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A pillar[5]arene-based fluorescent sensor for sensitive detection of L-Met through a dual-site collaborative mechanism

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Abstract

L-Methionine (L-Met) is one of the essential amino acids in human health, efficiently detect L-Met is a significant issue. Herein, a concept "dual-site collaborative recognition" had been successfully introduced into the design and achieved high selective and sensitive recognition of L-Met. In order to realize the "dual-site collaborative recognition", we rationally designed and synthesized an ester functionalized pillar[5]arene-based fluorescent sensor (**SP5**). And it shows blue Aggregation-induced emission (AIE) fluorescence. In the **SP5**, the pillar[5]arene group act as C-H···π interactions site, and ester group serve as multi hydrogen bonding acceptor. Interestingly, the **SP5** exhibited high selectivity and sensitivity (2.84×10^{-8} M) towards L-Met based on the collaboration of eletron-rich cavernous pillar[5]arene group and ester group through C-H···π and H-bond interactions, respectively. This "dual-site collaborative recognition" mechanism has been investigated by ^{1}H NMR, ESI-MS and theoretical calculation including frontier orbital (HOMO and LUMO), electrostatic potential (ESP) and the noncovalent

interaction (NCI). These theoretical calculations not only support the proposed host-guest recognition mechanism, but also provided visualized information on the "dual-site collaborative recognition" mode. Furthermore, the concept "dual-site collaborative recognition" is an effective strategy for easily detecting biological molecules.

Keywords: Fluorescent sensor; Dual-site collaborative recognition; AIEgen; Pillar[n]arenes; DFT calculation.

1. Introduction

As we all know, amino acids play significant roles in different biological areas and participate in various life activities, such as sustaining normal physiological processes, affecting Organs and tissues function and so on [1-4]. L-Methionine (L-Met) is one of the essential amino acids of human body. It can lower blood pressure, protect myocardium, resist cirrhosis and fatty liver, anti-depression and remove poison. Simultaneously, methionine is the most important methyl donor in DNA methylation [5, 6]. Based on the above, there are abundant research efforts devoted to create sensors for amino acids and their derivatives detection [7, 8]. Various methods for amino acid determination have been reported, such as high-performance liquid chromatography [9], electrochemistry, spectrophotometry [10-12] and mass spectrometry [13, 14]. However, these methods always suffer from high cost, low specificity, as well as complicated sample pretreatment. Therefore, it's still an important subject to develop novel method and sensor for conveniently and efficiently detecting L-Met.

Aggregation-induced emission (AIE), a very important concept presented by Tang and co-workers [15]. AIEgens are dim or no emission in dilute solution but much enhanced emission in aggregates or solid state [16]. The AIE phenomenon could be put down to the restriction of intramolecular motion (RIM), including rotation and vibration [17]. AIE probes (aggregation means local viscosity increase) are viscosity-sensitive probes, thus, if the analyte or environmental factor is not viscosity,

the application of AIE may have some limitations [18]. By far, a variety of AIEgen compounds had been designed and synthesized and widely applied in various important fields, such as organic light-emitting diode (OLED) [19], chemo and biosensor [20, 21], as well as fluorescent imaging techniques in the last twenty years [22-24]. Therefore, using the concept of AIE to design amino acids fluorescent sensor become a promising way.

Pillar[n]arene[25-27], a rising star of macrocyclic host, shows the merits including rigid electron-rich macrocyclic structure and various host-guest interactions [28]. The pillar[n]arenes have been applied in many fields, such as ions and molecules sensing [29-31], smart materials[32, 33], molecular machines [34, 35], drug controllable releasing systems [36, 37], adsorbents[38, 39], chemocatalysis and so on [40, 41]. Interestingly, recent research found that pillar[5]arene also possess AIE activity [42]. Therefore, although numerous applications in ions and molecules recognize have been developed [43, 44], the pillar[n]arene still supplied a new way for developing novel AIE-based fluorescent sensors.

In view of these and as a part of our research interests in supramolecular host-guest chemistry [45], herein, we design and synthesized an ester functionalized pillar[5]arene-based fluorescent sensor (**SP5**) through rationally introducing the concept “dual-site collaborative recognition” [46, 47]. Our strategies are as follows: firstly, the pillar[5]arene group can offer eletron-rich cavity and C-H···π interactions site to accommodate guest molecules. Secondly, the pillar[5]arene also could act as AIE signal group [42]. Moreover, the ester group could serve as multi hydrogen-bond acceptor. Benefited from these rational designs, the **SP5** shows effectively fluorescent detection for L-Met through the dual-site collaboration of pillar[5]arene group and ester group via C-H···π, H-bond interactions.

2. Experiment

2.1. Materials

All initial reagents and solvents were commercially available at analytical grade and were used without further purification. All amino acids were used as the L style and purchased from commercial suppliers without further purification. Fresh double distilled water was used throughout the experiment.

2.2. Instruments

Melting points were measured on an X-4 digital melting-point apparatus (uncorrected). ^{1}H NMR spectra were recorded on Varian Mercury-400 BB spectrometer (400 MHz) and Varian Inova 600 instruments (600 MHz). ^{1}H chemical shifts are reported in ppm downfield from tetramethylsilane. Mass spectra were performed on a Bruker Esquire 3000 plus mass spectrometer (Bruker-FranzenAnalytik GmbH Bremen, Germany) equipped with ESI interface and ion trap analyzer. The IR spectra were performed on a Digilab FTS-3000 Fourier transform-infrared spectrophotometer. Fluorescence spectra were recorded on a Shimadzu RF-5301PC spectrofluorophotometer. Ultraviolet-visible (UV-vis) spectra were recorded on a Shimadzu UV-2550 spectrometer. Study of scanning electron microscopy (SEM) was performed on a JSM-6701F FE-SEM microscope.

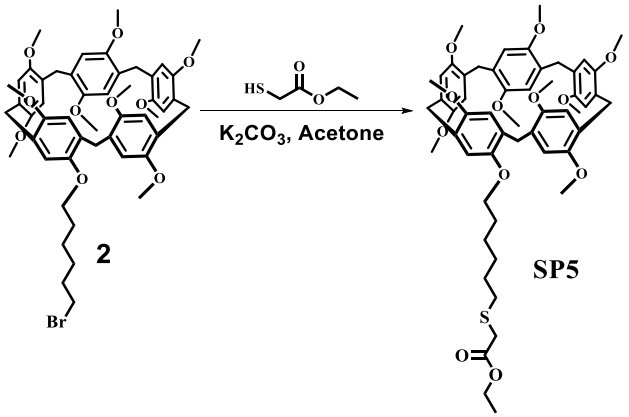
2.3. Synthesis of **SP5**

Synthesis of **SP5**: Pillar[5]arene 2 (0.90 g,1.0 mmol), K_2CO_3 (0.14 g, 1.0 mmol) and ethyl mercaptoacetate (0.60 mL,5.5 mmol) were added to acetonitrile (150 mL). The above solution was kept for another 24 h at 60℃. Then the precipitate was filtered off and the filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether: CH_2Cl_2 = 20:1) to produce **SP5** as a white solid (0.70 g, 75%). Mp: 168-170 °C. ^{1}H NMR (Fig. S3)(600 MHz, $CDCl_3$) δ (ppm): 6.79-6.75 (m, 10H), 4.17-4.14 (q, J = 6.0 Hz, 2H), 3.84-3.82 (t, J = 12 Hz, 2H), 3.78-3.75 (m, 10H), 3.67-3.64 (m, 27H), 3.20 (s, 2H), 2.60-2.59 (t, 2H), 1.79-1.76 (m, 2H), 1.58 (m, 2H), 1.49-1.43 (m, 4H), 1.26-1.23 (t, 3H). ^{13}C NMR (Fig. S4) (150 MHz, $CDCl_3$) δ (ppm): 170.51, 150.70, 150.65, 150.60, 149.96, 128.29, 128.22, 128.14, 114.79, 113.95, 113.90, 68.27, 61.25, 55.73, 53.66, 55.59, 33.75,

32.58, 29.69, 29.56, 29.34, 28.87, 25.85, 14.11. ESI-MS m/z: $(M+H)^+$ Calcd for $C_{54}H_{67}O_{12}S$ 939.43; Found 939.43 (Fig. S6).

3. Results and discussion

The synthetic route of fluorescent sensor **SP5** is shown in Scheme 1. The intermediates and product were characterized by ^1H NMR spectra, ^{13}C NMR spectra, FT-IR spectrum and ESI-MS (Fig. S1-S6). Then, a series of DMF/H_2O binary solutions with different water contents of **SP5** were used to conduct optical measurements at a fixed concentration (1.0×10^{-4} M). Because the DMF is a good solvent for **SP5**, while water is a poor solvent for it, upon the gradually increasing of water, the **SP5** solution exhibits fluorescence enhancing (Fig. 1). When water content increased to f_w=30%, the solution showed the strongest emission intensity at in 325 nm (λ_{ex} = 295 nm). This result indicated that the fluorescence enhancing of the **SP5** solution is AIE. Because with the increasing of water content, the **SP5** carried out an aggregation process and led to the restriction or absence of intramolecular motions in ring structures, which induce the AIE. So, the **SP5** could serve as a novel AIEgen. The fluorescence quantum yields of **SP5** in pure DMF and DMF/ H_2O binary solution (f_w=30%) were determined as 19.33% and 36.25%, respectively, according to the corresponding formula, using quinine sulfate as standard [48]. In addition, the AIE feature of **SP5** could be directly observed by the fluorescence color changes taken under 300 nm UV lamp (Fig. 1, inset). However, when the water volume fraction was higher than 30%, because water is a poor solvent for **SP5**, the **SP5** precipitated out from the solution, which induced the decreasing of the fluorescent emission.



Scheme 1. Synthesis of the pillar[5]arene **SP5**.

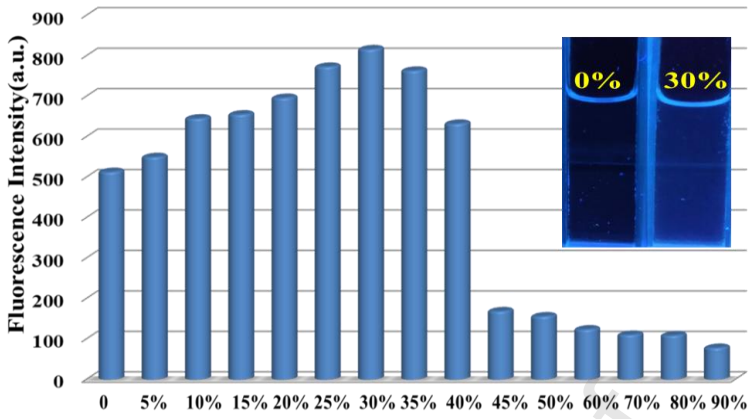


Fig. 1. Fluorescence spectra of **SP5** in DMF/H_2O binary solution with different water fraction, solution concentration: 1.0×10^{-4} M (λ_{ex}=295 nm). Inset: photographs of **SP5** in DMF/H_2O binary solution taken under 300 nm UV lamp.

Tyndall phenomenon and SEM had been carried out, interestingly, with increasing of the water content, especially when the water content reached 30%, a significant Tyndall phenomenon (Fig. 2a) was observed in DMF/H_2O binary solution, indicating that the aggregation of **SP5** induced enhancement of AIE fluorescence. Meanwhile, after aggregation of **SP5** in DMF/H_2O binary solution, the surface morphology showed microspheres (Fig. 2b), this could be attributed to the hydrophobic effect.

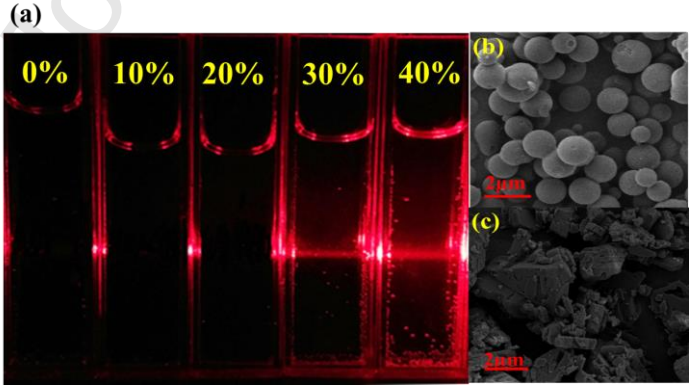


Fig. 2. (a) The Tyndall effect of **SP5** (1.0×10^{-4} M) with different volumetric fractions of water, (b) the SEM image of **SP5**, (c) the SEM image of **SP5+L-Met**.

In order to investigate the amino acids recognition property of the fluorescent sensor **SP5**, we carried out a series of host–guest recognition experiments. The responses of fluorescent sensor **SP5** to some natural amino acids (L-Phe, L-Gln, L-Ile, L-Thr, L-Glu, L-Ala, L-Ser, L-Met, L-Val, L-Tyr, L-Arg, L-Asp, L-Pro, L-His, L-Leu, L-Gly, L-Trp, L-Lys, L-Asn, and L-Cys) were primarily investigated by using fluorescence spectroscopy. In the fluorescence spectrum, the maximum emission of **SP5** appeared at 325 nm, with the addition of 2.0 equivalents of various amino acids, only L-Met induced the fluorescence intensity of **SP5** quenched obviously, but the addition of other amino acids exhibited almost no changes (Fig. 3). Therefore, the **SP5** showed specific fluorescence selectivity for L-Met. In addition, the selectivity of the **SP5** for L-Met over other competitive amino acids was investigated by competitive experiments (Fig. 4). The results also showed that the **SP5** could recognize L-Met with high selectivity.

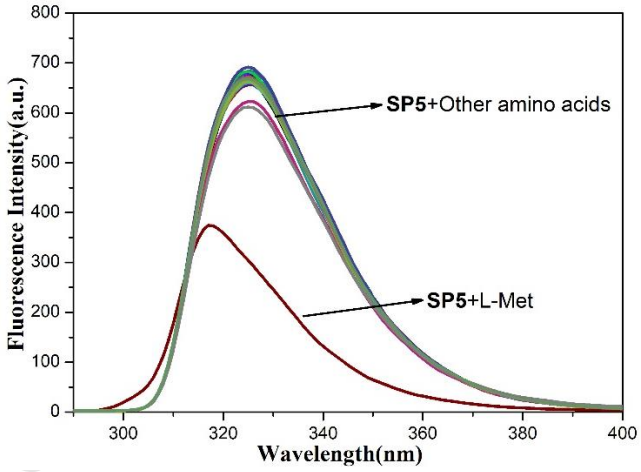


Fig. 3. Fluorescence spectra responses for **SP5** and each of the various amino acids (0.1 M, 2.0 equiv.) in the DMF/H_2O (7:3, v/v) binary solution (λ_{ex} = 295 nm).

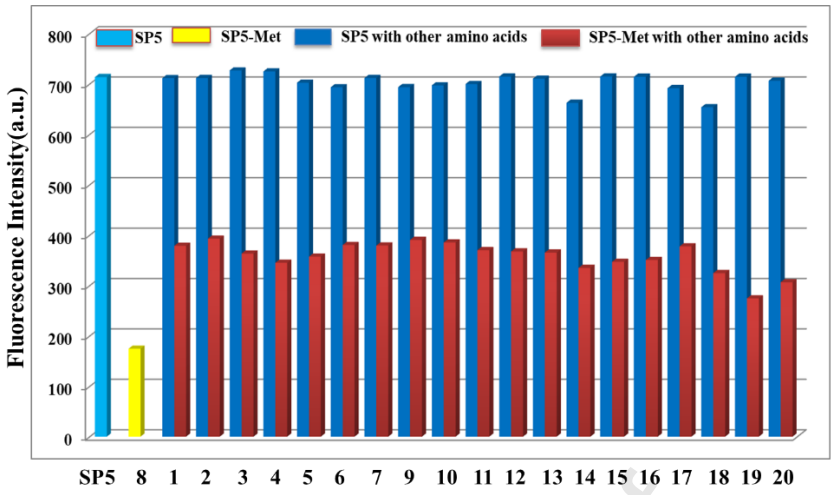


Fig. 4. Fluorescence response of **SP5** (1.0×10^{-4} M) in the presence of L-Met (2.0 equiv.) and the addition of other amino acids (0.1 M, 2.0 equiv.) in DMF/H_2O (7:3, v/v) binary solution (λ_{ex} = 295 nm): L-Phe, L-Gln, L-Ile, L-Thr, L-Glu, L-Ala, L-Ser, L-Val, L-Tyr, L-Arg, L-Asp, L-Pro, L-His, L-Leu, L-Gly, L-Trp, L-Lys, L-Asn and L-Cys.

To further investigate the efficiency of the fluorescent sensor **SP5** toward L-Met detection, we carried out fluorescence emission titration experiments. In the fluorescence spectrum, when adding L-Met (0-4.48 equiv.) to the solution of **SP5**, the fluorescence emission was quenched gradually (Fig. 5). The detection limit from the fluorescence spectrum changes calculated on the basis of 3δ/S is 2.84×10^{-8} M (Fig. S8), and the association constant Ka was also determined to be 1.24×10^{6} M^{-1} (Fig. S9), indicating the high sensitivity of the fluorescent sensor towards L-Met [49].

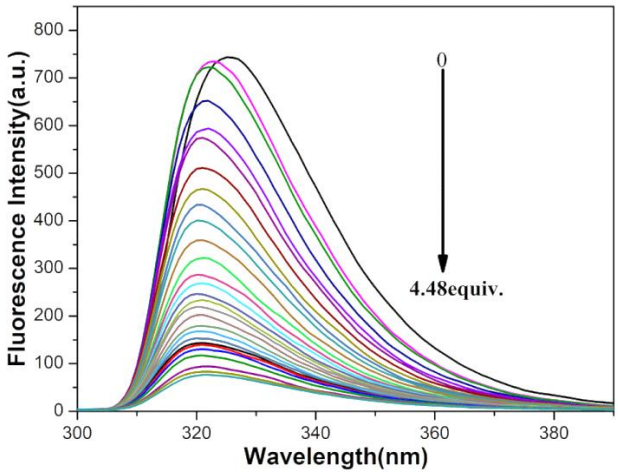


Fig. 5. Fluorescence spectra of **SP5** (1×10^{-4} M) in the presence of different concentration of L-Met in DMF/H_2O (7:3, v/v) solution (λ_{ex} = 295 nm).

Furthermore, in order to investigate the recognition mechanism of **SP5** and L-Met, the ^{1}H NMR titration, 2D NOESY, ESI-MS, the Job's plot and SEM experiments were carried out. In the partial ^{1}H NMR spectra (Fig. 6), after the addition of L-Met, the signal peaks H_1 of **SP5** showed downfield shift, and the signal peaks of Ha at L-Met showed upfield shift, suggesting that these protons were located in the shielding region of the cyclic pillar structure, like C-H···π interactions, and the signal peaks H_b of L-Met showed downfield shift, which indicated that the N-H···O hydrogen bond interaction between amino-group of L-Met and ester group of **SP5**. Besides, the signal peaks H_2 of **SP5** also showed downfield shift, which indicated that the C-H···O hydrogen bond interaction between ethyl group of **SP5** and carboxyl group of L-Met. Based on the above researches, we proposed this dual-site collaborative mechanism (Scheme 2). In addition, the 2D NOESY spectrum (Fig. S10) of an equimolar solution of **SP5** and L-Met shows cross peaks representing the correlations. These signs indicated that the assembly of **SP5** with L-Met took place in solution. Additionally, ESI-MS of an equimolar solution of **SP5** and L-Met exhibited a peak at m/z = 1086.48 (Fig. S11), corresponding to [**SP5**+L-Met-H]$^-$ which revealed a 1:1 stoichiometry for the complexation between **SP5** and L-Met. In the Job's plot, the slope turning point appears at the mole fraction of 0.5 ([L-Met]/[**SP5**] + [L-Met]) indicates that **SP5** and L-Met formed a 1:1 complex (Fig. S12). Meanwhile, the SEM image also shows surface morphology changed from microspheres to block structures after adding L-Met into the **SP5** solution (Fig. 2c).

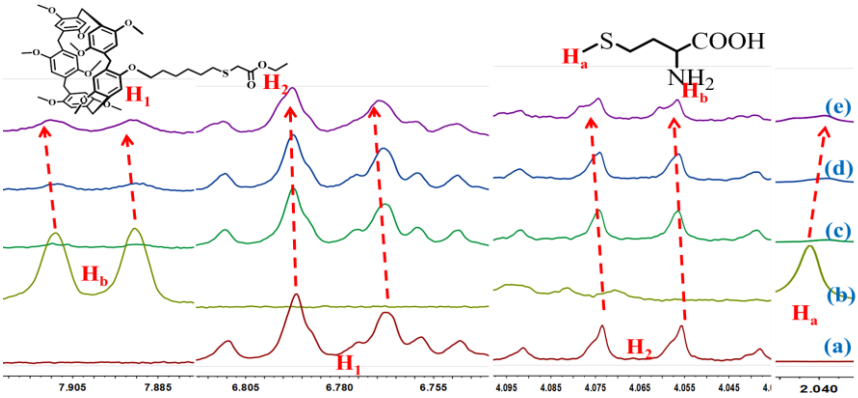
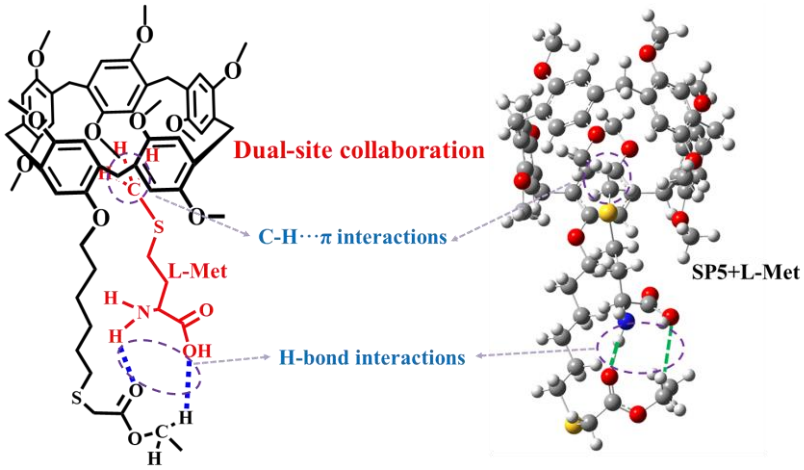


Fig. 6. Partial ^{1}H NMR spectra of **SP5** (400 MHz, DMSO-d_6) (a) **SP5**, (b) L-Met, and various equivalents of L-Met:(c) 0.2 equiv., (d) 0.5 equiv., (e)1.0 equiv.

Moreover, in order to better understand the interactions and mechanism between **SP5** and L-Met, the **SP5**, L-Met and **SP5**+**L-Met** optimized structure were obtained at B3LYP/6-311G* level of theory using the Gaussian 09 package suite [50], Multiwfn software (Fig. S13) [51]. The electron cloud on the benzene ring can interact with a C-H bond to form a C-H···π bond, which provides a favourable condition for holding L-Met in the cavity. Based on Fig. S13, it is reasonable to exist the C-H···π interactions, C-H···O and N-H···O hydrogen bond interactions [52, 53].

So as to elucidate the electronic structure properties of the host-guest interaction system, the frontier orbital (HOMO and LUMO) and electrostatic potential (ESP) are also performed. The highest occupied molecular orbitals (HOMO), lowest unoccupied molecular orbitals (LUMO), and electrostatic potential (ESP) maps of **SP5**, L-Met and host-guest complexes **SP5+L-Met** are shown in Fig. 7. About the **SP5**, the HOMO extends over oxygen atoms as well the adjacent C=C bonds of aromatic rings, whereas the LUMO extends over the ester group. The L-Met fragment only has a minor contribution to the frontier orbitals. This finding indicates that the structural stability of guest in host-guest complex is increased. And for the **SP5+L-Met** complex, HOMO and LUMO are asymmetric and complicated, which means the obvious multiple supramolecular interactions between **SP5** and L-Met [54].



Scheme 2. The proposed detecting mechanism of **SP5** for L-Met.

In the ESP map of **SP5**, the cavity of pillar[5]arene shows negative charge distribution, the sulfur methyl group of L-Met shows positive unit charge distribution therefore **SP5** possesses the ability of attracting the linear molecule L-Met to form C-H···π interactions. Meanwhile, the oxygen atom is negatively charged of the ester group from **SP5**, the nitrogen atom is positively charged of the amino group from L-Met, and the carbon atom is positively charged of ethyl group from **SP5**, the oxygen atom is negatively charged of the carboxyl group from L-Met, so the N-H···O and C-H···O multiple hydrogen bonds are easily formed due to the electrostatic attractions[55, 56].

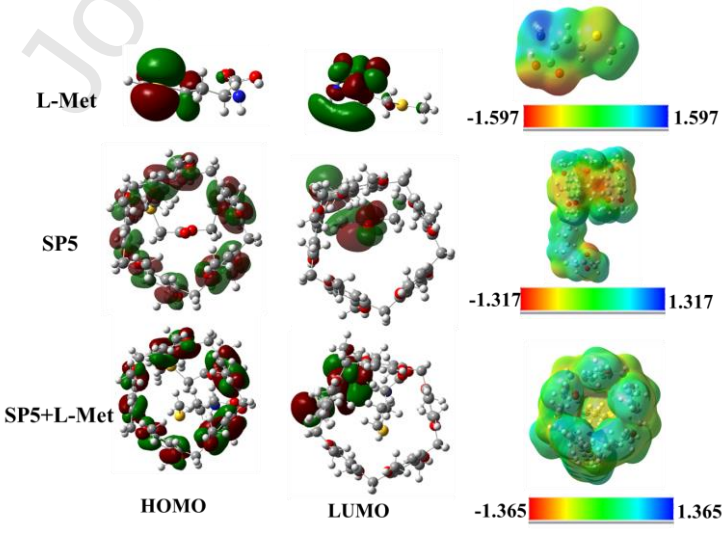


Fig. 7. The frontier orbitals (HOMO and LUMO) and electronic potential maps (ESP) of L-Met, **SP5** and **SP5+L-Met**.

For the purpose of reveal the supramolecular interactions intuitively, the noncovalent interaction (NCI) graph were obtained through the IGM (the so-called Independent Gradient Model) approach (Fig. 8). It further visualizes the interactions between **SP5** and L-Met, green represents the van der Waals force, which are C-H···π interactions, blue represents the attractions, so, the presence of N-H···O and C-H···O hydrogen bonding interactions are thus evident [51, 54].

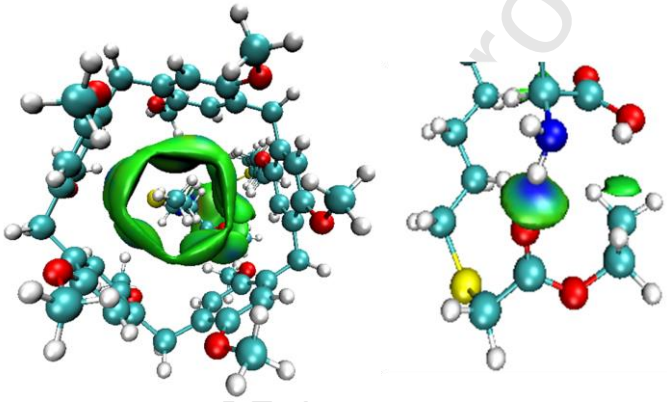


Fig. 8. the NCI graph of **SP5+L-Met**.

Based on the above researches, theoretical calculations vividly show the interactions between **SP5** and L-Met, and the accuracy of results that dual-site collaborative effects have also been proved. In other words, the synergy of eletron-rich cavity and ester group strengthen the **SP5** recognition of L-Met through multiple supramolecular interactions.

4. Conclusion

In summary, based on the "dual-site collaborative recognition" strategy, an ester functionalized pillar[5]arene fluorescent sensor (**SP5**) was designed and synthesized. It shows AIE fluorescence in DMF/H_2O (7:3, v/v) binary solution, it can detect L-Met with specific selectivity and high sensitivity (2.84×10^{-8} M). It is worth noting that other natural amino acids did not afford any obvious interfering response.

Simultaneously, the results showed the **SP5** could dual-site collaboratively recognize L-Met by multiple supramolecular interactions, and the theoretical calculations support the proposed host-guest recognition mechanism clearly, also showed the C-H···π, H-bond interactions between **SP5** and L-Met visibly. Therefore, this work provides a new idea and method for conveniently detecting amino acid. It may also offer a theoretical basis for enriching the host-guest chemistry and understanding the supramolecular interactions.

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Conflicts of interest

The authors declare no conflicts of interest.

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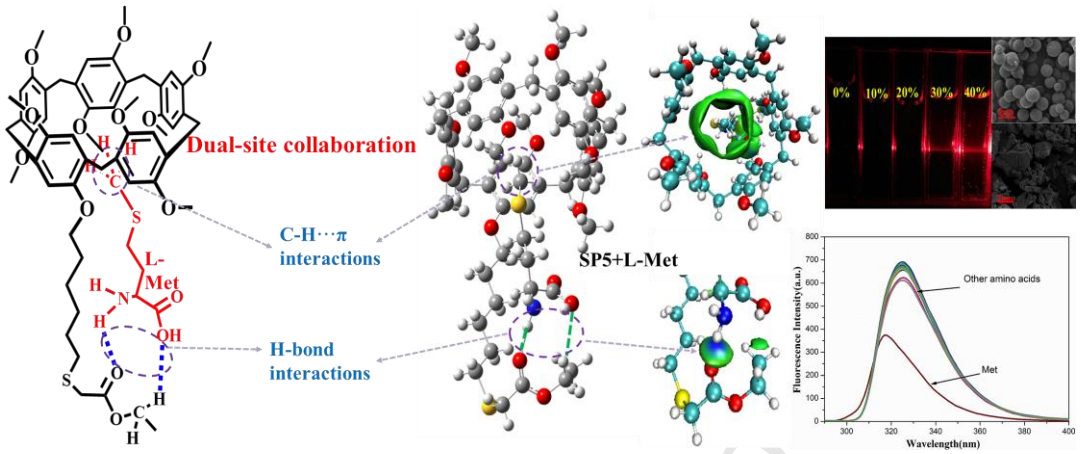
Declaration of interests

☒ 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.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Graphical Abstract



The ester functionalized pillar[5]arene-based fluorescent sensor **SP5** shows selective fluorescent sensing for L-Met through dual-site collaborative multiple supramolecular interactions.

Highlights

1. Pillar[5]arene-based fluorescent sensor (**SP5**) was designed and synthesized.
2. The **SP5** shows blue Aggregation-induced emission (AIE) fluorescence.
3. The **SP5** shows fluorescent sensing for L-Met by a dual-site collaboration way.
4. The LODs of **SP5** for detecting L-Met is reach up to 2.84×10^{-8} M.
5. Theoretical calculations support the proposed dual-site collaboration mechanism.