



Aggregation-enhanced excimer emission (AEEE) based on pyrenylchalcone and 2-to-4 molecular decoder by biothiols and polyanions in aqueous media



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ABSTRACT

An aggregation-enhanced excimer emission (AEEE) fluorophore was successfully synthesized by introducing chalcone into pyrene. Compared with the traditional AIE structure (tetra-phenylethene derivatives), pyrenylchalcone was more available under mild conditions. It exhibited weak emission when molecularly dissolved but strong excimer emission when aggregated. Then we designed a probe with good water solubility based on pyrenylchalcone for polyanion detection in aqueous media. An orange emission could be observed upon simple addition of polyacrylic acid sodium salt. Better than the other "blue-to-green" pyrene probes, this "turn-on" AEEE probe was more likely visible to eyes. Moreover, unlike the double bond in tetra-phenylethene, the unsaturated double bond in chalcone could be easily opened by thiols. It could lead to another different "turn-on" change in fluorescence. Adding biothiol and adding polyanion were two different methods to reduce the intra-molecular rotations and cause different emissions, thus we built a 2-to-4 molecular decoder in aqueous media which could be observed by naked eyes.

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1. Introduction

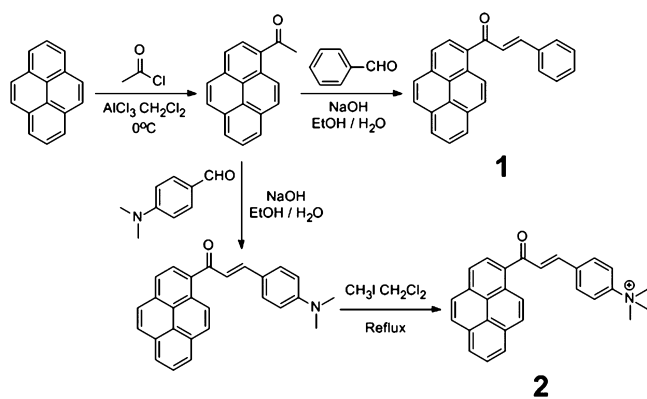
According to the past studies, common luminescent materials emit strongly when dissolved in good solvents but weakly when aggregated in poor solvents or in the solid state. This phenomenon is defined as aggregation-caused quenching (ACQ) and is harmful to practical applications such as the fabrication of organic light-emitting diodes (OLEDs) [1]. In 2001, a new phenomenon was discovered exactly opposite to this ACQ effect that was aggregation-induced emission (AIE) [2]. With the help of the restriction of intra-molecular rotations (RIR) process in these new materials, the notorious ACQ problem in π - π stacking is successfully resolved. Because of this exciting pioneering success, more and more groups have worked on design of new AIE luminophores [3]. In addition, pyrene can form excited dimeric structures known as excimers. The formation of excimers makes the emission band very broad and red-shifted. And recently, the excimer emission has been successfully applied to signal the presence of metal ions, nucleic acids, proteins and so on [4]. In 2011, Tang's group found aggregation-enhanced excimer emission (AEEE) in pyrene-substituted ethenes based on the traditional AIE structure: tetra-phenylethene (TPE) [5]. On the one hand, unlike AIE, its strong emission in aggregation

state was from the excimer. On the other hand, different from the emission of common pyrene monomer, the energy of its emission in monomer state was greatly consumed by the intra-molecular rotations. And the high emission of these new materials in the solid state was used in the development of non-doped organic light-emitting diodes [5a]. After that, this new concept hardly appears in the following literatures and seems to be forgotten.

The chalcone structure has been applied in many fields such as the synthesis of heterocycles and drugs in organic and medicinal chemistry [6]. Our group used it as the reaction substrate to develop a series of polysubstituted benzenes via one-pot green synthesis [7]. Nevertheless, which is usually ignored by researchers, there are rotary joints in such a simple chalcone structure that could meet the condition of AIE. What's more, unlike the double bond in the TPE, unsaturated double bond in chalcone could be opened easily by thiols. Thus, AEEE-active pyrenylchalcone dye **1** was synthesized. Then, soluble in the aqueous media, **2** was designed and successfully applied in sensing of polyanions.

In digital electronics, decoder is a kind of logic circuits which can convert binary information from n input lines to a maximum of 2^n unique output lines. Generally, it is used to undo the encoding so that the original information can be retrieved. The common decoders include 2-to-4 decoder, 3-to-8 decoder and 4-to-16 decoder. Nowadays, the functions of many logic circuits have been realized at the molecular scale, such as encoder, comparator, demultiplexer and keypad lock [8]. Though a lot of molecular logic

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Scheme 1. Synthesis of **1** and **2**.

gates have been developed, the molecular decoders are very few [9].

In this paper, we found that the AEEE-active **2** could be made into the molecular decoder. Environmentally-friendly inputs (Cys and Polyacrylic acid sodium salt (PAA_{Na})) were used to obtain four outputs. Better than other 2-to-4 molecular decoders, our system could work in aqueous media and be visible to naked eyes.

2. Materials and methods

2.1. Materials

Pyrene and polyacrylic acid sodium (PAA_{Na}) (Average Mw ~ 5100 by GPC) were purchased from Sigma–Aldrich. Homocysteine (Hcy) and glutathione (GSH) were purchased from TCI. Quinine sulphate was purchased from Alfa Aesar. Acetyl chloride, MeI, benzaldehyde, 4-(dimethylamino)benzaldehyde, cysteine (Cys) and other amino acids (Ala, Arg, Gly, His, Lys, Phe, Ser, Tyr) were purchased from Aladdin (China). All other common reagents and solvent were purchased from commercial sources and used without further purification.

2.2. Instruments

UV–vis absorption spectra were obtained with PerkinElmer-Lambda 950. Emission spectra were obtained using Varian-FLR006 and Edinburgh Instrument FLS920 with an excitation wavelength of 355 nm and 390 nm. ¹H and ¹³C NMR spectra were obtained with Varian Mercury (300 MHz for ¹H and 75 MHz for ¹³C) and Bruker Avance (400 MHz for ¹H and 101 MHz for ¹³C). Mass spectra and HPLC–HRMS were obtained with Bruker MicroTOF QII.

2.3. Synthesis

1-(Pyren-1-yl)ethanone was prepared by following the reported procedure [10]. **1** and **2** were prepared according to the synthetic routes shown in Scheme 1. Compared with TiCl₄/Zn and *n*BuLi at –78 °C used in the synthesis of TPE derivatives, pyrenylchalcone was very easy and cheap to be synthesized under mild conditions. **1** was soluble in CH₃CN, THF, DMF, DCM and EA, slightly soluble in ethanol and completely insoluble in water. And **2** could be dissolved in water and its solubility in water was approximately 0.2 mM at room temperature. UV–vis spectra of **1** in acetonitrile and **2** in water could be found in Supporting information, Fig. S1.

2.3.1. Synthesis of compound **1**

To a mixture of benzaldehyde (100 μL, 1 mmol) and 1-(pyren-1-yl)ethanone (0.24 g, 1 mmol) in EtOH (10 mL) was added dropwise aqueous solution of NaOH (2 mL 40%) in an ice-water bath. After

stirring 3 h at RT, the product was poured into 100 mL water and yellow precipitate was filtered off. The crude mixture was purified by recrystallization in methanol. **1**: Yellow powder; Yield 0.30 g (91%) Melting point: 90 °C. ¹H NMR (300 MHz, cdCl₃) δ 8.63 (d, *J* = 9.3 Hz, ¹H), 8.31–8.03 (m, ⁹H), 7.70–7.38 (dd + m + m, ⁶H). ¹³C NMR (75 MHz, cdCl₃) δ 195.96, 146.04, 134.82, 133.88, 133.35, 131.22, 130.79, 129.49, 129.28, 129.20, 129.10, 128.63, 127.57, 127.26, 126.47, 126.33, 126.21, 126.05, 124.99, 124.83, 124.16. HRMS(M+H⁺): Calcd. for C₂₅H₁₇O 333.1274; found: 333.1269.

2.3.2. Synthesis of 3-(4-(dimethylamino)phenyl)-1-(pyren-1-yl)prop-2-en-1-one

1-(pyren-1-yl)ethanone (0.24 g, 1 mmol) and 4-(dimethylamino)benzaldehyde (0.15 g, 1 mmol) were used as reaction materials, the produce was carried out in accordance with the method of synthesis of **1**: orange powder. 0.28 g (Yield 75%) Melting point: 167 °C. ¹H NMR (300 MHz, dmsO) δ 8.51 (d, *J* = 9.2 Hz, ¹H), 8.34 (m, ⁷H), 8.14 (t, *J* = 7.9 Hz, ¹H), 7.61 (d, *J* = 8.4 Hz, ²H), 7.45 (dd, *J* = 40.6, 15.8 Hz, ²H), 6.71 (d, *J* = 8.5 Hz, ²H), 2.99 (s, ⁶H). ¹³C NMR (75 MHz, dmsO) δ 194.58, 152.07, 146.82, 134.69, 132.19, 130.75, 130.12, 128.72, 128.59, 127.25, 126.64, 126.08, 125.78, 124.43, 121.57, 111.71, 39.62. HRMS(M+H⁺): Calcd. for C₂₇H₂₂NO 376.1696; found: 376.1691.

2.3.3. Synthesis of sensor **2**

0.19 g of 3-(4-(dimethylamino)phenyl)-1-(pyren-1-yl)prop-2-en-1-one (0.5 mmol) and 1 mL of methyl iodide (16 mmol) were added to 10 mL DCM. And the mixture was refluxed overnight under N₂ atmosphere. After the mixture was cooled to room temperature, the precipitate was filtered and washed with ether and dried under vacuum to give the product **2** (0.18 g, 70%). **2**: yellow powder; melting point: 175 °C. ¹H NMR (400 MHz, DMSO) δ 8.70 (d, *J* = 9.3 Hz, ¹H), 8.56 (d, *J* = 7.8 Hz, ¹H), 8.52–8.30 (m, ⁶H), 8.27–8.04 (t + dd, ⁵H), 7.88 (dd, *J* = 83.0, 15.9 Hz, ²H), 3.66 (s, ⁹H). ¹³C NMR (101 MHz, DMSO) δ 196.45, 150.36, 144.63, 138.38, 135.27, 134.91, 132.83, 132.31, 131.60, 131.45, 130.94, 129.41, 129.21, 129.02, 128.71, 128.33, 126.61, 126.44, 125.67, 123.32, 58.53. HRMS (M⁺): Calcd. for C₂₈H₂₄NO 390.1852; found: 390.1849.

3. Results and discussion

3.1. Aggregation-enhanced excimer emission (AEEE)

Pyrenylchalcone is a poor fluorescent dye in its good solvent. Due to free rotations in chalcone structure, it displayed weak peak (black line in Fig. 1a) in acetonitrile solution (50 μM). As **1** was not soluble in water, with the increase of the proportion of water, the peak gradually went up and in line with AEEE. Similar to pyrene-substituted ethenes, RIR process made pyrenylchalcone AEEE-active and highly emissive in aggregation state. In the end, over 80% water, small decline of the peak was observed. The possible reason was that the solutions became turbid and some molecules were precipitated from CH₃CN–H₂O. The AEEE phenomenon was also observed in some other organic solvents (Fig. 1b and c, Supporting information, Fig. S2). Moreover, the fluorescence of its solid power could be observed under UV lamp/365 nm (Fig. 1d).

In contrast, the monomer fluorescence of pyrene-substituted ethene in the solution was not as weak as pyrenylchalcone. It was most likely that the intra-molecule rotations in chalcone consumed more energy than the pyrene-substituted ethene. As a result, the fluorescence quantum yield [11] of the **1** in aggregated state could increase more than six times compared to its monomer (Fig. 1c).

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