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# **Accepted Article**

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This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Chem. Eur. J. 10.1002/chem.202002712

Link to VoR: https://doi.org/10.1002/chem.202002712



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# Flexible $\pi$ -Conjugated 2,5-Diarylamino-terephthalates: A New Class of Mechanochromic Luminophores with Tunable Aggregation States

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**Abstract:** The generation of different thermodynamically (meta)stable states is crucial for the development of smart solid-state luminescent materials. However, the design of luminophores with tunable aggregation states is remaining a grand challenge. Herein, we present a family of mechanochromic luminophores with tunable metastable states, based on the dynamically controllable  $\pi$ - $\pi$  stacking of the flexible  $\pi$ -conjugated structure of 2,5-diarylamino-terephthalates in the solid-state. The experimental data revealed that both the kinetically controlled metastable state and thermodynamic controlled stable state can be generated via tuning the intermolecular interactions such as  $\pi$ - $\pi$  stacking and hydrogen bonds. As a result, the highly sensitive mechano-stimuli response of these luminophores has been successfully achieved.

#### Introduction

Smart luminescent materials that exhibit tunable luminescent properties in the solid-state under mechanical stimuli have received considerable attention in the development of optical data recording and storage devices, as well as fluorescent sensors.<sup>[1]</sup> Several mechano-responsive luminescent systems derivate from metal (Au,<sup>[2]</sup> Cu,<sup>[3]</sup> Pt<sup>[4]</sup> and Ir<sup>[5]</sup>) and boron complexes,<sup>[6]</sup> anthracene-,<sup>[7]</sup> pyrene-,<sup>[8]</sup> and perylene bisimide-based dyes,<sup>[9]</sup> oligo(*p*-phenylenevinylene) derivatives,<sup>[10]</sup> and aggregation-induced emission (AIE) compounds<sup>[11]</sup> have been reported, and various mechanistic explanations such as phase transformation, excimer formation or dissolution and mechanical stress-induced

chemical changes have been proposed.<sup>[1a]</sup> However, even with the help of those proposed mechanisms, the development of new mechanochromic luminescent materials (MCLs) still heavily depends on random screening, which makes the rational design of new materials, especially those with high sensitivity to mechanical stimuli, remains a challenging work.

Mechanical stimuli trigged phase transformation of a luminophore from its metastable state to a more stable state is a promising strategy to generate MCLs with high sensitivity and high contrast fluorogenic signal.<sup>[1a, 10d, 12]</sup> Hence, luminophores, which can generate both of their metastable and stable states in a controlled way, have gained a great interest in the development of MCLs. Compared with luminophores with large and rigid  $\pi$ -configurations, flexible  $\pi$ conjugated systems are preferred to generate kinetically trapped metastable states, with luminescent properties that are sensitive to the surrounding environment, which make them promising platforms for the construction of stimulussensitive materials.<sup>[10,12c]</sup> It can be predicted that if a metastable state of flexible  $\pi$ -conjugated system is highly sensitive to mechanical stimuli, it would be easily converted to a more stable state in the presence of mechanical stimuli such as shearing, grinding or rubbing, accompanied by the distinct change of luminescence. Although flexible  $\pi$ conjugated luminophores such as oligo(p-phenylenevinylene) derivatives have been successfully employed for the construction of MCLs,<sup>[10]</sup> the development of flexible  $\pi$ conjugated luminophores with tunable aggregation states remains a grand challenge. In the present work, we report a

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2

new family of flexible  $\pi$ -conjugated mechanochromic luminophores (**MCL1-4**) that show tunable metastable and stable aggregation states.



Figure1. Chemical structures of MCL1-4 and the proposed molecular packing modes of MCL1-4 in the solid-state.

#### **Results and Discussion**

The design of MCL1-4 relies on the dynamically controllable  $\pi-\pi$  stacking of the flexible  $\pi$ -conjugated structure in the solid-state. Firstly, MCL1-4 are more likely to have a twisted conformation and large Stokes shift because of their flexible structure. As a result, molecular packing and energy transfer caused emission quenching would be efficiently inhibited, resulting in high emission intensity in the solid-state.[13] Secondly, dimethyl 2,5-diphenylamino-terephthalates are expected to generate different aggregation states corresponding to their four different packing modes:  $\pi - \pi$ stacking between B and B' (I), A-B-C and A'-B'-C' (II or III), and A and A' (IV) (Figure 1). After incorporating long alkyl chain or halogen atom to 2,5-diarylamino groups, different molecular packing modes would be tuned by varying the intermolecular interactions such as  $\pi-\pi$  stacking and hydrogen bonds. Therefore, mechanical stimuli triggered phase transformation from a metastable aggregation state to a stable one is highly expected. MCL1-4 are constructed by incorporating of arylamine groups to the 2,5-positions of methyl terephthalates. The synthetic route for MCL1-4 is shown in Scheme S1. The chemical structures of MCL1-4 are confirmed by NMR, mass data, and single-crystal X-ray structure analysis.

We first investigated the photophysical properties of **MCL1-4** in the solid-state (Tables S1–2). Slowly evaporation of the dichloromethane (DCM) solution of **MCL1-3** resulted in the precipitation of reddish-emissive crystals (R-form, **MCL1-3-R**). As shown in Tables 1 and S2, **MCL1-3-R** shows weak red fluorescence around 620 nm ( $\lambda_{em}$ ) with quantum yield ( $\Phi_{f}$ ) and decay time ( $\tau_{f}$ ) ranging from 2–5% and 2.5–8.9 ns, respectively. When the solvents are rapidly evaporated, yellow pristine powder of **MCL2-4** (Y-form, **MCL2-4-Y**) with bright orange luminescence (560-584 nm) and increased  $\varPhi_{\rm f}$  (9–17%) and  $\tau_{\rm f}$  (6.7–10.9 ns) can be obtained. Moreover, **MCL2-4-Y** powders can also be obtained by the method of rapid aggregation such as adding a large amount of water into the tetrahydrofuran (THF) solution of **MCL2-4**. These results strongly indicate that **MCL1-3-R** and **MCL2-4-Y** are the thermodynamically stable and kinetically trapped metastable states of **MCL1-4**, respectively.



Next, we examined the mechanical stimuli responses of MCL1-4. As shown in Figure 2 and S1, MCL1-3-R, MCL2-Y, and MCL4-Y showed relatively poor mechanochromic response. After shearing with the mortar, none emission band shift was observed for MCL1-R and MCL3-R (Figure S1a and S1d), while a 20 and 16 nm red-shifted  $\lambda_{em}$  were observed for MCL2-Y and MCL4-Y (Figure 2a and 2b), accompanied by the emission color change from light to deep orange for MCL2-Y and yellow to orange for MCL4-Y, respectively. Interestingly, the  $\lambda_{em}$  of MCL2-R was blueshifted from 627 to 614 nm upon shearing force stimuli, indicating the relatively unstable state of MCL2-R in comparison with MCL1-R and MCL3-R. MCL3-Y is highly sensitive to mechanical stimuli and can be easily converted to MCL3-R in the presence of shearing stimuli. After shearing the MCL3-Y powders using a spatula or mortar, the yellow fluorescence converted to red immediately, and the emission spectrum of ground powders (MCL3-Y-G) is the same with MCL3-R, suggesting the shearing stimuli triggered phase transformation from MCL3-Y to MCL3-R (Figures 2b and S1d). This phase transformation was further confirmed by powder X-ray diffraction (PXRD) measurements. PXRD results showed that MCL3-Y forms different molecular stacking architectures compared with MCL3-R, while MCL3-Y-G shows the same diffraction patterns with MCL3-R, suggesting the same molecular stacking structures of MCL3-Y-G and MCL3-R (Figure 2c). In addition, compared with MCL2-R and MCL2-Y, MCL2-R-G showed a different PXRD pattern, indicating that a new molecular packing mode was formed. In the case of MCL2-Y, and MCL4-Y, the initial powder, and the ground powder showed similar PXRD patterns (Figure S2a and S2c). This result indicates that no phase transition has occurred.

The mechanical stimuli sensitivity of MCL2-Y, MCL2-R, MCL3-Y, and MCL4-Y was also investigated using an automatic roller pressing machine. As shown in Figure S3, when the pressure is increased from 0 to 2 MPa, the MCL3-Y powders changed the colour from orange to dark orange, and the emission colour from bright yellow to dark yellow.

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#### **FULL PAPER**

However, under the same pressure, MCL2-Y, MCL2-R, and MCL4-Y showed almost no colour change. Only under the pressure of 10 MPa, the MCL2-Y, MCL2-R, and MCL4-Y powders can observe an obvious colour change. These results further confirm that MCL3-Y is sensitive to mechanical stimuli than MCL2-Y, MCL2-R, and MCL4-Y.

The high-contrast and highly sensitive mechanochromic fluorescence of **MCL3-Y** was further realized in a recording device. An as-spin cast film of **MCL3** was prepared by spin-coating of **MCL3** on a glass substrate from a THF solution. The as-spin cast film exhibited strong yellow fluorescence, which is coincidence with the emission of **MCL3-Y**. The yellow emission changed to red high sensitivity in response to very small shear forces, allowing for sensitive piezo-writing with a high contrast ratio (Figure 2d, Supplementary Video 1-2).

On the other hand, the reversibility of MCL behaviour was explored by subjecting the ground samples to heat treatment. After heating the ground powders at 160 °C, the original fluorescence can be restored except for MCL2-R-G, which shows that MCL2-Y-G, MCL3-Y-G, and MCL4-Y-G have higher thermochromic sensitivity than MCL2-R-G (Figure S1b-1e). Unexpectedly, the recovered powders showed poor sensitivity compared to the original form, indicating that these compounds are less reversible. As shown in Figure S2, the heated ground powders showed different PXRD diffraction patterns compared with the initial powders and the ground powders, indicating a phase transition caused by the heating-cooling cycle. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) further proved this speculation. The TGA trace showed that MCL1-4 are stable at temperatures up to 220 °C (Figure S4). During the

heating process, the DSC thermogram of MCL1-R, MCL2-Y, MCL2-R, MCL3-Y, and MCL4-Y showed one endothermic peak in the range of 124–160 °C. Such a low phase transition temperature proves the flexible  $\pi$ -conjugated nature of MCL1-4. During the cooling process, an exothermic transition was detected around 72–115 °C, indicating the formation of different crystalline states (Figure S5). These results are consistent with the aforementioned PXRD results, which rationalize the irreversibility of the MCL behaviour of MCL2-4.

To understand the generation, photophysical and mechanochromic properties of metastable and stable states of MCL1-4, the photophysical properties in solution state and the molecular packing mode in the crystalline state of MCL1-4 were investigated. In THF solution, the absorption maximum and shoulder bands of MCL1-4 are around 465 and 315 nm, respectively, which can be assigned to the intramolecular charge transfer (ICT) band and  $\pi - \pi^*$  band, respectively (Figure S6a). MCL1-4 show weak fluorescence with an emission maximum of around 565 nm (Figure S6b). The  $\Phi_{\rm f}$  and  $\tau_{\rm f}$  are determined to be 8% and 3.8 ns for MCL1. 3% and 2.2 ns for MCL2, 2% and 0.69 ns for MCL3, and 2% and 0.8 ns for MCL4, respectively. The large Stokes shift of 3584-4035 cm<sup>-1</sup> suggested a significant conformation change in the excited state, which should be attributed to the flexible structure of MCL1-4 (Table S2). The solvent effects on the absorption and fluorescence of MCL1-4 are examined. The absorption bands of MCL1-4 are hardly affected by solvent polarity, while the emissions of these compounds are quenched and red-shifted with the increment of solvent polarity, supporting the ICT nature of MCL1-4 (Figures S7 and S8).



Figure 2. Fluorescence spectra and photographs of (a) MCL2-Y, MCL2-Y-G, MCL2-R-G, and MCL2-R and (b) MCL3-Y, MCL3-Y-G, and MCL4-Y and MCL4-Y-G (c) PXRD spectra of MCL3-Y, MCL3-Y-G, and MCL3-R. (d) Fluorescence and colour change upon drawing of an "I" on a thin film of MCL3-Y on the glass. The drawing was made by sequential sketching with a spatula. The excitation wavelength for the fluorescence spectra measuring and photograph taking are 450 and 365 nm, respectively.

3

### FULL PAPER

When water as poor solvent was added into THF solution of MCL1 at varied volumetric fractions  $(f_w)$ , the emission intensity was distinctly decreased with the increment of  $f_w$ from 0 to 70%, accompanied by red-shifted  $\lambda_{em}$  from 565 to 585 nm (Figure 3a and 3e), demonstrating the aggregation caused emission quenching (ACQ).<sup>[14]</sup> When fw reaches 80%, the emission wavelength was blue-shifted from 585 to 570 nm, and the emission intensity was slightly increased in comparison with that of  $f_w = 70\%$ . Then the emission wavelength was red-shifted and the intensity was decreased again with  $f_w$  from 90 to 99%. This progress suggests that unstable aggregates were formed with  $f_w = 80\%$ , and these aggregates may be easily converted to MCL1-R with increased aggregation induced by high  $f_w$ . MCL2 and MCL4 showed decreased emission with  $f_w$  increasing from 0 to 40% for MCL2 (Figure 3b and 3f) and 0 to 70% for MCL4 (Figure 3d and 3h), respectively. However, when  $f_w$  reaches to 50% and 80%, a new fluorescence peak at 565 nm appeared and enhanced with  $f_w$  increasing. Similar to MCL2 and MCL4. **MCL3** showed ACQ caused by  $f_w$  increment from 0 to 50%. The emission intensity was then slightly increased with  $f_w$ ranging from 60 to 80%, and decreased with  $f_w = 90\%$ , demonstrating the unstable state of the AIE aggregates. Finally, these unstable aggregates were transformed into stable MCL3-Y aggregates to give an intense fluorescence peak at 562 nm with  $f_w = 95\%$  (Figure 3c and 3g). These results demonstrate that MCL2-4 are preferred to form the Yform aggregates during the fast molecular aggregation process. The aggregation-induced intramolecular motions restriction and twisted ICT inhibition may responsible for the AIE and blue-shifted emission.

To further disclose the relationship between molecular packing mode and mechanofluorogenic properties of MCL1-4, single-crystal X-ray analysis was performed. Single crystals of MCL1-R, MCL2-R, MCL2-Y, MCL3-R, and MCL4-Y were obtained by slow evaporation of DCM solution of these compounds. Unfortunately, single crystals of MCL3-Y suitable for X-ray analysis cannot be obtained due to the poor quality of the crystals. The ORTEP drawings and molecular packing structures of MCL1-R, MCL2-R, MCL2-Y, MCL3-R, and MCL4-Y are shown in Figures 4 and S9-18. All the molecules in their crystals showed twisted conformations due to the flexible  $\pi$ -conjugation structure.

MCL1-R and MCL2-R crystallized in a P21/c lattice, while MCL2-Y, MCL3-R, and MCL4-Y crystallized in a P-1 lattice (Table S3). Each MCL1-4 molecules are connected via interactions such as  $\pi - \pi$  stacking and H-bonds. In **MCL1-R**,  $\pi-\pi$  stacking between phenyl rings **B** and **B'** (3.47 Å for MCL1-R) dominated the type-I molecular packing mode (Figure 1), while weak C-H…O, H-bond and C-H… $\pi$ interactions such as C46-H46····O6 (3.07 Å, 106°) give fewer contributions. The closely-packed MCL1 molecules in MCL1-R should contribute to its poor mechanical response. Interactions including  $\pi - \pi$  stacking between phenyl rings **B** and B' (3.44 and 3.42 Å in MCL2-R and MCL2-Y, respectively) and weak C-H···C between the phenyl rings A and A' were observed in MCL2-R and MCL2-Y to give almost the same type-II molecular packing mode. However, their long alkyl chains arrayed slightly differently. In comparison with MCL1-R, the introduction of long alkane chains made the looser packing structure, leading to the better mechanical response of MCL2-R and MCL2-Y than MCL1-R.

(e)

(a.u.)

(a)

Figure 3. Fluorescence spectra of MCL1 (a), MCL2 (b), MCL3 (c), and MCL4 (d) in THF-water binary solvents  $(1.0 \times 10^{-5} \text{ mol } \text{L}^{-1})$  with varied  $f_w$  ( $\lambda_{ex} = 450 \text{ nm}$ ), and emission intensity ( $\lambda_{em}$ ) and wavelength changes of MCL1 (e), MCL2 (f), MCL3 (g), and MCL4 (h) with different varied fw.

**MCL3-R** was found to packed in type-IV packing mode. Strong  $\pi$ - $\pi$  interactions between the phenyl rings **A** and **C'** (3.47 Å) and the weak C11-H11...O3 (3.48 Å, 148°) H-bond interactions were observed within the packing structure. This head-to-tail type  $\pi - \pi$ stacking should attribute its red-shifted emission wavelength. Moreover, C19-H19...Br1 (3.82 Å, 157°) H-bond was also found within the crystal, which facilities the organization of long alkyl chains. The head-to-tail type  $\pi$ - $\pi$  stacking and H-bond synergistically stabilized MCL3-R, resulting in its poor mechanical response. Molecules within the MCL4-Y crystals were packed in type-III packing mode. The flexible conjugated  $\pi$ -skeletons were arranged shoulder to shoulder, with the help of strong  $\pi-\pi$ interactions between phenyl rings **B** and **B**', and weak C-H $\cdots\pi$ interactions between **A** and **A'** (C11-H11 $\cdots \pi$  3.76 Å, from H atom to phenyl center). Most importantly, strong N1-H...Cl1 (3.47 Å,



# **FULL PAPER**

138 °) H-bond was observed within the crystal, which should be helpful for the stabilization of the molecular arrangement of each molecule, and may give a major contribution for the formation of **MCL4-Y** as stable aggregation states rather than the type-**IV** packing mode like **MCL3-R**.



Figure 4. Molecular packing structures of MCL1-R, MCL2-R, MCL3-R, MCL3-Y, and MCL4-Y.

As mentioned above, the formation of yellowish-emissive crystals is attributed to the shoulder to shoulder type arrangement of flexible conjugated  $\pi$ -skeleton and intermolecular H-bond. While reddish-emissive crystals are preferred to formed *via*  $\pi$ - $\pi$  stacking interactions between phenyl rings **B** and **B'** or **A** and **C'**. As shown in Table 2, the emission color of these two aggregates is closely related to the dihedral angles between rings **B** and **A** and rings **B** and **C**. The calculated dihedral angles between rings **B** and **A** and rings **B** and **C** are same to each other, demonstrating the high symmetry of the molecules in the packing structure. The dihedral angles of 64–76° in Y-form are larger than those of 40-56° in R-form, demonstrating the more twisted molecular structure in Y-form than R-form. On the other hand, the substituted groups such as long alkyl chains and halogen atoms also play important roles in tuning the generation of Y-form and R-form aggregates.

Because MCL2-Y, MCL3-Y, and MCL4-Y showed intense PXRD peaks around  $2\theta = 4^{\circ}$ , but the R-form did not. In addition, MCL2-Y and MCL4-Y showed type-III molecular packing mode. Therefore, although we did not obtain the crystal structure of MCL3-Y, based on the information obtained from the XRD and single-crystal X-ray analysis, it can be expected that MCL3-Y may have the similar packing mode as MCL4-Y. However, because the electronegativity of the bromine atom is lower than that of chlorine atom, the intermolecular N-H---Br H-bonds in MCL3-Y should be weakened than N-H---Cl H-bonds in MCL4-Y, which makes MCL3-Y has higher energy than MCL4-Y.<sup>[15]</sup> The theoretical calculation results primarily proved this speculation. In the optimized MCL3-Y molecular packing structure (Figure S19), the length of the intermolecular N-H---Cl (3.47 Å, 138°) H-bond

observed within the single crystal of **MCL4-Y**. In addition, no other strong intermolecular interactions, such as  $\pi$ - $\pi$  stacking, were observed. The weak intermolecular interaction makes the **MCL3-Y** more unstable than that of **MCL2-Y** and **MCL4-Y**. Accordingly, the excellent mechanical fluorescence properties of **MCL3** can be rationalized.

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Table 2. Dihedral angles between rings B and A, and rings B and C of MCL1-4			
	Compounds	Y-form	R-form
	MCL1		46.7/43.4°
	MCL2	64.0°	55.8°
	MCL3	-	40.1°
	MCI4	76.1°	_

#### Conclusion

family In summary, a of dimethyl 2,5-diphenylaminoterephthalate-based mechanochromic luminophores (MCL1-4) that display tunable molecular packing mode in the solid-state, has been designed and synthesized. By varying the intermolecular interactions such as  $\pi$ - $\pi$  stacking and hydrogen bonds between molecular assemblies, different kinetically and/or thermodynamically controlled molecular packing modes with highly contrast emission colors have been generated. Moreover, highly sensitive mechanical stimuli fluorescence response of these luminophores has been successfully achieved by the transformation from the metastable state to the stable state. The understandings obtained from the experimental investigations will inspire the development of a new class of mechanochromic luminescent materials with tunable responsibility and provides important insights into the solid-state luminescent properties of molecules with flexible  $\pi$ -conjugated structure.

#### Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (21971115) and the Key University Science Research Project of Jiangsu Province (17KJA150004). We thank Dr. Dan Tian and Mr. Houting Liu for single-crystal structure solvation.

**Keywords**: Mechanochromic materials • Aggregation-induced emission • Dyes and Pigments • Fluorescence • Tuneable

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A new class of mechanochromic luminophores with tuneable aggregation states has been developed.