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original powder grinding powder n-C₆H₁₂ PhCH₃ EtOAc THF CH₂Cl₂ CH₃COCH₃ CH₃CN CH₃CN :H₂O =10: 90

Journal

1 Rational Design of Coumarin Fluorophore with Solvatochromism,

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AIE and Mechanofluorochromic Enhancement Properties

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10 Abstract

A new fluorophore 7-(diphenylamino)coumarin-4-yl pivalate (DPACP) with solvatochromism, 11 aggregation-induced emission (AIE) and mechanofluorochromic (MFC) enhancement 12 13 characteristics was rationally designed and synthesized by attaching bulky diphenylamine 14 electron-donor and pivalate ester electron-acceptor to coumarin. With solvent polarity increase 15 from n-hexane to acetonitrile, this molecular displayed a bathochromic shift in the emission wavelength (from 436 nm to 553 nm) and a decrease in the quantum yield (from 81.1% to 2.8%), 16 17 indicating solvatochromic effect. Also, the AIE behaviors were observed in CH₃CN/water and 18 THF/water mixture systems. For example, the PL intensity increased 6 times in mixed solvent 19 $(CH_3CN : water = 10 : 90)$ compared to that in pure CH_3CN . Moreover, the emission of original 20 powder samples was red-shifted (from 438 nm to 483 nm) with fluorescence enhancement (the solid-state quantum yield increase from 19% to 28%) upon grinding, and the emission behaviors 21 22 of grinding powder samples could be reverted to original state by wetting with n-hexane. 23 Furthermore, the relationship among the molecular structure, intermolecular interactions and 24 emission properties was investigated by single-crystal diffraction analysis. DPACP had a twisted 25 conformation because of steric hindrance from diphenylamine and pivalate ester groups, which 26 played a decisive role in realizing AIE and MFC enhancement behaviors. The absence of π - π 27 stacking observed in single-crystal structure was the main reason for the AIE property. The MFC 28 enhancement property could be ascribed to the disturbance of weak electrostatic interaction of 29 adjacent molecules upon grinding. The bulky group of pivalate ester was first used to construct 30 MFC molecule, and this work provided insights for developing AIE and MFC materials based on 31 conventional planar fluorophore which was always subject to ACQ effect.

32 1. Introduction

33 The design and synthesis of mechanofluorochromic (MFC) materials showing reversible

solid-state emission change upon external mechanical stimuli have attracted considerable 1 2 scientific interest [1-18]. Normally, fluorophores with AIE (such as tetraphenylethylene, 3 triphenylethylene, cyanoethylene and diarylvinylanthracene) have always been used as building 4 blocks to construct MFC materials [19-27], because AIE-active molecules often afford twisted 5 molecular conformations and loose packing, which facilitates the destruction of molecular 6 arrangements upon external mechanical stimuli, resulting in MFC behavior. For example, at least 7 100 MFC molecules based on tetraphenylethylene (TPE, a typical AIE compound) have been 8 reported [19]. But, it should be noted that not all AIE-core molecules exhibit mechano-responsive 9 behavior, some influences including crystallinity, velocity of crystallization and polymorphism play 10 important roles in MFC property and predictability was difficult to achieve [28].

11 Conventional planar organic dyes always display strong fluorescence in dilute solution but their 12 luminescence decays obviously in aggregate or solid states, known as aggregation-caused 13 quenching (ACQ) [29, 30], which is against to solid-state emission and stimuli-responsive 14 behaviors. However, ACQ can be restrained by virtue of structural modification to prevent the 15 aggregation, making conventional fluorophore potential candidates as promising AIE and MFC 16 materials. Therefore, in view of a known fluorescent structure unit, the molecular skeleton 17 modification is important and significant for achieving the AIE and MFC activities, which deserves 18 further exploration.

19 Coumarins are extensively applied to design fluorescent probes for biomedical imaging 20 because of their simple molecular structures, convenient skeleton modifications and excellent 21 photophysical properties in solution state [31]. But their derivatives that show both MFC and AIE 22 activities are scarce, which probably arise from fluorophore ACQ effect. Recently, several 23 mechanoresponsive molecules based on coumarin have been reported. For example, Yu and 24 co-workers reported a mechanoresponsive coumarin hydrozone compound by breaking of 25 hydrogen-bonded dimers under pressure [32]. By disturbing the π - π stacking upon grinding, Peng 26 and co-workers developed a novel TPE-fused coumarin molecule exhibiting MFC properties [33]. 27 Very recently, our group reported a MFC coumarin oxime compound based on the destroying of 28 H-aggregate induced by mechanical stimulus [34]. Even so, coumarin derivatives showing obvious 29 fluorescence in solution and aggregate states and MFC behavior are still very limited, and the 30 relationship among the molecular structure, intermolecular interactions and emission properties 31 requires to be revealed.

32 Herein we designed and developed a new coumarin-based fluorophore 33 7-(diphenylamino)coumarin-4-yl pivalate (**DPACP**) (Scheme 1) with solvatochromism, AIE and 34 reversible MFC enhancement properties. The fluorophore had a D- π -A molecular framework and

2

displayed remarkable solvatochromic effect. Importantly, by introducing the diphenylamine 1 2 (electron donor) and pivalate ester (electron acceptor) as steric hindrance moieties into the 3 molecular system, DPACP had a highly twisted conformation, which could reduce the 4 intermolecular π - π stacking and restrain the fluorescence quenching in aggregation state, thus 5 resulting in its AIE attribute. Moreover, twisted molecular structure could be beneficial to weaken 6 intermolecular interaction and eventually lead to MFC behavior of DPACP. In particular, the 7 solid-state quantum yield of **DPACP** increased from 0.19 to 0.28 upon grinding. To our knowledge, 8 the bulky group of pivalate ester was first used to construct MFC molecule. 9



10

Scheme 1. Synthetic route to target compound **DPACP** 12

13 2. Experimental

14 2.1. Measurements and material

All reagents and solvents were purchased from commercial sources and used as received 15 16 without further purification. NMR spectral measurements were carried out on a Bruker AV III 17 HD 600 NMR spectrometer. Mass spectrometric measurements were performed on a Bruker 18 micrOTOF-Q-II mass spectrometer. UV-Vis spectra were recorded on a Purkinje TU-1950 19 spectrophotometer. Photoluminescence (PL) spectra were recorded on an Agilent Cary Eclipse 20 fluorescence spectrophotometer. The fluorescence quantum yields in solutions were measured 21 by comparing a standard (quinine sulfate in 0.1 N H_2SO_4 aqueous solution, $Q_F = 0.54$). The 22 absolute fluorescence quantum yields of the solids were measured on an Edinburgh FLS1000 23 fluorescence spectrophotometer. The X-ray diffraction (XRD) measurements were carried out on 24 a Skyray DX-2600 X-ray diffractometer. Single crystal XRD measurements were carried out on a 25 Bruker smart apexii single crystal X-ray diffractometer. The photographic images were taken 26 under a 365 nm UV lamp.

Preparation of the samples for photophysical properties study. The UV-Vis absorption and PL spectra of **DPACP** in various organic solvents were measured using freshly prepared 1.0×10^{-5} M solutions. The CH₃CN/water (or THF/water) mixtures (concentration of 1.0×10^{-5} M) with different

1 water fractions were prepared by slowly adding distilled water into the CH₃CN (or THF) solution

2 of sample under ultrasound at room temperature.

The crystal of **DPACP** was grown from CH₃OH solution by slow evaporation at room
 temperature. CCDC 2011067 provided supplementary crystallographic data for this paper.

5 2.2. Synthesis

6 Compound 1 (8.0 g, 65 mmol), iodobenzene (29.2 g, 143 mmol), 1,10-phenanthroline (1.0 g, 7 5.5 mmol), Cul (1.1 g, 5.5 mmol) and t-BuOK (21.8 g, 195 mmol) were added in dry toluene (130 8 mL). The mixture was heated to reflux for 24 h under N₂. After cooling, the suspension was 9 filtered and the filtrate was washed with 100 mL H₂O and 100 mL brine. The organic layer was 10 dried over Na₂SO₄ and the solvent was removed in vacuum. Further purification was performed 11 by column chromatography with petrol ether/EtOAc to obtain 2 as colorless oil (13.8 g, 77%). 12 ¹H NMR (600 MHz, CDCl₃) δ 7.24 (t, J = 7.7 Hz, 4H), 7.14 (t, J = 8.1 Hz, 1H), 7.09 (d, J = 7.9 Hz, 4H), 13 7.01 (t, J = 7.3 Hz, 2H), 6.65 (d, J = 8.3 Hz, 1H), 6.62 (s, 1H), 6.55 (d, J = 8.2 Hz, 1H), 3.71 (s, 3H). 14 ¹³C NMR (150 MHz, CDCl₃) δ 160.56, 149.26, 147.84, 129.91, 129.33, 124.57, 122.98, 116.56, 15 109.87, 108.06, 55.36. LRMS (ESI): [M+H]⁺, 276.35.

16 Compound 2 (12.0 g, 43.5 mmol) was added drop-wise into melting pyridine hydrochloride 17 (60.0 g), and the mixture was stirred for 2 h at 180 °C. After cooling, the 200 mL water and 200 18 mL EtOAc were added, phases were separated under stirring and the aqueous layer was 19 extracted. The combined organic layers were dried over Na₂SO₄ and the solvent was removed in 20 vacuum. Further purification was performed by column chromatography with ether/EtOAc to obtain **3** as light green solid (6.8 g, 60%). ¹H NMR (600 MHz, CDCl₃) δ 7.25 (d, *J* = 6.1 Hz, 4H), 7.24 21 (s, 1H), 7.09 (d, J = 8.0 Hz, 4H), 7.02 (t, J = 7.3 Hz, 2H), 6.63 (d, J = 8.1 Hz, 1H), 6.52 (s, 1H), 6.46 (d, 22 J = 8.0 Hz, 1H).¹³C NMR (150 MHz, CDCl₃) δ 156.29, 149.34, 147.61, 130.05, 129.25, 124.67, 23 24 123.04, 116.04, 110.37, 109.36. LRMS (ESI): [M+H]⁺, 262.32.

25 Compound 3 (5.2 g, 20 mmol) and bis(2,4,6-trichlorophenyl) malonate (12.0 g, 26 mmol) were 26 added in dry toluene (22 mL). The mixture was heated to reflux for 6 h under N2. After cooling, a 27 large amount of solid precipitation separated out from the mixture. The precipitate was filtered off and washed with cold toluene to yield **4** as green solid (3.2 g, 48%). ¹H NMR (600 MHz, DMSO) 28 29 δ 12.28 (s, 1H), 7.62 (d, J = 8.8 Hz, 1H), 7.44 – 7.37 (m, 4H), 7.21 (td, J = 7.4, 1.0 Hz, 2H), 7.18 (dd, J = 7.6, 0.8 Hz, 4H), 6.75 (dd, J = 8.8, 2.2 Hz, 1H), 6.52 (d, J = 2.3 Hz, 1H), 5.39 (s, 1H). ¹³C NMR 30 (151 MHz, DMSO) δ 165.89, 162.17, 154.92, 151.44, 145.67, 130.00, 126.15, 125.27, 124.23, 31 32 115.29, 108.48, 105.01, 88.28. LRMS (ESI): [M+H]⁺, 330.36.

To a stirred solution of compound **4** (1.0 g, 3 mmol), pivaloyl chloride (0.5 g, 4.5 mmol) in dry CH₂Cl₂ (15 mL) were added dry Et₃N (0.61 g, 6 mmol). The mixture was stirred for 2 h at room

1 temperature under N₂, then was diluted with 20 mL CH₂Cl₂ and washed with H₂O and brine. The

2 organic layer was dried over Na₂SO₄ and the solvent was evaporated in vacuum to obtain **DPACP**

3 as yellowish solid (1.1 g, 91%). ¹H NMR (600 MHz, CDCl₃) δ 7.34 (t, J = 5.3 Hz, 4H), 7.31 (d, J = 5.9

4 Hz, 1H), 7.17 (t, J = 5.7 Hz, 6H), 6.86 (dd, J = 5.9, 1.4 Hz, 1H), 6.83 (d, J = 1.5 Hz, 1H), 1.40 (s, 9H).

5 13 C NMR (151 MHz, CDCl₃) δ 174.58, 162.29, 159.51, 155.38, 152.36, 146.00, 129.94, 126.43,

6 125.47, 123.16, 116.39, 108.58, 106.67, 101.62, 40.09, 27.19. LRMS (ESI): [M+H]⁺, 414.46.

7 3. Results and discussion

8 3.1. Synthesis and characterization

The chemical structure and synthetic route of DPACP were shown in Scheme 1. The 9 10 Buchwald-Hartwig coupling reaction of starting compound 3-methoxy aniline 1 with iodobenzene in the presence of 1,10-phenanthroline/Cul as catalyst gave compound 2 [35], which could be 11 12 converted to compound **3** by demethylation using pyridine HCl. The reaction of **3** with 13 bis(2,4,6-trichlorophenyl) malonate in toluene yielded compound 4 [36]. The target compound **DPACP** was prepared from the hydroxyl-acylation reaction of **4** with pivaloyl chloride in the 14 presence of triethylamine. All compounds were characterized by ¹H NMR and ¹³C NMR 15 16 spectroscopy and mass spectrometry. Furthermore, the structures of DPACP were demonstrated 17 by the single-crystal X-ray analysis.

18 *3.2. Solvatochromic properties*

19 UV-Vis absorption and photoluminescence properties of DPACP were studied in solvents with 20 increasing polarities (polarity parameter, Δf , was chosen as the measure of solvent polarity). As 21 shown in Fig. 1a and Table 1, the polarity of solvents had a negligible influence on the absorption 22 spectra of DPACP, indicating ground state energy was almost not influenced by solvent polarity 23 changes. In contrast, the fluorescence spectra were greatly affected by changes in solvent 24 polarity (Fig. 1b and Table 1). With solvent polarity increase the maximum emission wavelength 25 displayed significant red shift from 436 nm in $n-C_6H_{14}$ to 553 nm in CH_3CN , and the relative 26 emission intensity also decreased simultaneously due to the large solvent relaxation effect. For 27 example, the quantum yield in acetonitrile was about 40 times lower than that in n-hexane. Such 28 large solvatochromic effect brought about distinct fluorescence colors and intensities, which 29 could be differentiated by the naked eye through a 365 nm UV lamp. All these demonstrated 30 that photo-induced twist intramolecular charge transfer (TICT) occurred in the molecular 31 structure [37, 38]. Remarkably, the high fluorescence quantum yields of DPACP in n-hexane 32 implied that it was a potentially good blue fluorophore [39].



1

2 Fig. 1. (a) Normalized UV-vis absorption spectra and (b) PL spectra and photographic images

3 (inset) of **DPACP** in various solvents.

Table 1 Flotophysical properties of DFACF in various solvents						
solvent	Δf	$\lambda_{ m Abs}$ (nm)	$\lambda_{ t PL}$ (nm)	Δν (cm⁻¹)	$\Phi_F(\%)$	
n-hexane	0.001	368	436	4238	81.1	
toluene	0.014	371	464	5402	66.3	
ethyl acetate	0.20	373	491	6443	54.3	
tetrahydrofuran	0.21	376	500	6595	42.8	
methylene chloride	0.22	377	508	6840	36.6	
acetone	0.29	379	522	7228	7.7	
acetonitrile	0.31	381	546	7931	2.8	

4 Table 1 Photophysical properties of **DPACP** in various solvents

5 ^{*a*} The polarity parameter is calculated as $\Delta f = (\varepsilon - 1)/(2\varepsilon + 1) - (n^2 - 1)/(2n^2 + 1)$, where ε is the 6 static dielectric constant and *n* is the optical refractive index of the solvent.

7 Then the Lippert-Mataga mode was adopted to insight into the solvatochromic behaviors of **DPACP.** The Stokes shifts (Δv) in different solvents with orientation polarity parameter (Δf) were 8 listed in Table 1. And the Lippert-Mataga plot was shown in Fig. 2, which exhibited a good linear 9 correlation ($R^2 = 0.90$) of Stokes shifts versus orientation polarizability. The result demonstrated 10 DPACP could be applied to detect and discriminate the organic solvents. The transition dipole 11 12 moment between the ground state and the excited state ($\Delta \mu = \mu_e - \mu_g$) was estimated to be 12.4 D (see the Supporting Information) according to the slope of the fit curve (9480 cm^{-1}). So the 13 dramatic solvent-dependent fluorescent shifts and color changes of DPACP in various solvents 14 15 mainly were ascribed to large transition dipole moment induced by changes of solvent polarities. 16



1

2 Fig. 2. Lippert–Mataga plot for **DPACP** in various solvents.

3 To better understand the origin of large transition dipole moment and solvatochromic 4 behaviors of DPACP, density functional theory (DFT) calculations based on the single-crystal 5 structure were performed to examine the charge distribution in the ground state and the excited state. As can be seen in Fig. 3, the highest occupied molecular orbital (HOMO) was mostly 6 7 localized on the diphenylamino unit, whereas the lowest unoccupied molecular orbital (LUMO) 8 was primarily distributed on the lactone core and -O-C=O group of pivalate ester. The distinct 9 distribution of the electron cloud in HOMO and LUMO energy levels suggested a large transition 10 dipole moment during the ground-excited state transition. Also, the transfer of electrons from 11 donor to acceptor created a more polarized excited state, which could be stabilized through the 12 reorganization of polar solvent molecules. Therefore, the solvent polarity increase could lead to 13 lowered energy of the excited state and red-shifted emission spectrum.



Fig. 3. Molecular orbital energy levels of the HOMO and LUMO for **DPACP** based on DMol³
 calculations.

17 *3.3. AIE properties*

14

To explore the fluorescence behaviors of **DPACP** in aggregation state, the photoluminescence spectra in CH₃CN/water and THF/water mixtures with different fractions of water (f_w) were performed (Fig. 4). **DPACP** emitted a weak emission in strong polar solvent CH₃CN, which displayed further reduction of emission intensity up to 0.6 of f_w . However, when the f_w reached to 0.7, the fluorescence was notably enhanced. Eventually, the PL intensity increased 6 times in mixed solvent with 0.9 of f_w compared to that in pure CH₃CN. This down-up phenomenon of emission intensity was observed in some compounds with AIE attribute [40, 41]. From 0 to 0.6 of

fw, the decreased PL intensity could be ascribed to ICT effect arising from the increased solvent 1 2 polarity. With a further increase of fw from 0.6 to 0.9, the increased PL intensity was attributed to 3 the domination of the AIE effect caused by the aggregate formation at higher water percentage. Similar fluorescence behaviors were also observed in THF/water mixture system for DPACP. As 4 5 the f_w increased from 0 to 0.7, the PL intensity was significantly weakened and eventually 6 quenched due to the influence of the polarity of solvents on the TICT state. Nevertheless, 7 fluorescence was enhanced at $f_w = 0.8$, and reached the intensity maximum at 0.95 of water 8 content, reflecting a typical AIE phenomenon. The above results suggested the AIE properties of 9 DPACP.



10

Fig. 4. Fluorescence spectra of **DPACP** in (a) CH₃CN/water and (c) THF/water mixtures with different water fractions. The effect of water fractions on the maximum emission intensity and emission images (insets) of **DPACP** in (b) CH₃CN/water and (d) THF/water mixtures.

14 *3.4. MFC properties*

15 Considering that the twisted molecular conformations and obvious AIE properties, the 16 fluorescence behaviors of **DPACP** in the solid states were studied under mechanical stimuli. As 17 shown in Fig. 5a, the original powders obtained from the evaporation of the n-hexane solvent 18 emitted blue fluorescence centered at 438 nm with quantum yield of 0.19. Upon grinding with a 19 pestle, ground samples displayed green fluorescence and the emission peak was red-shifted to 20 483 nm with quantum yield of 0.28. Moreover, the fluorescence spectra and colors could be 21 reverted to its original state by wetting with n-hexane solvent. Thus, **DPACP** exhibited remarkable

MFC turn-on behaviors. Furthermore, powder X-ray diffraction measurements were performed 1 2 for interpretation of the reversible MFC properties (Fig. 5b). The pristine sample of **DPACP** 3 displayed sharp diffraction peaks, meaning good microcrystalline phase. By contrast, the ground 4 powder showed rather weak or broad peaks, indicating partial disordered molecular packing or 5 decrease of the crystallinity. However, the sharp diffraction patterns recovered through n-hexane 6 wetting, implying reversion to the crystalline nature. The reversible MFC behavior could be 7 assigned to morphology change between crystalline and partial amorphous states due to 8 modification of the molecular arrangement.



9

Fig. 5. (a) Normalized emission spectra and emission images (inset) and (b) XRD patterns of the corresponding samples for **DPACP**.

12 3.5. X-ray single-crystal diffraction analysis

13 The optical behaviors had closely relation to the molecular conformation, intermolecular 14 interactions and packing modes, so X-ray single-crystal diffraction analysis was necessary for 15 investigating the solid-state luminescence and MFC property of **DPACP**. The single crystal was 16 obtained from saturated methanol solution by slow evaporation at room temperature. As shown 17 in Fig. 6a, DPACP adopt twisted structure, the dihedral angles between the central coumarin plane and two phenyl group, pivalate ester group(-O-C=O) were 64.81°, 69.38° and 60.36°, 18 19 respectively. There existed three specific intermolecular interactions between adjacent molecules, 20 including C7-H···O4 (2.326 Å) hydrogen bond interaction (Fig. 6b), C24-H··· π (2.873 Å) aromatic interaction and C8...C12 (3.296 Å) electrostatic interaction (Fig. 6c). These interactions restrained 21 22 the intramolecular motions and blocked nonradiative decay to some extent. Furthermore, no π - π 23 stacking was observed between the adjacent molecules due to large twisted conformation and 24 steric hindrance from diphenylamine and pivalate ester moieties, avoiding the quenching of 25 fluorescence in the solid state. Thus DPACP exhibited AIE nature and acceptable solid-sate 26 quantum yield. It was noted that electrostatic interaction of adjacent molecules between 27 electron-deficient C8 and electron-rich C12 was relatively weak and sensitive to 28 mechano-stimulus due to the absence of shielding from dipole-dipole or π - π interactions. Upon

grinding, monomers were slipped along the short axis with respect to each other, possibly making adjacent molecules distance increases and electrostatic interaction (between C8 and C12) decreases. It meant that the nonradiative decay caused by electrostatic interaction was inhibited, which may account for the solid-state luminescence change together with quantum yield enhancement after grinding treatment of **DPACP**. Additionally, the red-shifted emission upon grinding should be mainly ascribed to more planar molecular conformation and better electronic conjugation of **DPACP** [42, 43].



8

9 Fig. 6. Crystal structures of **DPACP** revealing (a) large dihedral angle and (b and c) three specific
 10 intermolecular interactions between adjacent molecules.

11 4. Conclusions

12 In summary, we designed and synthesized a new coumarin fluorophore DPACP with bulky 13 diphenylamine donor and pivalate ester acceptor. It exhibited solvatochromism, AIE and 14 reversible MFC enhancement behaviors. The Lippert-Mataga plot study and theoretical 15 calculation indicated that solvatochromism was ascribed to intramolecular charge transfer and 16 large transition dipole moment affected by changes of solvent polarities. With the conformation 17 confirmed by single crystal structure, the relationship between intermolecular interactions and 18 emission properties were investigated. DPACP had a twisted conformation which was crucial for 19 AIE and MFC enhancement behaviors. The absence of π - π stacking avoided the non-radiative 20 decay in aggregation state, leading to AIE. The destruction of weak electrostatic interaction of 21 adjacent molecules upon mechanical stimuli was considered to be responsible for MFC 22 enhancement nature. This design strategy allowed molecular skeleton modification of 23 conventional planar fluorescence making them potential AIE and MFC materials.

24 Declaration of competing interest

25 The authors declare that they have no known competing financial interests or personal

1 relationships that could have appeared to influence the work reported in this paper. 2 Acknowledgements 3 This work was supported by the Sichuan University of Science & Engineering (Grant 2015RC25), 4 Key Laboratory of Green Chemistry of Sichuan Institutes of Higher Education (Grant LZJ1807), and 5 Chemical Synthesis and Pollution Control Key Laboratory of Sichuan Province (Grant CSPC 6 201908). 7 Appendix A. Supplementary data 8 Supplementary data to this article found online at https://doi. can be 9 org/10.1016/j.dyepig.xxxx.xxxxxx. 10 References 11 [1] Sagara Y, Kato T. Mechanically induced luminescence changes in molecular assemblies. Nat Chem 12 2009;1:605-10. 13 [2] Pucci A, Bizzarri R, Ruggeri G. Polymer composites with smart optical properties. Soft Matter 2011;7:3689-700. 14 [3] Chi Z, Zhang X, Xu B, Zhou X, Ma C, Zhang Y, et al. Recent advances in organic mechanofluorochromic materials. 15 Chem Soc Rev 2012;41:3878-96. 16 [4] Zhang X, Chi Z, Zhang Y, Liu S, Xu J. Recent advances in mechanochromic luminescent metal complexes. J 17 Mater Chem C 2013;1:3376-90. 18 [5] Sagara Y, Yamane S, Mitani M, Weder C, Kato T. Mechanoresponsive Luminescent Molecular Assemblies: An 19 Emerging Class of Materials. Adv Mater 2016;28:1073-95. 20 [6] Xue P, Ding J, Wang P, Lu R. Recent progress in the mechanochromism of phosphorescent organic molecules 21 and metal complexes. J Mater Chem C 2016;4:6688-706. 22 [7] Li Q, Li Z. The Strong Light-Emission Materials in the Aggregated State: What Happens from a Single Molecule 23 to the Collective Group. Adv Sci 2017;4:1600484. 24 [8] Ubba E, Tao Y, Yang Z, Zhao J, Wang L, Chi Z. Organic Mechanoluminescence with Aggregation-Induced 25 Emission. Chem Asian J 2018;13:3106-21. 26 [9] Di B-H, Chen Y-L. Recent progress in organic mechanoluminescent materials. Chinese Chem Lett 27 2018;29:245-51. 28 [10] Mellerup SK, Wang S. Boron-based stimuli responsive materials. Chem Soc Rev 2019;48:3537-49. 29 [11] Dong YQ, Lam JW, Tang BZ. Mechanochromic Luminescence of Aggregation-Induced Emission Luminogens. J 30 Phys Chem Lett 2015;6:3429-36. 31 [12] Ciardelli F, Ruggeri G, Pucci A. Dye-containing polymers: methods for preparation of mechanochromic 32 materials. Chem Soc Rev 2013;42:857-70. 33 [13] Pucci A, Ruggeri G. Mechanochromic polymer blends. J Mater Chem 2011;21:8282-91. 34 [14] Ma Z, Wang Z, Teng M, Xu Z, Jia X. Mechanically Induced Multicolor Change of Luminescent Materials. 35 Chemphyschem 2015;16:1811-28. 36 [15] Varughese S. Non-covalent routes to tune the optical properties of molecular materials. J Mater Chem C 37 2014;2:3499-516. 38 [16] Mukherjee S, Thilagar P. Stimuli and shape responsive 'boron-containing' luminescent organic materials. J 39 Mater Chem C 2016;4:2647-62. 40 [17] Wang C, Li Z. Molecular conformation and packing: their critical roles in the emission performance of

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Highlights

- 1. A new coumarin fluorophore with AIE and MFC enhancement properties was developed.
- It was shown that twisted molecule conformation was crucial for AIE and MFC behaviors.
- 3. The bulky group of pivalate ester was first used to construct AIE and MFC molecule.
- 4. The fluorescence quantum yields of the compound in n-hexane reached to 0.81.

Auther Statement

- All authors have seen and approved the final version of the manuscript being submitted. We warrant that the article is the authors' original work, hasn't received prior publication and isn't under consideration for publication elsewhere.
- 2. All authors declare that we have no financial and personal relationships with other people or organizations that can influence our objectivity, there's no financial/personal interest or belief that could inappropriately affect our work.
- 3. This work was supported by the Sichuan University of Science & Engineering (Grant 2015RC25), Key Laboratory of Green Chemistry of Sichuan Institutes of Higher Education (Grant LZJ1807), and Chemical Synthesis and Pollution Control Key Laboratory of Sichuan Province (Grant CSPC 201908).
- 4. There is no any material in the manuscript such as figures etc. which isn't original content.

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Conflict of Interest

All authors declare that we have no financial and personal relationships with other people or organizations that can inappropriately influence our work entitled "Rational Design of Coumarin Fluorophore with Solvatochromism, AIE and Mechanofluorochromic Enhancement Properties'.

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