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A red fluorogen: AIEE characteristic, photoluminescence mechanism and its application as chemosensor for ClO⁻

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ABSTRACT

Red material is widely used in many fields because it has a lot of high performances such as strong penetrability, little trauma to cell and tissue, easy to prepare, and low background interference. However, a lot of organic materials were troubled with the aggregation caused emission quenching (ACQ) effect, which really limits their practical applications. In contrast, aggregation induced emission (AIE) and aggregation-induced enhanced emission (AIE) effects provide an efficient method to break the obstacle of ACQ effect. Herein, a red light molecule was developed by integrating cyano and alkyl sulfide moieties. Its photoluminescence mechanism was further revealed by fluorescence spectrum, density functional theory (DFT) and X-ray single crystal diffraction, respectively. It is found that this compound has good planar construction and has no rotatory unit, it showed typical AIEE performance because of intramolecular D- π -A structure and the formation of J-aggregation. This molecular design principle may be able to offer an effective strategy to exploit red AIE/AIEE organic materials. Meanwhile, this fluorogen showed excellent response capability to CIO⁻ including high selectivity and sensitivity, and cell imaging performance.

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1. Introduction

Luminescent materials based on organic molecules have been focused widely and continuously in organic light-emitting devices, optical sensing, liquid crystal display, and stimuli-responsive due to rich colors, simple synthesis, adjustable structure, good light stability, and no heavy metal pollution [1–10]. However, many organic luminescent molecules exhibit intense fluorescence in benign solvent solution while show significant fluorescence quenching in the aggregation state or in the solid state for the formation of excimer and exciplex by the strong intermolecular π - π stacking interaction [11,12]. This is known as aggregation caused emission quenching (ACQ) effect, which really limits their practical applications. In contrast, aggregation induced emission (AIE) and aggregation-induced enhanced emission (AIEE) effects provide an efficient method to break the obstacle of ACQ effect [13]. AIE and AIEE luminescent materials have no fluorescence or weak emission in solution, but fluoresce strongly.

At present, more and more AIE and AIEE organic molecules have been prepared [14,15]. Nevertheless, the vast majority of them are blue and green light materials [16–25], the number of red light materials is still very limited including quinoline nitrile derives, diphenyl fumaronitrile substituted by carbazole derives, TPE-BODIPY derives and so on [26–30]. These red AIE molecules share a common character of complex molecular structure consisting of phenyl rotor, electrondonating group (*N*,*N*-dialkyl group) and electron-withdrawing group (cyano group). In solution, the energy of the excited state molecule is exhausted because of the free rotation of phenyl rotors via the singlebond axes. In aggregates, such intramolecular rotation is restricted (RIR) due to the steric hindrance [31]. In addition, the Cyano group provides an appropriate twisted molecular conformation that prevents the intermolecular π - π stacking interaction [32–35]. The non-radiative decay thus turns off, while fluorescence turns on.

Herein, we constructed a cleverish fluorogens with AIEE characteristic and red emission by integrating multiple Cyano groups (acceptor, A) and methylthio group (donor, D). This molecule exhibited pronounced fluorescence in solution due to intramolecular D- π -A structure and showed fluorescence enhancement in solid state because of the formation of J-aggregate. Additionally, it can response to ClO⁻ with high specificity and sensitivity, and can be used as fluorescence chemosensor for ClO⁻ detection (Scheme 1).

2. Experimental

2.1. Apparatus and materials

¹H and ¹³C NMR spectra were measured on nuclear magnetic resonance spectrometer (AVANCE III HD 600 MHz, Bruker, Switzerland) using TMS as the internal standard. Mass spectrum was recorded with

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Scheme 1. Synthetic route of compound 1.

a Bruker solan X70 FT-MS. Fluorescence spectra were recorded by Cary Eclipse fluorescence spectrophotometer (Varian, America). Fluorescence quantum efficiency was measured with a Fluorolog 3-TSCPC and integrating sphere accessory (Horiba Jobin Yvon Inc. France). Ultraviolet visible absorption spectrum was tested using UV-vis spectrometer (Lambda 950, PerkinElmer, USA). Cell images were got under laser scanning confocal microscopy (LSM700, Zeiss, Germany). Diffraction data was collected on Agilent G8910A CCD diffractometer. Fluorescence microscopy images were taken under fluorescence microscope (Olympus CX33). FTIR spectra were acquired by a Bruker TENSOR27 infrared spectrophotometer with KBr pellet in the range of 4000 cm⁻¹ to 400 cm⁻¹. All of the reagents and organic solvents are analytically pure. They were purchased from Sahn chemical technology (Shanghai) corporation and were used directly. Deionized water was used throughout the test process.

2.2. Syntheses

2-(3-Cyano-4,5,5-trimethylfuran-2(5H)-ylidene)malononitrile (2) was synthesized by the reaction between 3-hydroxy-3methylbutan-2-one (3) and malononitrile according to the published literature [36].

Compound 2 (1.0 g, 5.0 mmol), 4-methylmercaptobenzaldehyde (0.76 g, 5 mmol) and EtONH4 (0.77 g, 10 mmol) were dissolved in the mixture solution (THF/EtOH = 4:1, 60 mL). The reaction mixture was stirred for 24 h at room temperature. The deep red precipitate was obtained after filtration and was further purified by silica gel column chromatography with CH₂Cl₂ as mobile phase and recrystallization from the mixture solution of CH₂Cl₂ and ethanol. Compound 1 (yield: 78.4%). ¹H NMR (600 MHz, DMSO-*d*₆), δ (ppm): 7.93, 7.89 (d, *J* = 24 Hz, 1H); 7.86, 7.84 (d, *J* = 12 Hz, 2H); 7.38, 7.36 (d, *J* = 12 Hz, 2H); 7.20, 7.16 (d, *J* = 24 Hz, 1H); 2.56 (s, 3H); 1.79 (s, 6H). ¹³C NMR (151 MHz, DMSO-*d*₆), δ (ppm): 177.59, 175.76, 147.55, 145.53, 131.10, 130.36, 126.01, 114.55, 113.21, 112.38, 111.45, 99.75, 98.92, 54.52, 25.66, 14.47. EI-MS: calculated for C₁₉H₁₅N₃OS 333.09, found 334.1 [M + H]⁺.

2.3. X-ray crystallography

X-ray single crystal diffraction data was collected on Agilent G8910A CCD diffractometer with graphite-monochromated Mo-Ka radiation ($\lambda = 0.71073 \text{ Å}$). The structure was solved by the SAINT program. The crystallographic data has been uploaded to the Cambridge Crystallographic Data Centre (CCDC Number: 1915083), and the crystallographic data sheet has been shown in Table S1.

2.4. Cell imaging

A549 cells were purchased from Shanghai Chaoyan Biotechnology Co., Ltd. and were incubated for 24 h in Dulbecco's modified eagle medium at 37 °C. Then they were cultivated for approximately 20 min with compound 1 (20 μ M) and were imaged with a laser scanning confocal microscopy. Next, the cells were consequently cultivated with ClO⁻ (30 μ M) for another 10 min, and imaged using a laser scanning confocal microscopy again.

3. Results and discussion

3.1. Photophysical and AIEE characteristics

Ultraviolet absorption spectra (Fig. S4) and fluorescence spectra (Fig. S5) of compound 1 in different organic solution including dimethylsulfoxide (DMSO), *N*,*N*-dimethylformamide (DMF), acetoni-trile (CH₃CN), ethyl acetate (EA), absolute ethyl alcohol (EtOH) and dichloromethane (DCM). The absorption peaks are located at 449 nm, 448 nm, 444 nm, 450 nm, 442 nm and 450 nm, respectively. The maximum emission peaks are 610 nm, 604 nm, 596 nm, 581 nm, 593 nm and 586 nm, respectively.

AIEE characteristic of compound 1 was investigated in DMSO/H₂O mixture because it is soluble in organic solvents but insoluble in water, and compound 1 molecules must aggregate in DMSO/H₂O mixtures with a high water fraction (f_w , v:v). As shown in Fig. 1, compound 1 displayed purple fluorescence in pure DMSO solution, and its fluorescence quantum yield was 4.69%. Along with the increasing of f_w , the fluorescence enhanced gradually. When f_w reached 90%, the fluorescence quantum yield of compound 1 increased to 16.44%, which improved by 3.5-fold. In addition, the emission wavelength red shifted to 640 nm from 609 nm. The colour of compound 1 solution changed to red from pink (Fig. 1 inset). However, the fluorescence intensity decreased slightly when f_w was 95%, which can be caused by the precipitation of molecular aggregation. With the increase of water fraction, the fluorescence intensity enhancement (black square line) and the wavelength redshift (red dot line) of compound were revealed visually as shown in Fig. 2. These results proved that compound 1 has remarkable AIEE performance.

The aggregation process of compound 1 can be proved by fluorescence microscope (Fig. 3). When f_w were respectively 0% and 20%, no aggregation was observed under the fluorescence microscope. A small number of aggregates were not observed until the f_w reached 40%.



Fig. 1. Fluorescence spectra of compound 1 (10 μ M) in DMSO containing different rate of water ($\lambda_{ex} = 455$ nm).

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Fig. 2. Plot of maximum fluorescence intensity (black squares) and wavelength (red dots) of compound 1 (10 μ M) versus water fraction ($\lambda_{ex} = 455$ nm).

Dramatically, there were a lot of aggregates in solution when f_w was in the range of 50% to 80%. When f_w was 90%, lots of tiny particles were appeared. The fact that the change of aggregate state with increasing concentration of water also illustrated the existence of the aggregation process of compound 1 in DMSO/water mixtures. These results are consistent with the variation trend of fluorescence intensity.

3.2. Photoluminescence mechanism

The AIEE behavior of compound 1 encouraged us to explore the mechanism of fluorescence emission. The theoretical calculation was carried out by means of the Gaussian 09 program with the B3LYP/6-31G basis set. Optimized structure, energy levels and electron density distributions of compound 1 are displayed in Fig. 4. The optimized structure indicates that all the atoms except C7, C8, H25–27 of C7, H28–30 of C8, H38, H39 are in the same plane, which is very helpful to extend the π -conjugation system, easily resulting in a red-shifted fluorescence. Moreover, their HOMO and LUMO are distributed throughout most of molecule, which induce small energy gap between HOMO and LUMO. The energy levels of HOMO and LUMO and their energy gap are -6.14 eV, -3.39 eV and 2.95 eV, respectively. The small energy gap is

beneficial to enable the electron transition and is easy to result in a long wavelength fluorescence emission.

For AIEE molecule, the molecular packing mode has an important effect on the luminescence performance. Therefore, X-ray diffraction of compound 1 single crystal was also performed. The molecular conformation of compound 1 in the crystalline state is in accordance with its optimized structure, showing good planarity. Tactfully, two methyl groups and two hydrogen atoms out of the molecular plane can effectively hamper the intermolecular π - π stacking interaction (Fig. 5a), where the distance between the two molecular planes is 4.661 Å and the angle between the methyl group out of the plane and the molecular plane is 123.25 degrees. Furthermore, compound 1 could form rodshaped crystal (length L = 3 cm) from the mixture solution of CH_2Cl_2 and EtOH and show strong red fluorescence (Fig. 5a inset). In addition, molecules of compound 1 formed effective J-aggregates (Fig. 5b), thus prevent the fluorescence quenching in aggregate state. This leads to a conclusion that plane molecule without rotational units and rigid conjugate structure can also get AIE/AIEE and red fluorescence properties by introducing the right group.

3.3. Fluorescence response to ClO-

As one of reactive oxygen species, ClO⁻ has important effect on human health [37-41]. A moderate amount of ClO⁻ benefits people's health in aspects of bacteria disinfection in vivo and body immunization. However, abnormal concentration of ClO- will produce negative effects such as oxidative stress response and tissue lesion. Hence, the development of convenient detection technology for ClO⁻ is of great significance in the diagnosis and prevention of related diseases. It was found that compound 1 showed double optical response through ultraviolet absorption signal and fluorescence signal simultaneously, which can detect ClO⁻ with colorimetric and fluorescent changes with good selectivity and sensitivity for ClO⁻ over other analytes. The absorption spectra of compound 1 with ClO- were measured in aqueous solution containing 10% DMSO (pH = 7.4) (Fig. S6). Compound 1 has a strong absorption band around 459 nm and a weak absorbance band around 337 nm. With the addition of a series of concentration of ClO⁻, the peak at 575 nm reduced gradually, while the peak at 337 nm increased sharply. Additionally, with increasing concentrations of ClO⁻, the colour of probe 1 solution changed to colorless from yellow. The results



Fig. 3. Fluorescence microscopy images of compound 1 (10 µM) in DMSO containing different rate of water (scale bar: 50 µm).

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indicate the excellent colorimetric recognition ability of compound 1 for ClO⁻.

Similarly, the variation tendency of fluorescence with the increase of ClO⁻ concentration was also analyzed as shown in Fig. 6a. The fluorescence of compound 1 showed a reduced trend along with the gradual increase of ClO⁻ from 0 to 80 µM. In addition, It can be easily found that there is a good linear relation between the maximum values (640 nm) of fluorescence emission of compound 1 and the concentrations of ClO⁻ from 0 to 40.0 μ M: y = 895.1–18.8 x (R² = 0.9959) as shown in Fig. 6b. The limit of detection (LOD) of compound 1 can be calculated to be about 15.9 nM where the signal-to-noise ratio is 3 [42]. Moreover the fluorescence response of compound 1 is not disturbed by other analytes. As shown in Fig. 6c, the fluorescence intensity of compound 1 weaken only upon addition of ClO-, while didn't change obviously in the presence of other analytes (black bars). When ClO⁻ was added to the compound 1 solution in the presence of other competitive analytes, the fluorescence intensity displayed forceful quenching without significant interference (red bars). In addition, the response time of compound 1 to ClO⁻ was further examined as displayed in Fig. 6d.

The emission peak at 640 nm reduced quickly and was nearly stable value in 1 min after addition of 80 μ M ClO⁻. From these results it can be certainly inferred that compound 1 has high sensitivity and selectivity for quantitative detection of ClO⁻ with quick response time.

The fluorescence response mechanism was also explored by mass spectrum. After reacted with ClO⁻, the molecular peak at 334.10 in mass spectrum disappeared and a new peak at 350 grown up (Fig. S7). This can be attributed to the possible that alkyl sulfide of compound 1 was oxidized to carbonyl sulfide as shown in Fig. 7. Furthermore, the FTIR spectra also confirmed this shift of carbonyl sulfide. The peaks at 2997 cm⁻¹ and 2926 cm⁻¹ in the curve of compound 1 (Fig. S8) are the *st*(C—H) vibration of S—CH₃, and the peaks at 1299 cm⁻¹ and 1277 cm⁻¹ are the ν (C—H) vibration of S—CH₃. However, the four peaks disappeared and a new peak at 1048 cm⁻¹ appeared in the curve of compound 1 with ClO⁻ (Fig. S9). The peak at 1048 cm⁻¹ is the *st*(S=O) vibration, showing the transition form alkyl sulfide group to carbonyl sulfide group. Methylthio moiety is a strong electron withdrawing group, which can build D– π -A structure of compound 1 through intramolecular charge transfer (ICT) principle. When



Fig. 5. The molecular typical packing modes in the single-crystal structure of compound 1 along a direction (a) and b direction (b), respectively. Inset: Crystal photograph of compound 1 under UV light lamp (365 nm).

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Fig. 6. (a) Fluorescence changes of compound 1 (10 μ M) in the presence of a series of dopamine concentration of NaOCl in a water containing 10% DMSO (v:v). (b) The linear relation between fluorescence intensities of compound 1 and the concentrations of ClO⁻ in the range of 0–40 μ M. (c) Fluorescence intensity of compound 1 (10 μ M) in the presence of various analytes (80 μ M) (1. probe 1 only, 2. ClO⁻, 3. SO²⁻₄, 4. NO³⁻₃, 5. H₂PO₄⁻, 6. F⁻, 7. ClO₄⁻, 8. NO₂⁻, 9. O²⁻, 10. ¹O₂, 11. ·OH, 12. H₂O₂, 13. HSO₃⁻, 14. HCO₃⁻, 15. HS⁻). (d) The changes of fluorescence intensity of compound 1 (10 μ M) over time with ClO⁻ (80 μ M).

alkyl sulfide was oxidized to carbonyl sulfide by ClO⁻, the electron donating property of alkyl sulfide was replaced by the electronwithdrawing property of alkyl sulfide, breaking ICT process and D- π -A structure. As a result, the red fluorescence of compound 1 greatly decreased.

The biological application capacity was further investigated in living A549 cells. As shown in Fig. 8, A549 cells incubated with compound 1 were involved in obvious red fluorescence. However, after incubated successively with compound 1 and ClO⁻, the red fluorescence of A549 cells was almost completely quenched. The results indicated that compound 1 can penetrate cells very easily and display conspicuous changes

in the fluorescence signal, which is very applicable for the image of ClO⁻ in living cells.

4. Conclusions

In conclusion, a cleverish red fluorogen was developed by introducing D- π -A molecular structure. Though this compound has good planar construction and has no rotatory unites, it showed typical AIEE performance by regulating molecular stacking type and forming J-aggregation. This molecular design principle may be able to offer an effective strategy to exploit red AIE/AIEE



Fig. 7. Reaction mechanism of compound 1 to ClO-.

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Fig. 8. Laser confocal images. Bright-field image (a), fluorescence image (b) and merged image (c) of A549 cells incubated with compound 1. (d) Fluorescence image of A549 cells treated with compound 1 and then loaded with ClO⁻.

organic materials. Meanwhile, this fluorogen showed excellent response performances to ClO⁻ including high selectivity and sensitivity, and cell imaging performance, which has potential application for the detection of ClO⁻ in vitro and in vivo.

CRediT author statement

Liqiang Yan: Conceptualization, Methodology, Software, Formal analysis, Writing-original draft, Writing-review & editing.

Ya Xie: Validation, Visualization, Investigation.

Jianping Li: Funding acquisition, Project administration. Wenyuan Zhu: Resources.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi. org/10.1016/j.saa.2019.117794.

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