Insights into the isomeric effect on the self-assembly of donor-acceptor type aggregation-induced emission luminogens: Colour-tuning and shape-controlling

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ABSTRACT

In this study, we reported the synthesis and aggregation-induced emission (AIE) properties of a new molecular system, comprised of six positional isomers. The presence of electron donor (D) and acceptor (A) units endows them with intramolecular charge transfer (ICT) effects. We studied how changing the positions of the D/A units affects the AIE properties, ICT strength as well as the energy levels of the molecular orbitals. In addition, the self-assembly behaviors of them show distinct isomeric effect: With the D/A units repositioning, various self-assembly architectures with sizes ranging from microscale to nanoscale appear sequentially, including filaments, sheets, rods, irregular particles, needles, fibrous interlocking textures. It was verified that the D/A units on para-position that pose linear dipole-dipole interaction would favor the formation of well-defined structures, otherwise the resulting assembly would be underdeveloped or ill-shaped due to low degree of order in the molecular packing. This study probed the relationships between molecular structure and self-assembly behaviour, and further makes the self-assembly customizable.

1. Introduction

Molecular self-assembly describes the process in which spontaneous organization of molecules arranges themselves into well-ordered structures [1,2]. Self-assembling processes are common throughout nature, which are utilized increasingly in many disciplines, with a different emphasis and aim in each [3–5]. The beauty of self-assembly stems from the fact that it is one of the few practical strategies for fabricating various kinds of supramolecular architectures at micro- or nano-level as the prerequisite for functionalization of materials in countless areas [6–9]. Many examples have demonstrated that advances in sensors and smart materials would benefit tremendously from the unique well-ordered structures of molecular assemblies, or lose efficacy in their absence [10–12].

There is a major requirement for the application of self-assemblies, *i.e.*, controllability, which means the building blocks are able to assemble into the desired structures or patterns to fit for a given situation. Actually it is believed to rank as one of the twenty-five highlighted questions in the present century on account of its great significance [13]. To this end, the building blocks must be designed properly and wisely, and it applies equally for optical sensors and functional

materials that function based on molecular self-assembly [14–17]. Among all the building blocks for optics, the rapid expansion of aggregation-induced emission (AIE) systems are drawing worldwide attention [18,19]. They are designed to be highly twisted in conformation in order to avoid intermolecular π-π interaction in solid state [20]. Their solid-state emission is remarkably enhanced as a result of such propeller-shaped molecular configuration, offering great potential to serve as the functional subjects in solid state or on solid support, such as sensing films [21–23], mechanochromic fluorescent materials [24–26], organic light emitting diodes [27–29]. The advantages of AIE systems also facilitate the development of AIE-active building blocks for molecular self-assemblies to create supramolecular architectures with diversified morphologies, including rods [30], fibers [31,32], sheets [33], spheres [34] and helical structures [35,36]. Just as the investigation of structure-property relationships of the building blocks proceeds soon after the resulting materials profit from their characteristic architectures, so too has the investigation of AIE-based ones got started [37–39]. These studies are generally based on analogue compounds created by changing the species and positions of the substituents attached on the AIE cores. These substituent groups not only balance the attractions and repulsions in the self-assembly process *via* noncovalent

interactions, but also fine-tune the orientation and steric hindrance for the optimization of the molecular arrangement [40,41]. The systematic research on substituent effect would provide essential information on the relationships between supramolecular structures and properties, which helps us to get insights into the underlying working mechanisms and further offers the possibility to functionalize the materials or improve their performances through tiny modification of the molecular structure. And this applies equally to AIE-active functional materials.

Herein, we focus our attention to the isomeric effect on the self-assembly behaviour of a series of AIE isomers, which are created by attaching electron donor-acceptor (D-A) units in different positions of a conjugated core, *i.e.*, benzylideneaniline. The dipole-dipole interactions can be well controlled by repositioning D-A units of the luminogens, making the molecules to assemble in various ways. Our systematical study has led to the discovery of their remarkable isomeric effect on the self-assembled patterns. This would undoubtedly facilitate the customizable design of a functional material with the desired structure or surface morphology to satisfy the needs of a given application.

2. Experimental section

2.1. General information

Chemicals and organic solvents were purchased from J&K Scientific and Alfa Aesar. They are used as received without further purification. ^{1}H NMR and ^{13}C NMR spectra were measured on a Varian VNMRS 600 MHz spectrometer using tetramethylsilane as the internal reference. Mass spectra were recorded on an Agilent 7500-Ce inductively coupled plasma source mass spectrometer (ICP-Mass). UV–vis spectra were measured on a SHIMADZU-UV-2550 spectrophotometer. Photoluminescence (PL) spectra were recorded on a HITACHI-F-7000-FL spectrophotometer. The absolute fluorescence quantum yields (Φ_F) were determined by divided the absorbed photons by emitted ones on a HORIBA-FluoroMax-4 spectrophotometer equipped with calibrated integrating sphere. The ground-state geometries were optimized using density functional theory (DFT) with the B3LYP hybrid functional at the basis set level of 6-31G*. The calculations were performed with Gaussian 05 package. Fluorescence images were taken under an Olympus-CKX41 fluorescent microscope with UV excitation (365 nm). The morphologies were observed using a Hitachi SU-8010 scanning electron microscope (SEM).

2.2. Synthesis and structural characterization

The synthetic routes to the isomers including (E)-4-((2-hydroxy-5-methoxybenzylidene)amino)benzoic acid (MOBA1), (E)-3-((2-hydroxy-5-methoxybenzylidene)amino)benzoic acid (MOBA2), (E)-4-((2-hydroxy-3-methoxybenzylidene)amino)benzoic acid (MOBA3), (E)-3-((2-hydroxy-3-methoxybenzylidene)amino)benzoic acid (MOBA4), (E)-4-((2-hydroxy-4-methoxybenzylidene)amino)benzoic acid (MOBA5) and (E)-3-((2-hydroxy-4-methoxybenzylidene)amino)benzoic acid (MOBA6) are shown in Scheme 1. The synthetic procedure of MOBA1 is described as follows. To a round-bottom flask containing 4-aminobenzoic acid (3 g, 21.9 mmol, 1 equiv) was added anhydrous ethanol and two drops of acetic acid as the catalyst. The mixture was heated to 60 °C followed by the addition of 2-hydroxy-5-methoxybenzaldehyde (3.33 g mL, 21.9 mmol, 1 equiv). The reaction mixture was then stirred for 12 h, yielding MOBA1 as yellow precipitates. The products were collected by vacuum filtration using ethanol to rinse. No further purification was needed. Yield: 70%. MOBA2, MOBA3, MOBA4, MOBA5, and MOBA6 were prepared according to the same synthetic procedure. Their yields were 65%, 64%, 63%, 62% and 61%, respectively. The six compounds were characterized by ^{1}H NMR, ^{13}C NMR (Figs. S1-S12) and ICP-Mass spectra with satisfactory results. Data obtained from their structural characterization are listed as follows. ^{1}H NMR of MOBA1 (600 MHz, DMSO-d_6), δ (ppm): 12.93 (s, 1H), 12.01 (s, 1H), 8.93 (s, 1H), 8.00–7.98

(d, 2H), 7.44–7.42 (d, 2H), 7.27–7.27 (d, 1H), 7.06–7.04 (dd, 1H), 6.91–6.89 (d, 1H), 3.73 (s, 3H). ^{13}C NMR of MOBA1 (151 MHz, DMSO-d_6), δ (ppm): 167.30, 164.55, 154.80, 152.97, 152.39, 131.17, 129.13, 121.89, 121.63, 119.70, 118.06, 115.23, 56.00. ICP-Mass of MOBA1: calcd 274.3 [(M + 3H)$^+$, found 274.5]. ^{1}H NMR of MOBA2 (600 MHz, DMSO-d_6), δ (ppm): 13.12 (s, 1H), 12.16 (s, 1H), 8.97 (s, 1H), 7.88 (t, 1H), 7.86–7.84 (d,1H), 7.63–7.61 (d, 1H), 7.57–7.55 (t, 1H), 7.29 (d, 1H), 7.04–7.02 (dd, 1H), 6.90–6.89 (d, 1H), 3.73 (s, 3H). ^{13}C NMR of MOBA2 (151 MHz, DMSO-d_6), δ (ppm): 167.36, 164.26, 154.75, 152.35, 149.19, 132.58, 130.23, 127.92, 126.57, 121.96, 121.30, 119.64, 117.95, 115.51, 55.98. ICP-Mass of MOBA1: calcd 274.3 [(M + 3H)$^+$, found 274.4]. ^{1}H NMR of MOBA3 (600 MHz, DMSO-d_6), δ (ppm): 12.94 (s, 1H), 12.78 (s, 1H), 8.97 (s, 1H), 8.00–7.98 (dt, 2H), 7.47–7.45 (dt, 2H), 7.26–7.25 (dd, 1H), 7.15–7.13 (dd, 1H), 6.92–6.89 (t, 1H), 3.81 (s, 3H). ^{13}C NMR of MOBA3 (151 MHz, DMSO-d_6), δ (ppm): 167.29, 165.37, 152.39, 150.99, 148.38, 131.17, 129.24, 124.30, 121.94, 119.69, 119.23, 116.39, 109.99, 56.34. ICP-Mass of MOBA3: calcd 274.3 [(M + 3H)$^+$, found 274.4]. ^{1}H NMR of MOBA4 (600 MHz, DMSO-d_6), δ (ppm): 13.12 (s, 1H), 12.94 (s, 1H), 9.00 (s, 1H), 7.89–7.89 (t, 1H), 7.86–7.85 (dt, 1H), 7.65–7.63 (dq, 1H), 7.58–7.55 (t, 1H), 7.27–7.26 (dd, 1H), 7.13–7.11 (dd, 1H), 6.91–6.88 (t, 1H), 3.80 (s, 3H). ^{13}C NMR of MOBA4 (151 MHz, DMSO-d_6), δ (ppm): 167.35, 165.00, 150.92, 148.73, 148.33, 132.59, 130.23, 128.00, 126.41, 124.41, 122.19, 119.67, 119.13, 116.21, 56.32. ICP-Mass of MOBA4: calcd 272.1 [(M + H)$^+$, found 272.0]. ^{1}H NMR of MOBA5 (600 MHz, DMSO-d_6), δ (ppm): 13.32 (s, 1H), 12.90 (s, 1H), 8.90 (s, 1H), 7.98–7.96 (dt, 2H), 7.56–7.55 (d, 1H), 7.44–7.42 (dt, 1H), 6.57–6.55 (dd, 1H), 6.49–6.49 (d, 1H), 3.80 (s, 3H). ^{13}C NMR of MOBA5 (151 MHz, DMSO-d_6), δ (ppm): 167.32, 164.57, 164.36, 163.70, 152.28, 134.82, 131.17, 128.75, 121.72, 113.41, 107.60, 101.27, 55.99. ICP-Mass of MOBA5: calcd 272.1 [(M + H)$^+$, found 272.0]. MOBA6 (600 MHz, DMSO-d_6), δ (ppm): 13.40 (s, 1H), 13.10 (s, 1H), 8.92 (s, 1H), 7.86–7.85 (t, 1H), 7.82–7.81 (dt, 1H), 7.61–7.60 (dt, 1H), 7.57–7.53 (m, 2H), 6.56–6.54 (dd, 1H), 6.49–6.48 (d, 1H), 3.79 (s, 3H). ^{13}C NMR of MOBA6 (151 MHz, DMSO-d_6), δ (ppm): 167.40, 164.30, 164.01, 163.46, 148.72, 134.76, 132.55, 130.18, 127.51, 126.27, 121.95, 113.42, 107.39, 101.25, 55.96. ICP-Mass of MOBA6: calcd 272.1 [(M + H)$^+$, found 272.1].

3. Results and discussion

3.1. Aggregation-induced emission

It is obvious that the molecular designing including both twisted conformation and the incorporation of D-A pairs have motivated us to create these positional isomers, in which the N-benzylideneaniline moiety serves as conjugated core, while single bonds within the former offer the possibility of intramolecular rotation in solution state. According to previous reports [42,43], intramolecular hydrogen bonding would be readily formed between the phenolic hydroxyl group and the imine nitrogen, which helps to rigidify the molecular conformation to reinforce the solid-state emission. Fig. 1 shows the PL spectra of these molecules in solid state. Their photophysical data are summarized in Table 1 for better comparison. The emission of the starting molecule MOBA1 shows red colour with its peak located at around 591 nm in the PL spectrum. As the carboxylic acid shifts to the meta-position, the emission peak of the resulting compound MOBA2 exhibits a remarkable hypochromatic shift and locates at 567 nm due to weaker inductive effect. The solid powder of MOBA2 (Φ_F = 2.2%) fluoresce less efficiently than that of MOBA1 (Φ_F = 3.4%) as shown in Table 1. With the methoxy group repositioning and the carboxylic acid keeping unchanged, the compound MOBA3 also shows hypochromatic shift (591–581 nm) compared with the starting molecule MOBA1. And the Φ_F value continues to decrease as seen in Table 1. If both carboxylic acid and methoxy group have shifted, *i.e.*, MOBA4, the PL spectrum peaks at 568 nm. And the Φ_F value is 1.5%, which still remains a lower level (Table 1). When the D and A units both shift to para-position,