_{22}\text{H}_{15}\text{N}_3$ $[\text{M}+\text{H}]^+$ 322.1344, found 322.1340; $[\text{M}+\text{Na}]^+$ 344.1164, found 344.1157.



Scheme 1. Synthesis of DPAM

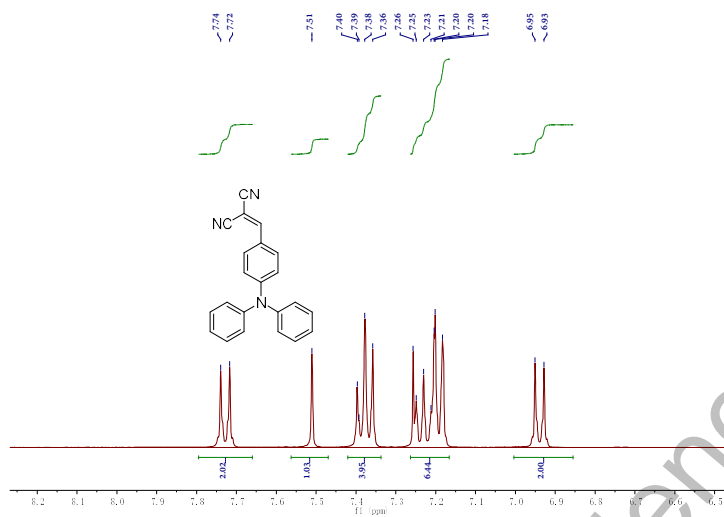


Figure 2. ¹H NMR spectra of DPAM

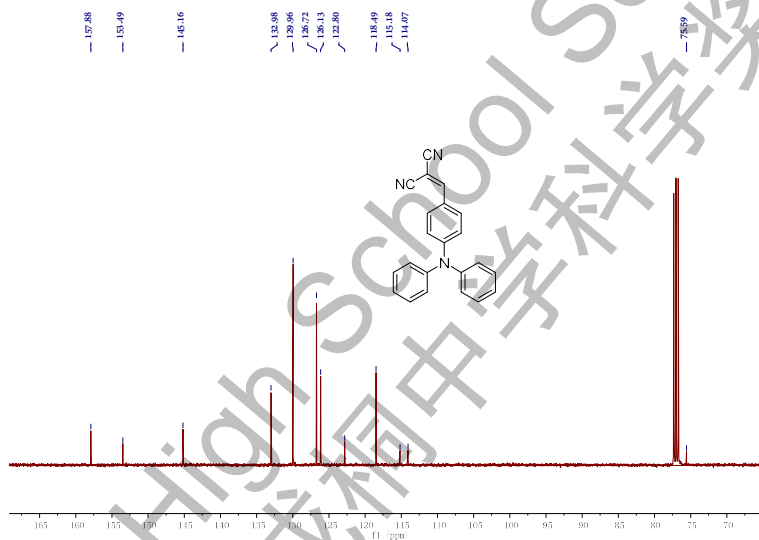


Figure 3. ¹³C NMR spectra of DPAM

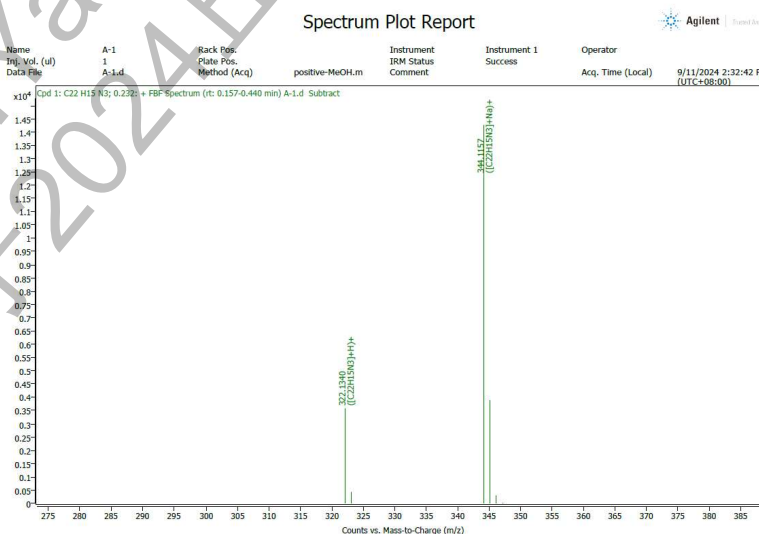


Figure 4. HRMS (ESI) spectra of DPAM

b) Relationships between physical color and crystal structure

The color of a substance is primarily determined by its molecular crystalline structure, as the molecular structure dictates its light absorption and reflection properties. Therefore, studying the relationship between a substance's color and its molecular crystalline structure helps us gain a deeper understanding of the substance's physical and chemical properties. To gain insight into the molecular organization of DPAM, the yellow needle-shaped single crystal A-1 suitable for structure analysis was obtained by slow evaporation of ethanol and water mixed solution of DPAM at room temperature for one week. The yellow needle-shaped crystal A-1 has been confirmed as a previously unreported new crystal form with an orthorhombic crystal system (Figure 5). The result indicated that A-1 molecule crystal existed in the orthorhombic space group $Pbca$ with $a = 11.2205(6) \text{ \AA}$, $b = 14.6394(10) \text{ \AA}$, $c = 20.9226(16) \text{ \AA}$ and $\beta = 90^\circ$. Crystallographic crystal data and processing parameters for A-1 were shown in Table 1.

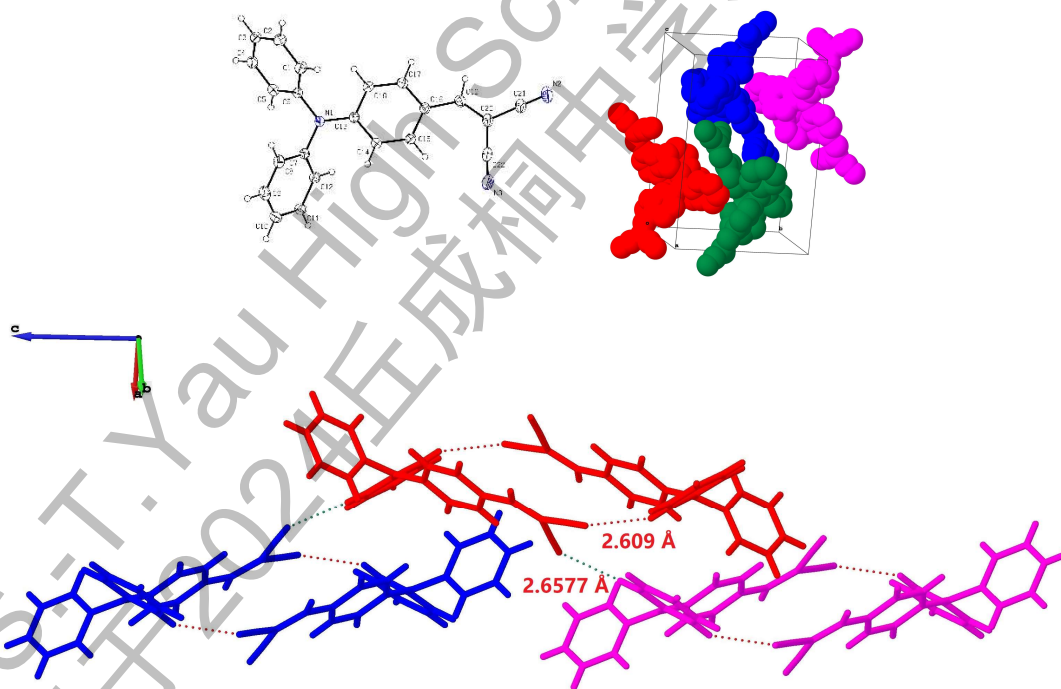


Figure 5. The X-ray single crystal diffraction pattern of crystal A-1

Table 1 Crystal data and structure refinement for A-1.

Empirical formula	$C_{22}H_{15}N_3$
Formula weight	321.37
Temperature/K	170.0

Crystal system	orthorhombic
Space group	Pbca
a/Å	11.2205(6)
b/Å	14.6394(10)
c/Å	20.9226(16)
α /°	90
β /°	90
γ /°	90
Volume/Å ³	3436.8(4)
Z	8
ρ_{calc} /cm ³	1.242
μ /mm ⁻¹	0.075
F(000)	1344.0
Crystal size/mm ³	0.48 × 0.05 × 0.02
Radiation	MoK α (λ = 0.71073)
2 θ range for data collection/°	4.972 to 54.252
Index ranges	-14 ≤ h ≤ 13, -18 ≤ k ≤ 17, -26 ≤ l ≤ 26
Reflections collected	23800
Independent reflections	3802 [R_{int} = 0.0672, R_{sigma} = 0.0419]
Data/restraints/parameters	3802/0/226
Goodness-of-fit on F^2	1.058
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0434, wR_2 = 0.0901
Final R indexes [all data]	R_1 = 0.0698, wR_2 = 0.1058
Largest diff. peak/hole / e Å ⁻³	0.13/-0.19

The orange red single crystal A-2 suitable for structure analysis was obtained by cooling the hot solution of DPAP in ethanol at room temperature for 6 hours. The orange red block-shaped crystal A-2 is a known crystal form with a monoclinic crystal system (Figure 6). The result indicated that A-2 molecule crystal existed in the monoclinic space group P2(1)/c with $a = 7.0262(9)$ Å, $b = 15.9319(16)$ Å, $c = 16.1075(19)$ Å and $\beta = 95.169(5)^\circ$. Crystallographic crystal data and processing parameters for A-2 were shown in Table 2.

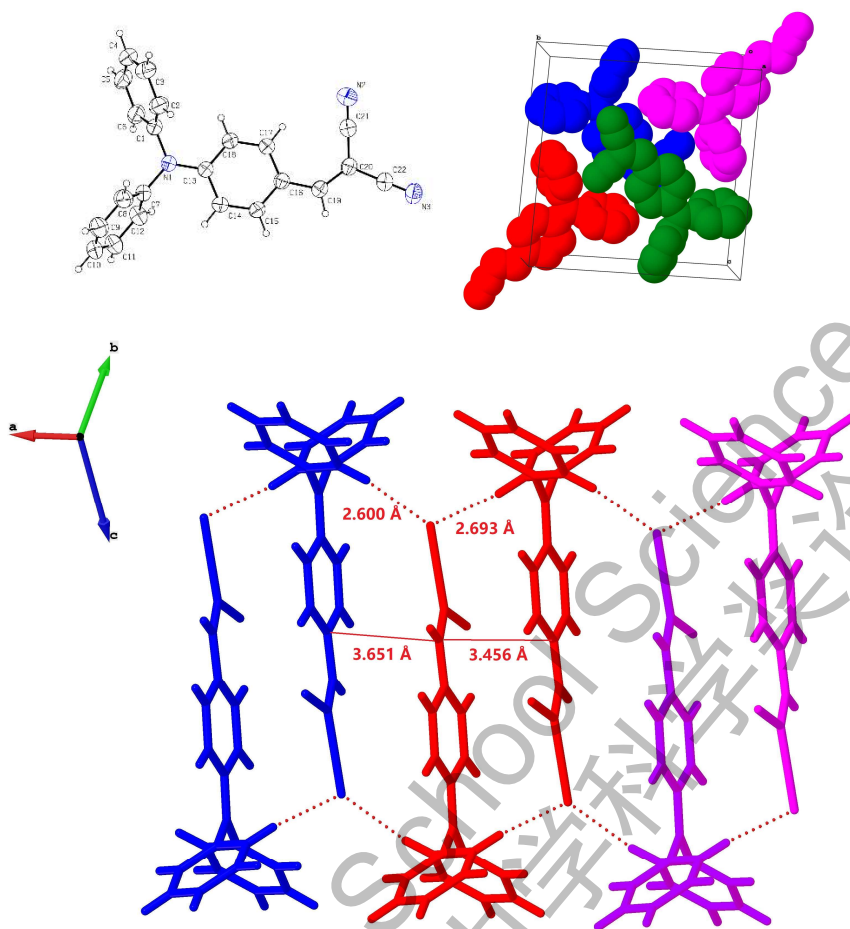


Figure 6. The X-ray single crystal diffraction pattern of crystal **A-2**.

Table 1 Crystal data and structure refinement for **A-2**.

Empirical formula	C ₂₂ H ₁₅ N ₃
Formula weight	321.37
Temperature/K	302.00
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	7.0262(9)
b/Å	15.9319(16)
c/Å	16.1075(19)
α/°	90
β/°	95.169(5)
γ/°	90
Volume/Å ³	1795.8(4)
Z	4
ρ _{calc} /cm ³	1.189
μ/mm ⁻¹	0.072
F(000)	672.0

Crystal size/mm ³	0.35 × 0.2 × 0.15
Radiation	MoK α (λ = 0.71073)
2 θ range for data collection/ $^\circ$	5.078 to 56.686
Index ranges	-9 \leq h \leq 9, -21 \leq k \leq 21, -21 \leq l \leq 21
Reflections collected	37280
Independent reflections	4468 [R _{int} = 0.0397, R _{sigma} = 0.0241]
Data/restraints/parameters	4468/0/226
Goodness-of-fit on F ²	1.163
Final R indexes [$I \geq 2\sigma(I)$]	R ₁ = 0.0888, wR ₂ = 0.2343
Final R indexes [all data]	R ₁ = 0.1317, wR ₂ = 0.3143
Largest diff. peak/hole / e \AA^{-3}	0.20/-0.30

The choice of crystallization solvents had a significant impact on the macro-scale morphology of the crystals. The yellow crystal A-1, belonging to the orthorhombic crystal system, was obtained from a mixed solvent of ethanol and water. In contrast, the orange red crystal A-2, which has a monoclinic crystal system, was obtained from pure ethanol. The crystalline structure reveals that the molecule of A-1 is arranged in antiparallel patterns characterized by hydrogen bonds. The highly twisted benzene rings within the crystal structure inhibit the formation of exciplexes or excimers, further promoting increased emissions. The crystalline structure reveals that the molecule of A-2 is arranged in antiparallel patterns characterized by $\pi \cdots \pi$ weaker interactions and hydrogen bonds. This arrangement helps to stabilize the conformations of the molecules, leading to enhanced emissions. The highly twisted stacking architecture results in shorter effective conjugation lengths, producing bluer emissions, while the planar conformation increases effective lengths, yielding redder emissions.

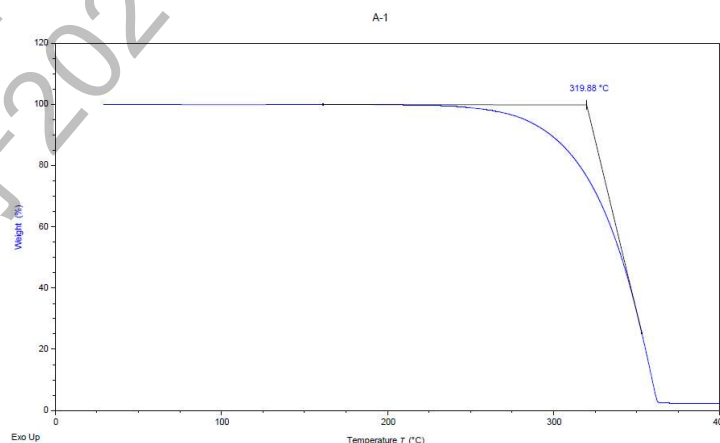


Figure 7. TGA test curve of crystal A-1.

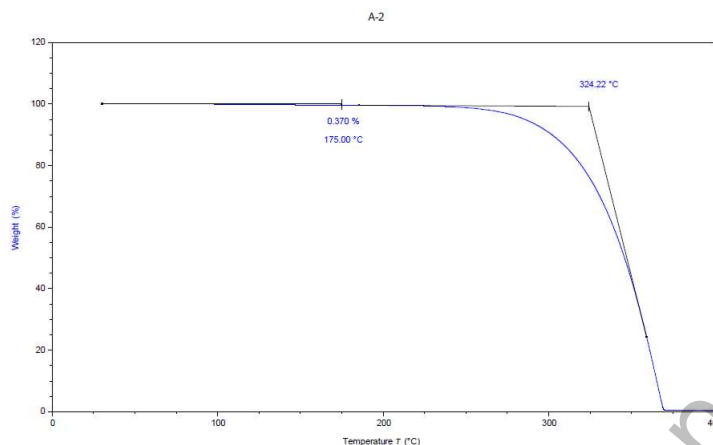


Figure 8. TGA test curve of crystal A-2.

Thermal stability is an important property of the organic crystal materials. The thermogravimetric analysis (TGA) test curves for A-1 and A-2 are shown in Figures 7 and 8, A-1 and A-2 exhibit high thermal stability. It can be observed that crystal A-1 exhibits significant mass loss for quickest decomposition only after reaching 319.88 °C, while the crystal A-2 exhibits little mass loss (0.37%) after reaching 175.00 °C, and exhibits significant mass loss for quickest decomposition after reaching 324.22 °C. The DSC test curves for A-1 and A-2 is depicted in Figures 9 and 10. It is evident that crystal A-1 exhibits a melting point around 138.02 °C and crystal A-2 exhibits a melting point around 139.43 °C.

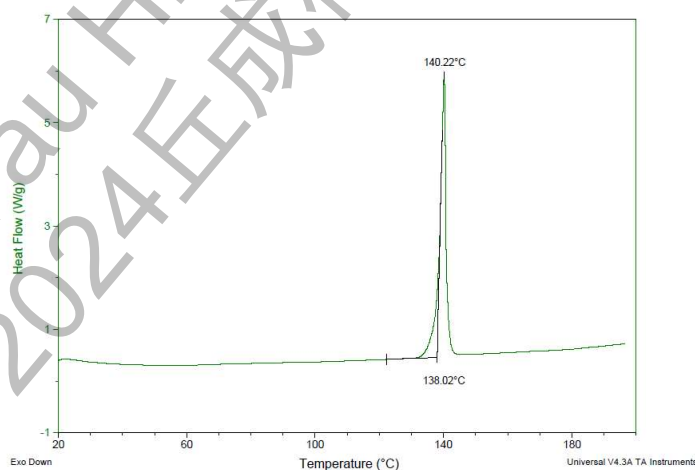


Figure 9. The DSC test curve of crystal A-1.

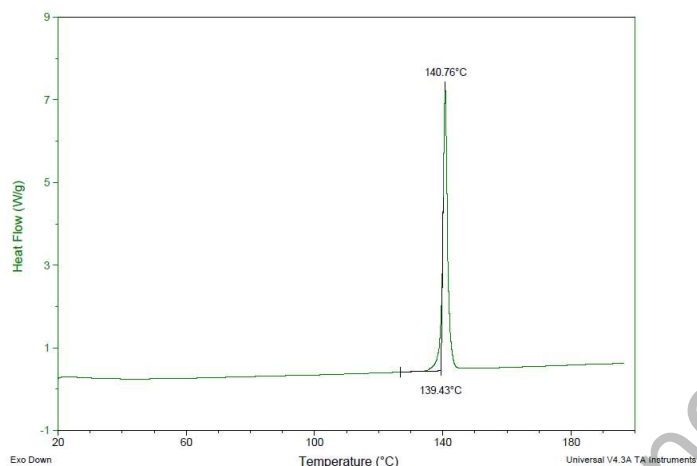


Figure 10. The DSC test curve of crystal A-2.

c) Mechanochromic phenomenon

In recent years, mechanochromically luminescent crystalline organic materials, which can reversibly alter the color of their solid-state emissions in response to mechanical stimuli, have garnered significant attention due to their diverse potential applications [8-11]. After grinding the orange red crystal A-2 in a mortar for 10 minutes, its color changed to yellow, as shown in Figure 11. Under excitation with UV light at 254 nm, the fluorescence color of A-2 shifted from red to yellow. This change may be attributed to alterations in the twisting angles of the three benzene rings within its crystalline structure due to the grinding process, resulting in the formation of yellow crystal form A-1. Furthermore, when crystal A-2 was subjected to a pressure of 10 MPa for 15 minutes affording yellow crystal A-1, the enhanced fluorescence property was also observed under the 254 nm UV light. Thus, the yellow crystal A-1 is a stable form, while the orange red crystal A-2 is a metastable form. The mechanism behind the mechanically induced change in emission color is attributed to transitions between crystalline and amorphous phases.

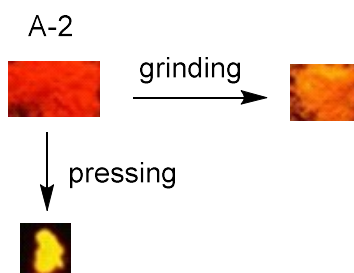


Figure 11. Mechanochromism of crystal A-2

d) Impact of solvent polarity on photophysical properties

The photophysical properties of DPAM in six different solvents (benzene, toluene, EtOAc, THF, ClCH₂CH₂Cl, and DMF) at the concentration of 1.0×10^{-6} mol/L are collected in Table 3. The fluorescence intensity decreases as solvent polarity increases. For instance, the maximum emission wavelength of DPAM is centered at 514 nm in benzene (emitting green fluorescence), while in the more polar solvent DMF, the peak shifts to 585 nm (emitting yellow fluorescence), resulting in a red shift of 70 nm and a one-third reduction in intensity due to the altered molecular environment. Significant Stokes shifts are observed for DPAM in the selected solvents, attributed to strong dipole-dipole interactions between the solvent and solute, which exhibit high orientational polarizability and dipole moments.

Table 3 Maximum emission wavelengths in different solvents.

benzene	toluene	EtOAc	THF	ClCH ₂ CH ₂ Cl	DMF
515	546	570	575	582	585

Organic compound DPAM contains both an electron-donating group (triphenylamine) and an electron-withdrawing group (dicyano), resulting in significant charge separation within the fluorophore, which contributes to its dipole moment in the ground state. In the excited state, the degree of charge separation increases, leading to an even larger dipole moment compared to that in the ground state. Furthermore, as solvent polarity increases, the charge separation becomes even more pronounced. Consequently, the emission spectra of the compound DPAM demonstrate notable sensitivity to solvent polarity.

4. Conclusions

In summary, 2-(4-Diphenylamino-benzylidene)malononitrile (DPAM) was synthesized in high yield via a piperidine-catalyzed Knoevenagel condensation reaction. A new crystal form, designated A-1, was obtained as needle-shaped yellow single crystals with an orthorhombic crystal system through careful selection of crystallization solvents. A systematic study encompassing the preparation process, spectroscopic data (including NMR and HRMS), thermal stability, single crystal X-ray diffraction, emission fluorescence spectra, and mechanochromism of the ICT-type organic crystal material DPAM has allowed us to derive significant structure-property relationships. Based on single crystal X-ray diffraction analysis, the highly twisted benzene rings within these crystal structures inhibit

the formation of exciplexes or excimers, thereby promoting enhanced emissions. The results of the mechanochromism study indicate that the mechanism underlying the mechanically induced changes in emission color is attributed to transitions between crystalline and amorphous phases. This research presents a promising organic crystalline material for applications in pressure sensing, anti-counterfeiting, and information encryption.

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指导教师顾昊睿简历：女，博士、实验师，2010年毕业于扬州中学；2014年毕业于浙江大学化学系获得学士学位；2019年毕业于浙江大学化学系获得理学博士学位，同年入职浙江大学化学系、化学国家级实验教学示范中心，承担化学实验教学工作和化学科普宣传等。跟林青文同学没有亲属关系，在本研究中作为科学实践导师，进行理论指导、实验指导、数据分析指导和论文写作指导等。属于无偿指导。

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本研究源自作者（林青文同学）参加浙江大学化学国家级实验教学中心组织的中学生科普实验暑期实践项目：利用Knoevenagel缩合有机人名反应制备有机发光晶体材料，展示此类有机分子的神奇发光效应，顾昊睿老师是该科普项目的指导教师。科普实验结束后，受好奇心驱动，作者主动提出要探究该类有机晶体材料的分子结构和发光性能之间的关系，希望继续参与作为科研实践课题并撰写作品参加丘成桐化学科学竞赛。在研究中发现利用不同重结晶溶剂可制备2种不同颜色的有机发光晶体，在顾昊睿老师指导下，通过查阅文献，其中一种是未被文献报道的新晶型，而且发现另一种已知晶型可通过研磨转晶，首次发现该晶体材料的力致变色现象。作者在指导老师帮助下进行了本课题的系统研究，该研究结果有助于揭示化合物DPAM的晶体结构、晶体形态与机械变色发光之间的关系，并希望促进该类晶体材料在压力传感器、防伪、信息加密等领域的潜在应用。

在研究过程中，作者首先要感谢顾昊睿老师无偿无私的指导。她给了我很多理论指导、和实验操作指导，并协助制定实验方案、表征方法，指导我如何查阅国内外文献，指导我具体的数据分析（含荧光测试分析、高分辨质谱测试与分析），最后指导论文写作和定稿等，一个月的科研实践经历都离不开顾老师的悉心指导。作者也要感谢我的高中化学任课教师刘晓青老师，认真细致指导我的论文写作，在研究报告起草过程中给与大量意见和建议。最后，作者欢要感谢浙江大学化学系大型仪器分析测试平台的一些老师的帮助：毛侦军实验师（核

磁测试)、陈林深正高级实验师(热分析)、刘继永实验师(单晶衍射测试与解析)。

在本项目研究中,其实碰到了无数的困难和挑战。比如新晶型发现,如何培养单晶?首先了解培养单晶方法,尝试各种溶剂体系并行安排实验。还有就是,好多测试项目,如何理解图谱?这方面,顾老师给我补了非常多的理论知识,但是短时间要完全掌握都是很大挑战,只能一边做测试,一边学习实际分析图谱案例。所幸在实验教学中心各位老师的大力支持和鼓励下,作者终于坚持下来,完成了本项目的挑战,必将受益终生。

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