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Shusheng Ge, Baoyan Li, Xinlei Meng, Han Yan, Mei Yang, Ben Dong, Yun Lu

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# 1 Aggregation-Induced Emission, Multiple Chromisms and

## 2 Self-Organization of N-substituted-1,8-Naphthalimides

3 Shusheng Ge, Baoyan Li, Xinlei Meng, Han Yan, Mei Yang, Ben Dong, Yun Lu\*

4 Department of Polymer Science and Engineering, State Key Laboratory of
5 Coordination Chemistry, Collaborative Innovation Center of Chemistry for Life
6 Sciences, Key Laboratory of High Performance Polymer Materials and Technology
7 (Nanjing University), Ministry of Education, School of Chemistry and Chemical
8 Engineering, Nanjing University, Nanjing 210093, P. R. China

9 \*Corresponding author.

10 E-mail: yunlu@nju.edu.cn

## 11 Abstract

12 Most aggregation-induced emission (AIE) luminogens possess propeller-like aromatic 13 stator-rotor structures, such as silole, tetraphenylethylene (TPE) and triphenylamine 14 (TPA), to restrict intra-molecular motions (RIM) and avoid aggregation-caused 15 quenching (ACQ) effects. In our work, two simple N-substituted naphthalimides were 16 designed and synthesized by the amide condensation to create novel AIE systems. 17 Except for the same aromatic stator (naphthalimide), N-phenyl-1,8-naphthalimide 18 (PhNI) contained aromatic (phenyl group) while an rotor 19 N-cyclohexyl-1,8-naphthalimide (CyNI) contained an aliphatic rotor (cyclohexyl 20 group). The PhNI samples obtained from different preparation processes showed

21	multiple chromisms (MC) effects and varied levels of luminescence. Despite of the
22	same intra-molecular structure, the crystal of PhNI had staggered parallel
23	inter-molecular conformation with weak emission but the precipitation of PhNI had
24	cross one with strong emission. Although without MC effects, CyNI gave an excellent
25	fluorescence quantum yield ( $\Phi_f = 0.55$ ). The experimental results and theoretical
26	analyses suggested that the AIE effects were decided by intra- and inter-molecular
27	structure simultaneously and the construction and destruction of inter-molecular $\pi$ - $\pi$
28	stacking between aromatic rotors in PhNI resulted in the MC effects.

Keywords: Naphthalimide; Aggregation-induced emission; Multiple chromisms;
Self-organization; Inter-molecular structure.

# 31 Introduction

32 Most common planar luminogens, such as pyrene, naphthalimide and others, are emissive in solution state but non-emissive in solid state due to aggregation-caused 33 34 quenching (ACQ). According to the reported quantum-chemical calculations, the 35 cofacial configurations ( $\pi$ - $\pi$  stacking) in the molecules are responsible for the decay of luminescence.[1] Theoretically, effective methods to solve this problem are 36 37 separating these molecules through the introduction of large steric hindrance groups 38 or achieving the rotation of the molecules around the stacking axis while keeping the 39 parallelism between the molecular planes.[2,3]

40 Nowadays, an abnormal phenomenon called aggregation-induced emission (AIE)
41 is observed, in which some non-planar luminogens are emissive in solid state while

42 none-emissive in solution state.[4,5] These AIE luminogens are usually composed of 43 a central stator, normally aromatic planar fluorescent molecule, and several steric 44 aromatic planar rotors linked to the stator.[6] The restriction of intra-molecular motion (RIM) in the aggregation is accounted as the reason for the brightening. This new 45 46 progress offers a large platform for exploring practically useful luminescent materials 47 in solid state. So far diverse AIE luminogens with tuneable emission colors and high quantum yields in solid state have been generated, which show the potential 48 49 applications in numerous fields including optics, electronics, energy and 50 bioscience.[7-9] Nevertheless, there are still some issues that need to be improved. 51 First of all, most non-planar AIE luminogens reported in recent years are prepared 52 based on coupling reactions with noble metal catalyst, which are neither convenient for preparation nor friendly to environment.[10,11] Secondly, for most stator-rotor 53 systems, the steric aromatic planar rotors, which are used to break up the  $\pi$ - $\pi$  stacking 54 between stators and increase the fluorescence quantum yield, could form extra  $\pi$ - $\pi$ 55 56 stacking between themselves and reduce the fluorescence quantum yield. Thirdly, the 57 relation between inter-molecular stacking modes and photoluminescent properties for 58 AIE luminogens is still not so clear owing to the uncertainty, complexity and variability of the stacking modes. 59

60 On the other hand, the multiple chromisms (MC) effect resulting from external 61 stimuli often appears in the poly-aryl AIE systems with plenty of  $\pi$ - $\pi$  stacking 62 structures.[12] These MC materials have showed the promising applications in 63 lighting, sensing and displaying.[13-17] But their complex inter- and intra-molecular

structures based on large amounts of aromatic rings make it difficult to describe themechanism clearly.

66 Herein, the naphthalimide moieties were first introduced into AIE systems as twisted structures rather than connecting ones or donors/acceptors.[18-24] On the 67 calculation, N-phenyl-1,8-naphthalimide (PhNI) 68 basis of reported and 69 N-cyclohexyl-1,8-naphthalimide (CyNI) shared similar twisted the cross conformation.[25] Compared with phenyl group, cyclohexyl group could be not only 70 71 a huge group with the occupation functionality to break up the  $\pi$ - $\pi$  stacking between 72 stators but also a non-conjugated one without forming extra  $\pi$ - $\pi$  stacking between rotors during aggregation. The samples of **PhNI** obtained from different preparation 73 74 processes showed changeable emission while the corresponding samples of CyNI 75 showed stable emission. The results demonstrated that the  $\pi$ - $\pi$  stacking between conjugated rotors (phenyl groups) affected the photoluminescent properties. Further 76 77 structural characterization illustrated that the crystals of PhNI and CvNI adopted 78 J-aggregation and X-aggregation respectively, suggesting that the inter-molecular 79 conformation had a profound impact on AIE and MC effects.

# 80 Experimental section

#### 81 Measurements

<sup>1</sup>H and <sup>13</sup>C NMR measurements were recorded on a Bruker AVANCE 400 MHz
spectrometer, using tetramethylsilane (TMS) as an internal standard. Electron
ionization mass spectra (EI-MS) was measured using ThermoFisher spectrometers

85 (TRACE 1300 GC-MS). Fourier transform infrared (FT-IR) spectra were obtained on 86 a BRUKER TENSOR 27 spectrometer (KBr pellet). UV-Vis spectra were recorded on 87 a SHIMADZU UV-3600 spectrophotometer. Photoluminescence emission spectra were obtained with HORIBA Fluoromax-4 spectrofluorometer. The absolute 88 luminescence quantum yield ( $\Phi_F$ ) was measured by a FLS920 fluorescence 89 was completed 90 spectrophotometer. Thermogravimetric analysis (TGA) PerkinElmer Pyris 1 TGA with heating rate of 20 °C/min from 50 °C to 600 °C under 91 92 nitrogen atmosphere. Differential scanning calorimetry (DSC) was conducted by PerkinElmer Pyris 1 DSC with heating rate of 10 °C/min from 50 °C to 300 °C under 93 94 nitrogen atmosphere. X-ray diffraction (XRD) patterns were obtained by using a Bruker X-ray diffractometer (D8 ADVANCE, Germany) with Cu Kα radiation source 95 (40kV, 40mA). Morphologies of the samples were observed by scanning electron 96 microscopy (SEM, Hitachi S-4800). The single-crystal X-ray diffraction data for the 97 crystal of **PhNI** prepared with 50 mg sample and 50 mL THF/water (1:1 by volume) 98 99 as solvent were collected from a BRUKER D8 VENTURE system with Cu-Ka 100 radiation ( $\lambda$ =1.54178 Å) at 280(10) K. The structure was solved using direct methods 101 following the difference Fourier syntheses. All non-hydrogen atoms were anisotropically refined through least-squares on  $F^2$  using the SHELXTL program 102 103 suite. The anisotropic thermal parameters were assigned to all non-hydrogen atoms. The hydrogen atoms attached to carbon were placed in idealized positions and refined 104 105 using a riding model to the atom from which they were attached. The pictures of

- structure were produced using Diamond 3.1. CCDC 1537487 contains thesupplementary crystallographic data of this paper.
- 108 Synthesis
- 109 N-phenyl-1,8-naphthalimide (**PhNI**)

1,8-Naphthalic anhydride (6.00 g, 30 mmol) and aniline (5.50 mL, 60 mmol) 110 111 were added to 50 mL acetic acid. After reflux for 6 h, the white suspension 112 turned into a black homogeneous solution. Then the reaction system was cooled to room temperature with continuous stirring and a white precipitate formed. 113 114 After filtration, the residue was washed with 20 mL acetic acid twice and dried 115 with a vacuum drying oven at room temperature for 24h. The **PhNI** compound was obtained as a white powder in 82% yield (6.76 g). <sup>1</sup>H NMR (400 MHz, 116 CDCl<sub>3</sub>, 25 °C, TMS)  $\delta$  (ppm):8.63 (dd, J = 7.3, 1.0 Hz, 2H); 8.25 (dd, J = 8.3, 117 1.0 Hz, 2H); 7.77 (dd, J = 8.1, 7.4 Hz, 2H); 7.62 – 7.53 (m, 2H); 7.53 – 7.46 (m, 118 1H); 7.38 – 7.30 (m, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>, 25 °C, TMS) δ (ppm): 119 164.18, 135.33, 134.14, 131.56, 131.41, 129.26, 128.56, 128.53, 128.33, 126.89, 120 122.62. FT-IR (KBr) υ (cm<sup>-1</sup>): 3403, 3353, 3137, 3071, 1870, 1777, 1703, 1662, 121 1488, 1583, 1357, 1239, 1190, 888, 779, 701. EI-MS: m/z: calcd: 273.08. 122 Found: 272.07 [M-1]<sup>+</sup>. Anal. Calc. for C<sub>18</sub>H<sub>11</sub>NO<sub>2</sub>: C 79.11%, H 4.06%, N 123 124 5.13%; found: C 79.14%, H 4.25%, N 5.18%.

- 125 N-cyclohexyl-1,8-naphthalimide (CyNI)
- 126 1,8-Naphthalic anhydride (6.00 g, 30 mmol), cyclohexylamine (6.90mL, 60

mmol), and piperidine (1.0 mL) were added to 50 mL 2-ethoxyethanol. After reflux 127 128 for 6 h, the white suspension turned into a black homogeneous solution. Then the reaction system was cooled to room temperature with continuous stirring and a pale 129 130 vellow precipitate formed. After filtration, the residue was washed with 20 mL 2-ethoxyethanol twice and dried with a vacuum drying oven at room temperature for 131 132 24h. The CyNI compound was obtained as a pale yellow powder in 55% yield (4.63 g). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS)  $\delta$  (ppm): 8.55 (dd, J = 7.3, 1.0 Hz,2H), 133 8.16 (dd, J = 8.3, 0.9 Hz,2H), 7.72 (dd, J = 8.1, 7.4 Hz,2H), 5.03 (tt, J = 12.2, 3.7 134 Hz,1H), 2.55 (qd, J = 12.3, 3.3 Hz,2H), 1.95 – 1.22 (m, 8H). <sup>13</sup>C NMR (101 MHz, 135 136 CDCl<sub>3</sub>, 25 °C, TMS) δ (ppm): 164.57, 133.40, 131.36, 130.96, 128.10, 126.85, 123.23, 53.70, 29.06, 26.52, 25.42. FT-IR (KBr) v (cm-1): 3400, 3133, 2928, 2853, 2866, 137 1694, 1655, 1589, 1399, 1237, 1185, 1101, 845, 774, 665, 542. EI-MS: m/z: calcd: 138 279.13. Found: 279.10 [M]<sup>+</sup>. Anal. Calc. for C<sub>18</sub>H<sub>17</sub>NO<sub>2</sub>: C 77.40%, H 6.13%, N 139 5.01%; found: C 77.43%, H 6.20%, N 5.07%. 140

# 141 **Results and discussion**

### 142 Synthesis of PhNI and CyNI

Scheme 1 described the synthesis of **PhNI** and **CyNI**. Both of them were synthesized *via* an one-step amide condensation[26,27]. Considering the different nucleophilicity of aniline and cyclohexylamine, different acid-base catalysts were used in the synthetic reactions. The structures of the two molecules were confirmed by <sup>1</sup>H NMR,<sup>13</sup>C NMR, gas chromatography-mass spectrometry (GC-MS) and

#### 148 elemental analysis.



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Scheme 1. Synthesis of PhNI and CyNI.

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# 152 AIE properties of PhNI and CyNI

The UV-vis absorption spectra and PL spectra of PhNI and CyNI 153 respectively in dilute THF solution and in THF solution with increasing water 154 content  $(f_w)$  were provided in Fig. 1. For both **PhNI** and **CyNI**, a characteristic 155 156 absorption maximum ( $\lambda_{max}$ ) appeared at ~330nm, implying their similar rigid 157 conjugated mother compound of naphthalimide. With increasing water content ( $f_w$ ) in THF solution, **CyNI** exhibited only one emission peak at ~470 nm (Fig. 158 159 1B), while **PhNI** showed two peaks at ~400 nm and ~470 nm respectively (Fig. 160 1A), suggesting its polymorphism or the possible solute-solvent interaction.

161 The photographs taken under UV light (inset in Fig. 1A and 1B) revealed that

162 PhNI and CyNI aggregated and brightened with increasing water content,

163 showing their typical AIE effects.



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**Fig. 1.** Normalized UV-PL spectra of (A) **PhNI** and (B) **CyNI** in THF with increasing  $f_w$  (the solution concentrations are  $10^{-5}$  M for UV test and  $10^{-3}$  M for PL test;  $\lambda_{ex} = 330$ nm), the insets in (A) and (B) are fluorescence images of **PhNI** and **CyNI** respectively in THF with increasing  $f_w$  under UV light ( $\lambda_{ex} = 365$  nm).

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170 The **PhNI** samples prepared under different conditions and with various

171 external stimuli showed different photophysical properties in solid state (Fig. 172 2A), suggesting the presence of MC effect. For instance, the crystal of PhNI (PhNI-C) was white solid with weak violet emission. After grinding with 173 sandpaper, it partly changed to white powder (PhNI-G) with strong 174 bluish-green emission. The precipitation of PhNI (PhNI-P) made by titrating 175 saturated THF solution of **PhNI** into large amount water quickly and filtrating 176 immediately gave pale-yellow powder with strong blue emission. After fuming 177 178 with THF vapor for 24h, it changed to white powder (**PhNI-F**) with weak violet emission. Treating the crystal at  $210 \square$  for 10 min, it melted into a transparency 179 180 liquid. If the cooling process was slow (annealing), the liquid turned into white powder (**PhNI-A**) with weak violet emission. But with a fast cooling process 181 (quenching), the liquid turned into yellow powder (PhNI-Q) with strong blue 182 emission. Such mechanochromism and thermochromism effects of PhNI 183 samples were further verified by PL spectra (Fig. 2B). After grinding, the 184 185 emission peak of **PhNI-C** red-shifted from 430 nmto 505 nm. After fuming, the emission peak of PhNI-P blue-shifted from 455nm to 420 nm. Through 186 different cooling process, the emission peak of PhNI-A was located at 430 nm 187 while PhNI-Q at 455 nm. Based on the fluorescence images and 188 189 photoluminescence spectra of PhNI samples, the two emission peaks in Fig. 1A could be attributed to the polymorphism of **PhNI** instead of the solute-solvent 190 191 interaction. By contrast, the luminous intensities and wavelengths of CyNI 192 samples were stable, disregarding preparation processes and external stimuli

(Fig. 2C and 2D), indicating the absence of MC effect. The UV-Vis absorption 193 194 spectra of PhNI samples (Fig. S1) showed that the stable samples (crystal, fume and anneal) have the maximum absorption peaks at about 350nm while the 195 196 unstable samples (precipitation, grind and quench) at about 390nm, indicating their different energy gaps between the ground state and the lowest excited state 197 as well as thus resulting different brightness. The photophysical data 198 199 (absorption, emission and fluorescence quantum yields) of PhNI and CyNI samples in different solid states and solution states were listed in Table 1. Since 200 PhNI and CyNI shared the same fluorescence core of naphthalimide, the 201 202 difference in their photophysical properties should be relevant to the different 203 stacking modes caused by the different substituents and the different 204 preparation process.

Table 1 Photophysical data (absorption, emission and fluorescence quantum
yields) of PhNI and CyNI samples in different solid states and solution states.

state	Sample	Abs. (nm)	Em. (nm)	$\Phi_{ m f}$
solution	PhNI	330nm	-	0
	CyNI	330nm	-	0
<b>Y</b>	PhNI-C	355nm	430nm	0.06
solid	PhNI-P	385nm	455nm	0.51
	PhNI-G	393nm	505nm	0.45
	PhNI-F	353nm	420nm	0.10

PhNI-A	345nm	430nm	0.15
PhNI-Q	396nm	455nm	0.45
CyNI	398nm	470nm	0.56



Fig. 2. Fluorescence images ( $\lambda_{ex} = 365 \text{ nm}$ ) and photoluminescence spectra ( $\lambda_{ex} = 330 \text{ nm}$ ) of the different **PhNI** samples (A and B) and the different **CyNI** samples (C and D).

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#### 213 MC properties of PhNI

214 To recognize the difference in inter-molecular structure ( $\pi$ - $\pi$  stacking) 215 between different **PhNI** samples and clear up the cause of the MC effect, the phase identification of PhNI was undertaken with powder X-ray diffraction 216 (XRD). In Fig. 3A, the XRD pattern of PhNI-C exhibited a sharp profile, 217 indicating its well-ordered microcrystalline structures. According to Bragg 218 equation, the peak at  $2\theta = 25.4^{\circ}$  (green circle) in the pattern of **PhNI-C** 219 220 corresponded with the interlayer distance of 3.48Å. Similarly, the peak at 221  $2\theta$ =30.3° (blue circle) corresponded with the interlayer distance of 2.95Å. Both of them matched well with the calculated interlayer distance from face index 222 223 (3.49 Å for the interlayer distance of  $\pi$ - $\pi$  stacking between naphthalimides and 2.96 Å for the interlayer distance of  $\pi$ - $\pi$  stacking between phenyl groups in Fig. 224 4) and the simulated pattern from single crystal diffraction of PhNI-C (Fig. 225 226 3B). But in the pattern of **PhNI-G**, the decrease of Ph-Ph peak (the interlayer distance of  $\pi$ - $\pi$  stacking between phenyl groups) and the retained NI-NI peak 227 (the interlayer distance of  $\pi$ - $\pi$  stacking between naphthalimides) implied the 228 destruction of  $\pi$ - $\pi$  stacking between phenyl groups. There were no difference 229

between the pattern of PhNI-P and PhNI-F, which suggested that only the 230 surface structure of **PhNI-P** was changed by fuming with THF vapor, thus 231 232 leading to the difference in fluorescence data but the similarity in XRD pattern. 233 Besides, PhNI-A had more peaks than PhNI-Q, indicating its more stability. 234 Moreover, the location of NI-NI peak and Ph-Ph peak in the pattern of heat-treated **PhNI** samples changed a little, different from other **PhNI** samples. 235 236 The above-mentioned XRD results (Fig. 3A) and fluorescence data (Fig. 2A 237 and 2B) of **PhNI** samples illustrated that the samples with strong Ph-Ph peak exhibited weak fluorescence and vice versa. Briefly, the fluorescence intensities 238 239 showed negative correlation with the presence of  $\pi$ - $\pi$  stacking between phenyl 240 groups.



Fig. 3. (A) XRD curves of the different PhNI samples, (B) simulated pattern from
single crystal diffraction of PhNI-C and (C) DSC curves of the different PhNI
samples.

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246 Further characterization on the  $\pi$ - $\pi$  stacking of the different PhNI samples was done with differential scanning calorimetry (DSC). Comparing the first 247 heating curves of **PhNI** samples (Fig. 3C), besides the common melting peak at 248 202, PhNI-Q exhibited an extra exothermic cold crystallization peak (1.5 249 250 kJ/mol) than **PhNI-A** at 168, implying its more instability. **PhNI-C** showed an extra endothermic phase transformation peak (2.0 kJ/mol) than PhNI-A at 251 252 181, explaining their different locations of NI-NI and Ph-Ph peaks (Fig. 3a). **PhNI-P** showed a set of strange overlap peaks at about 175 like a noise. 253 Since the exothermic cold crystallization peak of **PhNI-Q** and the endothermic 254 phase transformation peak of **PhNI-C** were located at the adjacent position in 255 256 DSC curves and had the same order of magnitudes in intensity, it could be imagined that the overlap peaks of PhNI-P resulted from the existence and 257 258 superposition of the above two peaks. Ignoring the same endothermic phase transformation peak, PhNI-P possibly contained an extra exothermic cold 259 crystallization peak than **PhNI-C**, implying that **PhNI-P** is relatively unstable 260 compared with **PhNI-C**. Because the energy of cold crystallization peak (1.5 261 kJ/mol) and the energy of forming  $\pi$ - $\pi$  stacking between phenyl groups (8.0 262

kJ/mol) were in the same order of magnitudes,[28] we could infer that **PhNI-P** had less  $\pi$ - $\pi$  stacking between phenyl groups than **PhNI-C**, agreeing with the XRD results.

To accurately explore the structure (inter-molecular  $\pi$ - $\pi$  stacking) of **PhNI** 266 samples and to figure out the MC mechanism, it was necessary to understand 267 the single-crystal structural information of **PhNI-C** (with  $\pi$ - $\pi$  stacking between 268 phenyl groups) and **PhNI-P** (without  $\pi$ - $\pi$  stacking between phenyl groups). As 269 270 shown in Fig. 4, PhNI-C adopted the twisted cross intra-molecular conformation with dihedral angle near 90°. In addition, there existed  $\pi$ - $\pi$ 271 stacking between naphthalimides (3.49Å) and  $\pi$ - $\pi$  stacking between phenyl 272 273 groups (2.96Å) simultaneously, forming the J-aggregate with staggered parallel 274 inter-molecular conformation. Although PhNI-P was unavailable for single-crystal structural analyses owing to its structure disorder, its 275 276 inter-molecular structure could be inferred by the conclusion of XRD that there were  $\pi$ - $\pi$  stacking between naphthalimides but no  $\pi$ - $\pi$  stacking between phenyl 277 groups in PhNI-P. Therefore, PhNI-P could take cross inter-molecular 278 279 conformation. In such case, naphthalimides stacked with each other while phenyl groups repulsed each other, which was called X-aggregate. The 280 emission of PhNI-C (J-aggregate) was weaker than that of PhNI-P 281 282 (X-aggregate), which has been confirmed from their fluorescence quantum yields displayed in Table 1 and corresponded with the reported computation 283 284 results that the inter-molecular parallel cofacial configurations are detrimental

to luminescence in the solid state.[1] On the other hand, the single crystal structure of **CyNI-C** was supposed to be helpful for the structure analysis of **PhNI-P** due to their similarity without the  $\pi$ - $\pi$  stacking between phenyl groups. However, the disorder in the crystal structure of **CyNI** hampered the measurement of its accurate structure which, from another side, reflected its unstable structure similar to that of **PhNI-P**.



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## 294 Self-assembly of PhNI and CyNI

Both **PhNI** and **CyNI** were capable of self-assembling due to the inter-molecular  $\pi$ - $\pi$  stacking. In the case of dissolving in a good solvent (e.g., THF) mixed with a poor solvent (e.g., water), by evaporating the good solvent slowly, microfibers with a diameter of several microns for **CyNI-C** (Fig. 5A) and hundred microns for **PhNI-C** (Fig. 5C) were formed respectively. According to the calculation results of reported articles,[29] the constraint in one direction resulted in fiber-like structures and the constraint in two

directions resulted in plate-like structures. In our case, such difference in 302 diameter suggested that plate-like structure (PhNI-C) was composed of 303 two-dimensional (2-D)  $\pi$ - $\pi$  stacking while fiber-like structure (CyNI-C) was 304 305 composed of one-dimensional (1-D)  $\pi$ - $\pi$  stacking. Precipitations obtained by titrating saturated THF solution of **PhNI/CyNI** into water quickly and filtrating 306 immediately respectively were broken microfibers with several microns in 307 diameter (Fig. 5B and 5D), suggesting that PhNI-P and CyNI-P might be built 308 by 1-D  $\pi$ - $\pi$  stacking. It could be imagined that **PhNI-P**, **CyNI-P** and **CyNI-C** 309 formed the similar X-aggregate for lacking the  $\pi$ - $\pi$  stacking between rotors 310 311 (Ph/Cy). Moreover, like PhNI-C and PhNI-P, the diameter of PhNI-A (Fig. 312 5E) was much larger than that of PhNI-Q (Fig. 5F), which implied the 313 difference in  $\pi$ - $\pi$  stacking (1-D/2-D) and corresponded well with the XRD data (Fig. 3A). 314



315

316 Fig. 5. SEM images of (A) CyNI-C, (B) CyNI-P, (C) PhNI-C, (D) PhNI-P, (E)

317 **PhNI-A** and (F) **PhNI-Q**.

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# 319 Interaction analysis

Based on the above results, we inferred that the AIE effects of **PhNI** and **CyNI** were influenced by intra-molecular and inter-molecular structures simultaneously. Up to now, there have been several theories about AIE, for example, restriction of intra-molecular motions (RIM), J/X-aggregate formation (JXAF), excited state intra-molecular proton transfer (ESIPT) and twisted intra-molecular charge transfer (TICT).[30] For the as-prepared two

326 naphthalimides without any hydrogen bonds interaction or cofacial 327 intra-molecular conformation, the RIM and JXAF theories should be more appropriate. In Fig. 6A, the excited state energy of PhNI and CvNI was 328 consumed by the intra-molecular motion in solution state, leading to weak 329 fluorescence. But in solid state, the intra-molecular motion was restricted 330 331 (RIM) by  $\pi$ - $\pi$  stacking and the energy could be transformed into emission, resulting in the fluorescence of PhNI and CyNI. Instead of changeless lacking 332  $\pi$ - $\pi$  stacking between cyclohexyl groups in **CyNI** samples, the changeable 333 presence and absence of  $\pi$ - $\pi$  stacking between phenyl groups in different **PhNI** 334 335 samples brought about varied inter-molecular structures (J/X-aggregate) and changed the energy gap between the ground state and the lowest excited state, 336 resulting in the varied fluoresce quantum yields ( $\Phi_{\rm F}$ ). To sum it up, AIE effects 337 were associated with both intra-molecular and inter-molecular structures. The 338 former provided the foundation of RIM and afforded the energy for generating 339 fluorescence, while the latter transformed the aggregate states, influenced the 340 341 energy gaps and adjusted the fluorescence intensity. As shown in Fig. 6B, the 342 fluorescence of AIE molecules with cross intra-molecular structures (RIM) 343 could be hidden due to the form of J-aggregate with parallel cofacial 344 inter-molecular configurations, which could be named implicit AIE (imAIE) effect. By means of different preparations and various external stimuli, some 345 implicit AIE effects (J-aggregate) could be transformed into explicit AIE effects 346 (X-aggregate), like PhNI-C and PhNI-P. As illustrated in Fig. 6C, PhNI-C, 347

PhNI-A and PhNI-F could be obtained by thermodynamic controlling process 348 349 and exhibited stable J-aggregates with weak fluorescence due to the  $\pi$ - $\pi$ stacking between substituents. To the contrary, **PhNI-P** and **PhNI-Q** might be 350 351 acquired by kinetic controlling process and displayed instable X-aggregates with strong fluorescence owing to the repulsion between substituents. Besides, 352 PhNI-G benefited from shear force and gained a similar instable structure. The 353 354 MC effect could be obtained by transformation between implicit AIE (imAIE) 355 effect and explicit AIE (exAIE) effect, which was controlled by thermodynamic/kinetic process and external stimuli. 356



358 Fig. 6. Proposed mechanisms of AIE/MC effects for PhNI and CyNI.

359

# 360 Conclusions

361 In summary, two N-substituted naphthalimides (PhNI and CyNI) with AIE effects 362 were synthesized. Among them, **PhNI** showed an interesting MC property, which was confirmed by PL spectra. Although without useful MC effect, CyNI showed stable 363 strong AIE effect. The studies by XRD, DSC and SEM indicated that the solid 364 365 fluorescent properties had a close relation with inter-molecular structures. The single-crystal X-ray structural analyses verified that conjugated and non-conjugated 366 substituents resulted in different  $\pi$ - $\pi$  stacking modes and different photoluminescent 367 properties. For the different PhNI samples, their MC property resulted from their 368 different inter-molecular structures and could be controlled by thermodynamic/kinetic 369 370 processes. These results suggested that AIE effect was decided by intra-molecular 371 (RIM) and inter-molecular (JXAF) structures simultaneously. We believed that our 372 studies would be helpful to obtain deeper insights into the AIE/MC phenomena and 373 mechanisms, and develop much more AIE/MC materials based on naphthalimides.

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# Highlights

- We explore a new AIE system using naphthalimide as twisted structure instead of linker or donor/acceptor.
- Two naphthalimides avoid noble metal catalyst in the synthesis.
- The relations between properties and structures of two naphthalimides reveal an opinion that the AIE effects were influenced by intra- and inter-molecular structures simultaneously.
- The multiple chromisms effects of AIE materials may result from the transformation of inter-molecular structures.
- Two naphthalimides exhibit excellent AIE effects ( $\Phi_f = 0.55$ ) and interesting multiple chromisms effects.