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Aggregation-induced emission, multiple chromisms and self-organization of *N*-substituted-1,8-naphthalimides

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

Department of Polymer Science and Engineering, State Key Laboratory of Coordination Chemistry, Collaborative Innovation Center of Chemistry for Life Sciences, Key Laboratory of High Performance Polymer Materials and Technology (Nanjing University), Ministry of Education, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, PR China

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ABSTRACT

Most aggregation-induced emission (AIE) luminogens possess propeller-like aromatic stator-rotor structures, such as silole, tetraphenylethylene (TPE) and triphenylamine (TPA), to restrict intra-molecular motions (RIM) and avoid aggregation-caused quenching (ACQ) effects. In our work, two simple *N*-substituted naphthalimides were designed and synthesized by the amide condensation to create novel AIE systems. Except for the same aromatic stator (naphthalimide), *N*-phenyl-1,8-naphthalimide (**PhNI**) contained an aromatic rotor (phenyl group) while *N*-cyclohexyl-1,8-naphthalimide (**CyNI**) contained an aliphatic rotor (cyclohexyl group). The **PhNI** samples obtained from different preparation processes showed multiple chromisms (MC) effects and varied levels of luminescence. Despite of the same intra-molecular structure, the crystal of **PhNI** had staggered parallel inter-molecular conformation with weak emission but the precipitation of **PhNI** had cross one with strong emission. Although without MC effects, **CyNI** gave an excellent fluorescence quantum yield (Φ_f = 0.55). The experimental results and theoretical analyses suggested that the AIE effects were decided by intra- and inter-molecular structure simultaneously and the construction and destruction of inter-molecular π-π stacking between aromatic rotors in PhNI resulted in the MC effects.

1. Introduction

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 quenching (ACQ). According to the reported quantum-chemical calculations, the cofacial configurations (π-π stacking) in the molecules are responsible for the decay of luminescence [1]. Theoretically, effective methods to solve this problem are separating these molecules through the introduction of large steric hindrance groups or achieving the rotation of the molecules around the stacking axis while keeping the parallelism between the molecular planes [2,3].

Nowadays, an abnormal phenomenon called aggregation-induced emission (AIE) is observed, in which some non-planar luminogens are emissive in solid state while none-emissive in solution state [4,5]. These AIE luminogens are usually composed of a central stator, normally aromatic planar fluorescent molecule, and several steric 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 progress offers a large platform for exploring practically useful luminescent materials 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 applications in numerous fields including optics, electronics, energy and bioscience [7–9]. Nevertheless, there are still some issues that need to be improved. First of all, most non-planar AIE luminogens reported in recent years are prepared 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 systems, the steric aromatic planar rotors, which are used to break up the π-π stacking between stators and increase the fluorescence quantum yield, could form extra π-π stacking between themselves and reduce the fluorescence quantum yield. Thirdly, the relation between inter-molecular stacking modes and photoluminescent properties for AIE luminogens is still not so clear owing to the uncertainty, complexity and variability of the stacking modes.

On the other hand, the multiple chromisms (MC) effect resulting

* Corresponding author.
E-mail address: yunlu@nju.edu.cn (Y. Lu).

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from external stimuli often appears in the poly-aryl AIE systems with plenty of π-π stacking structures [12]. These MC materials have showed the promising applications in 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 the mechanism clearly.

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

2. Experimental section

2.1. Measurements

^{1}H and ^{13}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 (TRACE 1300 GC-MS). Fourier transform infrared (FT-IR) spectra were obtained on a BRUKER TENSOR 27 spectrometer (KBr pellet). UV–Vis spectra were recorded on a SHIMADZU UV-3600 spectrophotometer. Photoluminescence emission spectra were obtained with HORIBA Fluoromax-4 spectrofluorometer. The absolute luminescence quantum yield (Φ_F) was measured by a FLS920 fluorescence spectrophotometer. Thermogravimetric analysis (TGA) was completed on PerkinElmer Pyris 1 TGA with heating rate of 20 °C/min from 50 °C to 600 °C under 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 nitrogen atmosphere. X-ray diffraction (XRD) patterns were obtained by using a Bruker X-ray diffractometer (D8 ADVANCE, Germany) with Cu Kα radiation source (40 kV, 40 mA). Morphologies of the samples were observed by scanning electron microscopy (SEM, Hitachi S-4800). The single-crystal X-ray diffraction data for the crystal of **PhNI** prepared with 50 mg sample and 50 mL THF/water (1:1 by volume) as solvent were collected from a BRUKER D8 VENTURE system with Cu-Kα radiation (λ = 1.54178 Å) at 280 (10) K. The structure was solved using direct methods following the difference Fourier syntheses. All non-hydrogen atoms were anisotropically refined through least-squares on F^2 using the SHELXTL program 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 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 the supplementary crystallographic data of this paper.

2.2. Synthesis

2.2.1. N-phenyl-1,8-naphthalimide (*PhNI*)

1,8-Naphthalic anhydride (6.00 g, 30 mmol) and aniline (5.50 mL, 60 mmol) were added to 50 mL acetic acid. After reflux 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 white precipitate formed. After filtration, the residue was washed with 20 mL acetic acid twice and dried with a vacuum drying oven at room temperature for 24 h. The **PhNI** compound was obtained as a white powder in 82% yield (6.76 g). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm):8.63 (dd, J = 7.3, 1.0 Hz, 2H); 8.25 (dd, J = 8.3, 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, 1H); 7.38–7.30 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm): 164.18, 135.33, 134.14, 131.56, 131.41, 129.26, 128.56, 128.53, 128.33, 126.89, 122.62. FT-IR (KBr) υ (cm^{-1}): 3403, 3353, 3137, 3071, 1870, 1777, 1703, 1662, 1488, 1583, 1357, 1239, 1190, 888, 779, 701. EI-MS: *m/z*: calcd: 273.08. Found: 272.07 $[M-1]^+$. Anal. Calc. for $C_{18}H_{11}NO_2$: C 79.11%, H 4.06%, N 5.13%; found: C 79.14%, H 4.25%, N 5.18%.

2.2.2. N-cyclohexyl-1,8-naphthalimide (*CyNI*)

1,8-Naphthalic anhydride (6.00 g, 30 mmol), cyclohexylamine (6.90 mL, 60 mmol), and piperidine (1.0 mL) were added to 50 mL 2-ethoxyethanol. After reflux 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 yellow 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 24 h. The **CyNI** compound was obtained as a pale yellow powder in 55% yield (4.63 g). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm): 8.55 (dd, J = 7.3, 1.0 Hz,2H), 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 Hz,1H), 2.55 (qd, J = 12.3, 3.3 Hz,2H), 1.95–1.22 (m, 8H). ^{13}C NMR (101 MHz, $CDCl_3$, 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) υ (cm-1): 3400, 3133, 2928, 2853, 2866, 1694, 1655, 1589, 1399, 1237, 1185, 1101, 845, 774, 665, 542. EI-MS: *m/z*: calcd: 279.13. Found: 279.10 $[M]^+$. Anal. Calc. for $C_{18}H_{17}NO_2$: C 77.40%, H 6.13%, N 5.01%; found: C 77.43%, H 6.20%, N 5.07%.

3. Results and discussion

3.1. 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 ^{1}H NMR,^{13}C NMR, gas chromatography-mass spectrometry (GC-MS) and elemental analysis.

3.2. AIE properties of PhNI and CyNI

The UV–vis absorption spectra and PL spectra of **PhNI** and **CyNI** respectively in dilute THF solution and in THF solution with increasing water content (f_w) were provided in Fig. 1. For both **PhNI** and **CyNI**, a characteristic absorption maximum (λ_{max}) appeared at ~330 nm, implying their similar rigid conjugated mother compound of naphthalimide. With increasing water content (f_w) in THF solution, **CyNI** exhibited only one emission peak at ~470 nm (Fig. 1B), while **PhNI** showed two peaks at ~400 nm and ~470 nm respectively (Fig. 1A), suggesting its polymorphism or the possible solute-solvent interaction. The photographs taken under UV light (inset in Fig. 1A and B) revealed that **PhNI** and **CyNI** aggregated and brightened with increasing water content, showing their typical AIE effects.

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