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Solvent-assistant self-assembly of an AIE + TICT fluorescent Schiff base for the improved ammonia detection



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ABSTRACT

Solvent-assistant self-assembly of an AIE + TICT fluorescent Schiff base into one-dimensional nanofilaments has been developed. The orientation of the assemblies can be controlled by a simple dewetting process: the filaments are interweaved when the self-assembly process is performed on a horizontal substrate, while tilting the substrate to a tiny angle results in the formation of highly oriented ones with long-range order as verified by microscopic examination. The compound shows remarkable fluorescent response to ammonia gas based on a TICT-LE transition. The self-assembled film presents higher detection sensitivity compared with the non-assembled test paper: the former enables 4.75 times faster response time and 6.86 times lower detection limit than the latter. Furthermore, the former demonstrates better selectivity toward ammonia gas in the presence of various organic amines. The sensing devices also enjoy the advantage of cyclic utilization. The fluorescence of the fumed devices can be converted back into the original state when they are heated at 100 °C for 5 min, as thermal treatment can desorb the ammonia gas that adsorbed in the sensing devices.

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1. Introduction

Self-assembly is one of the most unique features of organic soft matter. Nowadays, advances in sensors including chemosensors [1,2], bioprobes [3,4] and sensor arrays [5,6] benefit tremendously from the high ordering, simple fabrication and scalability of self-assembly. π -conjugated molecules allow the formation of stacked molecular arrangements, and therefore are ideal candidates for the building blocks of supramolecular assemblies [7]. It is frequently reported that π -conjugated molecules can self-assemble into various well-defined structures (eg., hollows, spheres, wires, tubes, vesicles and ribbons), which are driven by π - π interaction as well as further supramolecular interactions such as multiple hydrogen bonding, dipole-dipole interactions and axial coordination [8,9]. However, precise control over the size and orientation of these self-assemblies, which is very important aspect for ensuring desired functions, still remains a major challenge [10].

There is a recent surge in the “directed self-assembly”, which is generally achieved by templating a self-assembly process on a pre-patterned substrate [11–13]. In other cases, “directed self-assembly” implies a self-assembly process in the presence of an externally applied electric or magnetic field that introduces or

modifies the interactions between building blocks, leading to specific structure or orientation that would not otherwise form in their absence [14–16]. But the above-mentioned techniques are often imprecise and require energy-consuming instruments and complicated operations. While solvent regulation or dewetting process provides a simpler approach to direct self-assembly as solvents are capable of fine-tuning the intermolecular interactions and solute-solvent interactions, resulting in well-ordered patterns at the air-solvent interface [17–19].

Here we introduce a fluorescent Schiff base, (E)-4-((4-(diethylamino)benzylidene)amino)benzoic acid (DBBA) that undergoes both aggregation-induced emission (AIE) and twisted intramolecular charge-transfer (TICT) mechanisms. The relationship between the molecular structure and its PL properties were investigated in this work. We further studied the solvent-regulated self-assembly of DBBA and found that the long-range orientation of the assemblies can be realized by a simple dewetting process. Interestingly, the molecular assemblies can act as a fluorescent sensor toward ammonia gas and enable higher performances than the amorphous sample. The sensing devices also enjoy the advantages of reversibility and reproducibility during the repeated detection procedure.

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2. Materials and methods

2.1. Instruments

Chemicals involved in this study were purchased from Aldrich or Alfa Aesar and used as received without further purification. HRMS (MALDI-TOF) spectrum was recorded on a Bruker Autoflex III mass spectrometer. ^1H NMR and ^{13}C NMR spectra were recorded on a Varian VNMRS 600 MHz spectrometer using tetramethylsilane (TMS; $\delta=0$) as an internal reference. UV–vis spectra were measured on a SHIMADZU UV 2550 spectrophotometer. Emission spectra were measured on a HITACHI F-7000 FL spectrophotometer. 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 using the Gaussian 05 package. The fluorescence quantum yields (Φ_F) were determined using a calibrated integrating sphere. X-ray diffraction (XRD) intensity data were collected at 273 K on Bruker Smart Apex diffractometer equipped with a Mo-K α sealed-tube X-ray source. The crystal structure was solved by direct methods and refined on F2 by full-matrix least-squares using the SHELXTL-97 program systems. CCDC 1420713 contains the supplementary crystallographic data of DBBA for this paper. The morphologies of the DBBA assemblies were investigated using a Hitachi SU8010 Scanning Electron Microscope (SEM). Fluorescence images of DBBA were observed under an Olympus CKX41 phase contrast microscope at an excitation wavelength of 365 nm.

2.2. Synthesis and structural characterization

DBBA was prepared by a simple one-step reaction (Scheme 1). Detailed synthetic process is given as follows: 4-(diethylamino) benzaldehyde (5.00 g, 42.65 mmol) and 4-aminobenzoic acid (5.84 g, 42.65 mmol) were dissolved in dehydrated ethanol (300 mL) in a 500 mL round bottom flask equipped with a stir bar and a condenser. Two drops of acetic acid were added and the reaction was stirred at 50 °C for 8 h, then the yellow crystalline product precipitated. The product was filtered and washed several times by ethanol and hexane, respectively. Yield: 65%. Its structure was well characterized using single crystal X-ray diffraction, NMR and MS spectroscopies with satisfactory analysis results as listed in Fig. S1–S3. The ^1H NMR, ^{13}C NMR, MALDI-TOF and elemental analysis data of DBBA are given as below.

^1H NMR (400 MHz, DMSO- d_6), δ (ppm): 12.68 (s, 1H), 8.40 (s, 1H), 7.95–7.93 (m, 2H), 7.75–7.72 (d, 2H), 7.25–7.22 (m, 2H), 6.77–6.74 (d, 2H), 3.46–3.40 (m, 4H), 1.15–1.12 (m, 6H).

^{13}C NMR (600 MHz, DMSO- d_6), δ (ppm): 167.57, 161.59, 156.89, 150.62, 131.48, 131.00, 127.20, 123.15, 121.32, 111.28, 44.29, 40.38, 12.85.

HRMS (MALDI-TOF): m/z : 297.1597 ($[\text{M}+\text{H}]^+$ calcd 297.1525).

Anal. Calcd for $\text{C}_{18}\text{H}_{20}\text{N}_2\text{O}_2$: C, 72.95; H, 6.80; N, 9.45; O, 10.80. Found: C, 73.17; H, 7.18; N, 9.92; O, 9.73.

2.3. Fabrication of DBBA self-assembled sensing film

THF solution of DBBA (10 mM) was prepared and one drop of

the solution was drip on a quartz substrate. After dewetting in the air, the film was further dried in a vacuum oven.

2.4. Fabrication of DBBA test paper

A filter paper was cut into uniform paper strips and dipped into the THF solution mentioned above. After 1 min, the paper strips were taken out and dried in a vacuum oven.

2.5. Ammonia sensing

Paper strips and self-assembled films made through the above-mentioned methods was fixed in a quartz cell, then excess amount of ammonia water was added, after fuming for 5 min, the fluorescent signal was recorded using a PL spectrometer.

2.6. Selectivity test

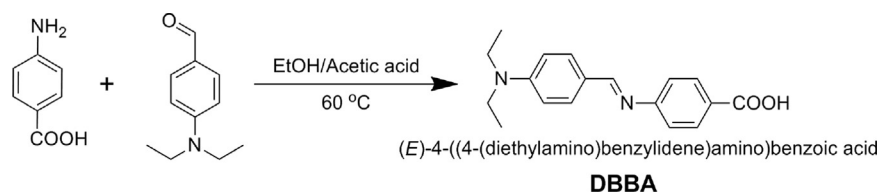
The selectivity of the sensing devices was investigated using competitive organic amines, including triethylamine, diisopropylamine, cyclohexylamine, isopropylamine and ethylamine. After 5 min of fumigation, the fluorescent response of the sensing devices was measured by a PL spectrometer. Each fumigation experiment was performed 8 times for accuracy.

3. Results and discussion

3.1. Photophysical properties

ICT compounds with long-wavelength emission are highly desired especially in the fields of biological imaging, electroluminescent devices and fluorescent probes owing to their non-destructive radiation energy and excellent propagation nature [9,20–22]. They can be fabricated by introducing electron donor (D) and acceptor (A) groups into a fluorophore to concomitantly drive up the highest occupied molecular orbital (HOMO) and pull down the lowest unoccupied molecular orbital (LUMO) [23]. Generally the fluorophores employed are planar aromatic compounds such as fluorene, pyrene, perylene, benzothiadiazole, etc., which suffer drastically from the aggregation-caused quenching (ACQ) problem [24,25]. Fortunately, the reports of AIE systems with highly twisted molecular conformation give a hint to end the dilemma [26,27]. DBBA is exactly designed via a combined concept of AIE and TICT, which endows the molecule with both intense light and long-wavelength emission color (535 nm) at solid state (Fig. S4). The as-synthesized product is crystalline as confirmed by powder X-ray diffractogram (Fig. S5). The AIE phenomenon was investigated through a typical experiment, which is done by dissolving DBBA in pure THF and then adding hexane as a bad solvent. As expected, DBBA shows greatly intensified PL emission at high hexane fraction (Fig. 1A and B). The absolute Φ_F of DBBA in THF solution (0.1 mM) is merely 0.88%, whereas it becomes much stronger (6.72%) in the solid state.

Owing to the presence of both D (diethylamino) and A (carboxylic acid) moieties in the molecule, DBBA exhibits a typical TICT solvatochromism (Fig. 1C): the maximum emission



Scheme 1. Synthetic route to DBBA.

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