Comparative study of the dicyanovinyl-functionalized 1,1-dimethyl-2,3,4,5-tetraphenylsilole derivatives on their structures, properties, and applications in thiol detection

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Integrating electron-accepting dicyanovinyl (DCV) moieties with aggregation-induced emission (AIE)-active 1,1-dimethyl-2,3,4,5-tetraphenylsilole (DMTPS) skeleton on the meta-positions of the 2,5-phenyl groups via simple Knoevenagel condensation derived the novel polar silole derivative, i.e. DMTPS-m-DCV. Systematic and comparative studies on the structures, properties and application in the thiol detection of DMTPS-m-DCV and its para-isomer DMTPS-p-DCV shed light on their structure-property relationships. The multiple rotors and non-planar 3D configurations bestow aggregation-enhanced emission (AEE) or AIE feature on them and the A-D-A type electronic structures impart intramolecular charge transfer (ICT) effect to them. The reactive DCV units endow these two isomers with the capability of specifically recognizing thiol species. The subtle variation in the substitution position of DCV units leads to a number of differences in the crystal and electronic structures, thermal stability, fluorescence properties, solvatochromism, ICT effect, thiol-reactivity, and thus detection performances. Benefiting from their AIE/AEE plus ICT attributes, both DMTPS-p-DCV and DMTPS-m-DCV perform well as ratiometric probes for thiols with minimal background noise, remarkable blue shift in fluorescence maxima, large enhancement in fluorescence intensity as well as high contrast in the biocompatible aqueous solutions or on the solid matrices. Intriguingly, DMTPS-p-DCV could differentiate cysteine (Cys) and homocysteine (Hcy) from glutathione (GSH) relying on the distinctive differences in kinetics. The fluorescence turn-on ratiometric probe DMTPS-m-DCV holds a superb sensitivity to Cys with a detection limit lower than 0.5 μM. Fast and sensitive responses of TLC plates with DMTPS-m-DCV spots to Cys in water demonstrated the practicability of these simple and handy test strips.

1. Introduction

Organic conjugated molecules, by virtue of their special optical and electronic properties, have been active objects in the research of advanced materials, and the exploration of them has continued to be a topic of interest. Since these optoelectronic materials are generally utilized as thin films or in aggregated state for practical applications [1], it is thus of great significance to understand and manipulate their emission behavior and performance in the solid or...
aggregated state. In the solid state or aqueous media, the molecules of aromatic luminophores are located close to each other and are apt to form aggregates. The aggregation of conventional luminogens is commonly adverse, because it usually causes quenching in the emission as a result of the formation of detrimental species such as excimers or exciplex. Such a phenomenon is noted as “aggregation-caused quenching (ACQ)”[2]. Diamentically opposite to ACQ, aggregation-induced emission (AIE) provides a solution to the development of highly efficient luminescent materials in the solid state [3]. The luminogens featured with AIE property are named as AIEgens [4], which are weakly or non-luminescent as molecular species but become highly emissive when they are aggregated in solutions or in the solid state. The weak or non-luminescence of AIEgen in molecularly dispersed state has been rationalized as a result of active intramolecular motions which dissipate the excitation energy nonradiatively, whereas, the intense emission in the condensed phase is ascribed to the restriction of intramolecular motions (RIM) that promotes the radiative decay of the excited state [4].

Amongst all the developed AIEgens, siloles (silacyclopentadienes) with propeller-like conformations are the archetypal AIEgens[3,4]. Besides their AIE characteristics, siloles are viewed as a new kind of AIE-active polar silole which shows efficient luminescent materials in the solid state. The unique electronic structure of silole ring endows them with high electron affinity and good electron mobility. In the light of their AIE motif and peculiar electronic features, a vast variety of functional materials have been developed by adopting silole as the fluorescent core, which have found applications in fields including organic-light emitting diodes [5], circularly polarized luminescence materials [6], fluorometric bioprobes [7], and chemosensors [8]. However, the overwhelming majority of AIE-active siloles developed so far are nonpolar and without reactive functional groups, which cause difficulties for the fine-tuning of their fluorescence emission, in particular for long-wavelength emission [9]. There have only been few reported silole derivatives which simultaneously possess long-wavelength emission and AIE properties. Fortunately, through judicious design, we have recently attained an AEE-active polar silole which shows efficiently possess long-wavelength emission and AIE properties. There have only been few reported silole derivatives which simultaneously possess long-wavelength emission and AIE properties.

2. Experimental section

2.1. Chemicals and materials

Tetrahydrofuran (THF) used for reactions was distilled with sodium and benzophenone under an atmosphere of dry nitrogen immediately prior to use. Dichloromethane (DCM) used for the electrochemical tests was freshly distilled from calcium hydride under the N2 atmosphere before use. Ultra-dry THF used for optical measurements was chromatographically pure and obtained from TEDIA Company, Inc. The chromatographically pure dimethyl sulfide (DMSO) was bought from Alfa Aesar (Thermo Fisher Scientific) and used for the detection experiments. Water used in all the tests was double-distilled. Common organic solvents were analytically pure and purchased from Sinopharm Chemical Reagent Co., Ltd. TMBFDPD [7d] and DMTPS-p-DCV [5a,10] were synthesized according to the procedures reported in our previously published papers. Malononitrile, Alanine (Ala), Arginine (Arg), Aspartic acid (Asp), Cysteine (Cys), Glutamic acid (Glu), Glutathione (GSH), Glycine (Gly), Histidine (His), Homocysteine (Hcy), Isoleucine (Ile), Leucine (Leu), Lysine (Lys), Methionine (Met), Phenylalanine (Phe), Phenylglycine (Pgl), Proline (Pro), Serine (Ser), Threonine (Thr), Tyrosine (Tyr) and Valine (Val) were purchased from Sigma-Aldrich Chemical Co., Inc. All the other chemicals and reagents were commercially available, of analytic grade, and used as received without further disposal. The thin-layer chromatography (TLC) plates were acquired from Merk KGaA.

2.2. General instrumentation

1H and 13C NMR spectra were measured on a Bruker AV 400 spectrometer in deuterated chloroform using tetramethylsilane (TMS; δ = 0) as the internal reference. FTIR data were recorded on a Bruker Vector 22 spectrometer. The high-resolution mass spectra (HRMS) were obtained on an XEVO-G2 mass spectrometer (Waters) operated in an ESI-TOF mode. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurement were conducted on Perkin–Elmer DSC 7 under N2 atmosphere at a heating/cooling rate of 10 K min⁻¹. Single crystal X-ray diffraction intensity data were collected at 173.2 K for DMTPS-p-DCV on an Xcalibur, Sapphire 3, Gemini ultra diffractometer with graphite monochromated Cu ka X-ray radiation. Empirical absorption correction was done by using spherical harmonics, implemented in SCALE 3 ABSPACK scaling algorithm. CrysAlisPro, Oxford Diffraction Ltd., Version 1.17133.55. The structure solution was measured by SHELXS-97 (Sheldrick, 1990), and the structure refinement were conducted using SHELXL-97 (Sheldrick, 1997) suite of X-ray programs. The analysis was carried out using Mercury Version 2.3. UV–vis absorption spectra were measured on a Varian CARY 100 Bio UV–visible spectrophotometer. Fluorescence (FL) spectra were recorded on a Perkin–Elmer LS 55 spectrophotofluorometer. Fluorescence quantum yields (ΦF) of DMTPS-p-DCV were estimated using quinine sulfate in 0.1 N sulfuric acid (ΦF = 54.6%) as a standard. The absorbance of the solutions was kept around 0.05 to avoid internal filter effect. The film-state ΦF values were recorded using a calibrated integrating sphere with a diameter of 4” (Labsphere Inc.). The films were excited at 325 nm utilizing a He–Cd laser.
ground-state geometries were optimized using density functional theory with B3LYP hybrid functional at the basis set level of 6-31 + G(d). All the calculations were preformed using Gaussian 09 package [11]. Cyclic voltammetry were performed at room temperature in a three-electrode cell using a CHI-600 Electrochemical Workstation at a scanning rate of 50 mV s^{-1}. Electrochemical investigations were conducted in anhydrous DCM with a Pt disk (d¼ 1.6 mm) as the working electrode, Pt wire as the auxiliary electrode, and saturated calomel electrode as a reference electrode. 0.1 M tetra-n-butylammonium hexafluorophosphate ([NBu4]PF6) was used as a supporting electrolyte. The electrolyte solution was purged with N₂ gas before and between electrochemical measurements.

2.3. Synthesis

2.2-(1,1-Dimethyl-3,4-diphenyl-1H-silole-2,5-diyl)bis(3,1-phenylene)bis(methanlylidene)dimalononitrile (DMTPS-m-DCV): 1.1-Dimethyl-2,5-bis(3-benzaldehyde)-3,4-diphenyilsilole (DMBFDPS; 0.120 g, 0.255 mmol) and malononitrile (0.070 g, 1.000 mmol) were dissolved in anhydrous ethanol (70 mL) and then refluxed at 88 °C for 48 h. After being cooled to room temperature, the orange yellow solution was evaporated to dryness under reduced pressure. The residue was purified by silica-gel column chromatography using petroleum ether/ethyl acetate as eluent (Rf¼ 0.25). Yellow solid of DMTPS-m-DCV was obtained in a yield of 51.4% (0.074 g). 1H NMR (400 MHz, CDCl₃): δ (TMS, ppm) 7.63–7.61 (d, 2 H), 7.55 (s, 2 H), 7.43 (s, 2 H), 7.32–7.29 (t, 2 H), 7.15 (d, 2 H), 7.04–7.00 (m, 2 H), 6.78–6.76 (d, 4 H), 0.53 (s, 6 H). 13C NMR (100 MHz, CDCl₃): δ (TMS, ppm) 160.4, 155.9, 141.7, 141.1, 137.5, 135.2, 130.8, 130.0, 129.5, 128.3, 128.0, 127.2, 114.1, 112.8, 82.5, –41. IR (KBr): ν (cm⁻¹) = 3037 (w), 2925 (w), 2229 (s), 1723 (w), 1584 (s), 1461 (s), 1368 (m), 1328 (m), 1271 (s), 1093 (w), 1026 (w), 787 (s), 735 (m), 697 (s), 628 (s), 581 (s), 513 (s). HRMS (ESI-TOF; m/z) Calcd: 567.2005, Found: 567.2006. Melting point: 198 °C (DSC). UV (THF): λ_{max} (ε_{max}) = 356 nm (1 × 10⁻³ mol L⁻¹).

2.4. Preparation of nanoaggregates

For the tests of AIE property, stock solutions of DMTPS-m-DCV in THF (1 × 10⁻³ M) were prepared. Aliquots (1 mL) of the stock solutions were transferred to 10 mL volumetric flasks. After appropriate amounts of THF were added, water was added dropwise under vigorous stirring to afford 10⁻³ M solutions with different fractions of water (f_w = 0–90 vol %). The photoluminescence (PL) measurements of the resultant solutions were performed promptly. While for the determination of detection medium, stock solutions of DMTPS-p-DCV and DMTPS-m-DCV (10⁻⁴ M) were prepared in DMSO respectively. Their DMSO/H₂O solutions (10⁻⁵ M) with different f_wS were prepared via the same procedures as stated above.

2.5. Detection of Cys/Hcy/GSH in the mixture of DMSO/H₂O (6/4, v/v)

Appropriate amount of Cys, Hcy or GSH was dissolved in H₂O (4 mL), and then chromatographically pure DMSO (5 mL) was added into the mixture and well mixed. At last, 1 mL stock solution of DMTPS-p-DCV or DMTPS-m-DCV (0.10 mM) in DMSO was added dropwise under vigorous stirring to afford the detection system with a probe concentration of 10 μM. The mixture was stood at room temperature for 60 min and then underwent the necessary measurements.

2.6. Detection of thiols on the TLC plates

The DCM solutions of silole isomers (DMTPS-p-DCV and DMTPS-m-DCV) were prepared with a concentration of 0.1 mM. Tiny aliquots of the silole solutions were dropped onto the TLC plates by means of capillary glass tubes to afford test strips of probes. The plates with the silole spot were then dipped into the DMSO or aqueous solutions of Cys, Hcy, GSH or other analytes for a certain period of time. The strips were afterwards taken out and the solvent over them was evaporated by the hot air from a hand-held electric blow drier. Ultimately, the TLC plates were examined using a hand-held UV lamp and the photographs of them were taken under UV illumination.

3. Results and discussion

3.1. Syntheses

The silole derivative DMTPS-p-DCV, whose para-positions of the 2,5-phenyl rings were symmetrically decorated with dicyanovinyl (DCV) groups, was prepared referring to the procedures we reported elsewhere [5a,10]. The isomer of DMTPS-p-DCV, namely DMTPS-m-DCV, which has DCV moieties situated on the meta-positions of the 2,5-phenyl rings, was readily prepared in one step via the Knoevenagel condensation reaction between the formyl groups of DMBFDPS and malononitrile with a moderate yield of 51.4%. The synthetic route is depicted in Scheme 1, where the aldehyde-functionalized silole derivative DMBFDPS was synthesized via a modified Tamao method as described in our previous publication [7d]. The silole isomers are very stable when stored under normal laboratory conditions.

3.2. Structures

The obtained new isomer, namely DMTPS-m-DCV, has been fully characterized by 1H NMR ([Fig. S1, Electronic Supplementary Information (ESI)]), 13C NMR ([Fig. S2, ESI]), FTIR, and HRMS ([Fig. S3, ESI]) with satisfactory results (see the Experimental Section for details). The structures of the para-isomer, i.e. DMTPS-p-DCV, were mentioned in our previously published papers [5a,10], some of which will be used here for comparison. Moreover, to further identify its chemical composition and structure, single crystals of DMTPS-m-DCV were grown from solutions. DMTPS-m-DCV (30 mg) was firstly transferred into a small glass spun bottle and dissolved by an appropriate amount of chloroform. Afterwards, this uncovered bottle was put into a wide-mouth container which was filled with anhydrous methanol. The container was firmly sealed and stored at room temperature. Slowly diffusing methanol vapour into the concentrated chloroform solution of DMTPS-m-DCV afforded yellow crystals which were perfect enough for X-ray crystallography analysis in three to five days.

The X-ray crystallographic data of DMTPS-m-DCV were summarized in Table S1 and the crystal structure is shown in Fig. 1. For comparison, the crystal structure of DMTPS-p-DCV was also
because the DCV units elongated the increment in comparison with the phenyl groups at the 2,5-positions of silole core could increase these results indicated that the introduction of DCV moieties onto
largely different, the crystal packing of DMTPS-
Furthermore, although the corresponding torsion angles are not
substituents are much more conjugated with the silole core.
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which could provide some insights into the molecular structure. The thermal properties of these silole isomers were hence investigat-
ed by TGA and DSC. As shown in Table S2 and Fig. S4 (ESI), DMTPS-m-DCV possesses high thermal stability with a temperature of 5%-weight loss (T_{d}) up to 347 °C, which is much higher than that of its parent (275 °C) [5a]; i.e., DMTPS, but a bit lower than that of DMTPS-p-DCV (371 °C). Moreover, DMTPS-m-DCV displayed a melting temperature (T_{m}) of 198 °C, which is higher than that of DMTPS (181 °C) but lower than that of DMTPS-p-DCV (229 °C). These results indicated that the introduction of DCV moieties onto the phenyl groups at the 2,5-positions of silole core could increase the thermal stability and para-substitution could give rise to larger increment in compare with meta-substitution. It is probably because the DCV units elongated the π-conjugation and the para-substituents are much more conjugated with the silole core. Furthermore, although the corresponding torsion angles are not largely different, the crystal packing of DMTPS-m-DCV is looser than that of DMTPS-p-DCV, which also contributes to the differences in the thermal properties.
3.3.2. Photophysical properties
The two silole isomers are readily soluble in most of the com-
mon organic solvents such as THF, DCM and DMSO, but insoluble in
water. DMTPS-p-DCV has been verified to be featured with aggregation-enhanced emission (AEE) property [5a]. When molecularly dispersed in the THF solution, DMTPS-p-DCV shows observable orange yellow fluorescence peaked at 553 nm with a Φ_{f} value of 1.4% (Table S2). Adding water into the THF solution caused gradual increase in its emission intensity and a large red-shift in the emission wavelength which is probably attributed to the J-aggre-
gates formed by the DCV groups as well as the polarity effect of water [5a]. The aggregates formed in the THF/water mixture (f_{w} = 90 vol%) displayed an intense orange-red luminescence with an emission maximum (λ_{em}) of 581 nm and a Φ_{f} value measured to be 8.5%, manifesting the AEE effect. Altering the DCV segments from para-positions to meta-positions greatly changed the optical behav-
iors. The absorption spectra of DMTPS-m-DCV shown in Fig. S5 (ESI); λ_{abs} = 356 nm) are similar to those of the intermediate DMBFDPs but quite different from those of DMTPS-p-DCV (λ_{abs} = 421 nm), implying that the meta-substitution exerts smaller influence on the overall conjugation as compared to para-substitu-
tion. The emission behaviors of DMTPS-m-DCV in the aqueous mixtures with varying f_{w} values are depicted in Fig. 2. In its dilute THF solution, DMTPS-m-DCV strongly luminesces with a Φ_{f} value estimated to be 2.1% (Fig. 2b). Upon the addition of water, the fluorescence was gradually decreased and the emission peak was red-shifted from 553 nm to 585 nm (f_{w} = 70 vol%), exhibiting a typical effect of intramolecular charge transfer (ICT). The ICT effect was ascribed to the A-D-A electronic structure formed between the electron-donating (D) silole core and the peripheral electron-accepting (A) DCV units. The addition of "small" amount of water increased the polarity of the microenvironment, stabilized the charge separation and drove the equilibrium to the ICT state, which accounts for the bathochromic shift in the fluorescence color and the dramatic drop in the fluorescence intensity. With a large amount of water, the solvating power of the resulting THF/water mixture became so poor that it can no more dissolve the DMTPS-m-
DCV molecules. As a result, the DMTPS-m-DCV molecules clustered into nanoaggregates where the luminogen molecules residing are in a less polar microenvironment and the intramolecular motions are physically constrained. The formation of nanoaggregates owing to its hydrophobic nature has been evidenced by the Mie effect of the absorption spectra (Fig. S5, ESI). Consequently, the emission

Fig. 1. Molecular structure, ORTEP drawing diagrams and single-crystal structure of these silole isomers. CCDC-829494 and 1528759 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk.
was blue-shifted to 545 nm and its intensity was enhanced with the \( \Phi_f \) value increased from 0.2\% (\( f_w = 70 \) vol\%) to 1.6\% (\( f_w = 90 \) vol\%), demonstrating the remarkable AIE effect.

DMTPS-p-DCV and DMTPS-m-DCV are highly fluorescent in their solid state with even higher \( \Phi_f \) values. The thin film of DMTPS-m-DCV fluoresces at 512 nm with an absolute \( \Phi_f \) value of 6.4\% (Table S2). In contrast, owing to the well-extended \( \pi \)-conjugation and \( J \)-aggregation-rigidified conformation, DMTPS-p-DCV in the film state shows an intense orange-red emission peaked at 593 nm with a \( \Phi_f \) value of 10.1\% [5a].

In view of the symmetric A-D-A electronic structure, the ICT effect of DMTPS-p-DCV has been clearly and specifically discussed in our previous publication [5a]. Its absorption spectra only exhibited a 16-nm variation when the solvent changed from nonpolar solvent (i.e., toluene) to polar ones (e.g., \( N,N \)-dimethylformamide; DMF), whereas, the photoluminescence spectra showed a dramatic bathochromic shift from 543 nm to 585 nm. Parallel investigations were carried out for the newly developed DMTPS-m-DCV and the results are shown in Fig. S6–S8 (ESI†). The absorption maxima of both DMTPS-m-DCV and its precursor DMBFDPs did not change significantly with solvent (Fig. S6, ESI†). In contrast to DMBFDPs, which displayed no solvatochromism with the emission peak kept at around 470 nm, DMTPS-m-DCV exhibited a distinct and obvious solvatochromism. As can be seen from Fig. S7 (ESI†), its fluorescence color was red-shifted from bluish-green (\( \lambda_{em} = 496 \) nm) to red (\( \lambda_{em} = 627 \) nm) by the increasing solvent polarity parameter (\( \Delta \pi \)), indicative of the strong electron push-pull effect. To gain deeper insights into the solvatochromism of these two silole isomers, the influence of \( \Delta \pi \) on the Stokes shift (\( \Delta \gamma \); Fig. S8a, ESI†) and the dependency of their emission wavelengths on the empirical parameters (\( E^\alpha_\pi \)) of solvent polarity were studied (Fig. S8b, ESI†). The Lippert-Mataga equation [12] for the correlation between \( \Delta \gamma \) and \( \Delta \pi \), and the calculation formula [13] for \( E^\alpha_\pi \) were illustrated in the ESI†. The nearly linear \( \Delta \gamma - \Delta \pi \) plot of DMTPS-m-DCV gives a positive slope as high as 10387.3, which is much larger than that of DMTPS-p-DCV (2464.7). Similarly, the slope of the emission wavelength versus \( E^\alpha_\pi \) plot is 167.6 for DMTPS-m-DCV. It is larger than that of DMTPS-p-DCV (148.1). Both of these methods suggest that DMTPS-m-DCV possesses a more significant solvatochromic effect than its para-isomer, implying that its excited state holds a larger dipole moment compared to the ground state as a result of substantial charge redistribution.

### 3.3.3. Electrochemical properties

For better understanding of the photophysical properties, the molecular calculations on the energy levels were performed by employing the density functional theory (DFT) method with a B3LYP/6-31 + G(d) basis set utilizing the Gaussian 09 package [11]. The electronic structures of the molecular orbitals calculated from their crystal structures are depicted in Fig. 3. Both the DMTPS-p-DCV and DMTPS-m-DCV adopt twisted conformations, which is consistent with the crystallographic data. Such a non-planar 3D configuration would prevent the \( \pi \)-\( \pi \) stacking interaction and the resultant fluorescence quenching.

The highest occupied molecular orbital (HOMO) of DMTPS-p-DCV is well-distributed over almost the whole molecule excepting the silicon atom and methyl groups, while the HOMO of DMTPS-m-DCV is mainly located on the DMTPS skeleton, suggesting that the DCV units on the meta-positions are less conjugated with the DMTPS framework. Intriguingly, the lowest unoccupied molecular orbital (LUMO) of DMTPS-p-DCV is mainly dominated by the orbitals from the silole ring and its 2,5-substituents, revealing an obvious outward ICT process from the silole core and 3,4-phenyl groups to the 2,5-DCV moieties [5a]. The LUMO of DMTPS-m-DCV is taken up by the orbitals from the 2,5-phenyl rings and their DCV substituents, manifesting an outward ICT from the DMTPS skeleton to the DCV groups as well as a complete charge separation between them. These results are in good agreement with the solvatochromism measurements.

To further confirm the electron affinities of these two isomers, cyclic voltammetry was employed to investigate their...
electrochemical properties. The measurements were carried out in anhydrous DCM solutions containing 0.1 M tetrabutylammonium hexafluorophosphate at a scanning rate of 50 mV s\(^{-1}\) with Pt as the working and saturated calomel electrode (SCE) as the reference electrode. The corresponding results are summarized in Table S3. DMTPS-p-DCV and DMTPS-m-DCV possess reduction onset potentials (**E**\(_{\text{onset}}\)) at -0.32 V and -1.80 V, respectively, which are lower than that of the DMTPS parent (**E**\(_{\text{onset}}\) \(= -2.35 \text{ and } -2.64 \text{ V}\)). The oxidation onset potential (**E**\(_{\text{onset}}\) of DMTPS-m-DCV was determined to be 1.14 V, whereas, as for DMTPS-p-DCV, only structureless oxidation profile was recorded, demonstrating that it does not possess electron-donating ability due to the electron-deficient DCV units. When compared with the DMTPS parent (**E**\(_{\text{onset}}\) \(= 0.93 \text{ and } 1.04 \text{ V}\)), it can be concluded that decorating the silole core with strong electron-accepting DCV moieties on its 2,5-phenyl rings could markedly decrease the reduction barriers and facilitates its reduction process. However, the decreasing amplitude is largely depends on the substituent position. Owing to the better conjugation, the para-substituted DCV groups could play a more efficient role in lowering the reduction barrier.

The energy levels of the HOMO and LUMO were estimated by the following equations [14]:

1. \(E_{\text{HOMO}} = -e(F_{\text{onset}} + 4.4V)\)
2. \(E_{\text{LUMO}} = -e(F_{\text{onset}} + 4.4V)\)

The LUMO energy levels of DMTPS-p-DCV and DMTPS-m-DCV were calculated to be -4.08 and -2.60 eV. The HOMO energy level of DMTPS-m-DCV was determined to be -5.54 eV and that of DMTPS-p-DCV was deduced to be -6.55 eV by subtracting the optical band gap energy \(E_{g}\) estimated from the onset absorption wavelength from the LUMO value (Table S3). The distinctive HOMO and LUMO values not only imply that the energy levels of DMTPS derivatives could be fine-tuned by altering the substitution position from para to meta, but also provide an explanation on the differences in the photophysical properties.

3.4. Detection of thiols

3.4.1. Detecting biothiols in the mixture of DMSO/H\(_2\)O (6/4, v/v)

Thiol-containing compounds possess unique chemical reactivity and hence play special roles in chemical reactions and biological processes. Biothiols are indispensable elements in biological systems including human body. Amongst all the biogenic thiols, Cys, Hcy, and GSH have received the most attention for their important physiological functions in the processes such as homeostasis, anti-aging, detoxification, and metabolism. It is believed that the abnormal levels of these thiol species in body fluids are indicative of certain diseases [15]. For example, the deficiency in Cys is closely associated with a number of syndromes including slow growth, hair pigmentation, liver damage, skin lesions and lethargy [16]. High concentration of Hcy in the serum is linked to a wide range of diseases such as cardiovascular diseases, neuropsychiatric disorders, renal dysfunction and Alzheimer’s disease [15c,15d]. Development effective methods for the detection of biothiol species is thus of great significance to both academic research and clinical diagnosis.

Among all the detection approaches developed by far, the fluorescence detection is the most appealing one for its rapidity, simplicity, cost-effectiveness, visual and real-time responses, and no requirement for sophisticated instrumentation. Ratiometric fluorometric probes that could reduce the interferences from probe molecule concentration and micro-environment using the ratio of two intensities of emission at different wavelengths have drawn considerable attention. Up till now, a large variety of fluorometric probes have been explored for biothiol detection [17–21], however, the ratiometric ones are relatively rare [7d,7e,21], not to mention AIE-based ratiometric fluorometric probes [7d,7e,21a].

Close study on the structures and properties gives us some enlightenment that the AIE-active silole derivatives presented here might be good candidates for the ratiometric fluorometric probes. It is because the \(\alpha,\beta\)-unsaturated DCV group is a widely used Michael acceptor and it is very sensitive to the nucleophilic thiol species. The reaction between DCV group and thiol would destroy the **C==C** double bond, breaking the conjugation between DCV and DMTPS core, and ultimately leading to the change in fluorescence spectra (Scheme S1). In this regard, it can be anticipated that both DMTPS-p-DCV and DMTPS-m-DCV could work as thiol probes with the DMTPS unit serving as a signaling moiety and the DCV groups acting as recognition moieties.

The possibility of applying DMTPS-p-DCV and DMTPS-m-DCV for thiol detection was firstly examined by mixing the silole derivative with excess Cys in the mixture of DMSO/H\(_2\)O. DMSO and water were chosen in consideration of their biocompatibility. The volume ratio of them was determined according to the AIE/AIE plots of these two isomers measured in the DMSO/H\(_2\)O mixtures with different volume ratios [7d,7e,21]. The fluorescence spectra of DMTPS-m-DCV in DMSO/H\(_2\)O mixtures are close to the abscissa and keep unchanged until the \(f_{\text{onset}}\) exceeded 40 vol% (Fig. S10, ESI†). In these solutions, the DMTPS-m-DCV molecules were dispersed, and thus their active intramolecular motions and the strong polarity of solvents cooperatively quenched the emission. After this point, the photoluminescence of DMTPS-m-DCV takes off with the increasing \(f_{\text{onset}}\). Therefore, to achieve the balance between the biocompatibility and “turn-on” effect, the threshold \(f_{\text{onset}}\) of its AIE plot (40 vol%) was set as the action ratio for thiol probing. The situation is different for DMTPS-p-DCV (Fig. S9, ESI†). The AIE property made it already emissive in pure DMSO solution. The addition of water initially caused an increase in the emission when \(f_{\text{onset}} \leq 20 \text{ vol%}\). Further addition of water (20 vol% < \(f_{\text{onset}} < 40 \text{ vol%}\) made the emission intensity drop a bit. Afterwards, the fluorescence intensity was monotonically boosted with the increasing amount of water. For the same reason, \(f_{\text{onset}} = 40 \text{ vol%}\) was also chosen as the working ratio for the following detection experiments.

The AEE-active DMTPS-p-DCV shows a strong orange red emission peaked at 602 nm in the detection medium at a concentration of 10 \(\mu\)M (Fig. 4a). When coexisting with 2 mM Cys in the detection medium, the fluorescence at 602 nm instantly declined while a new emission band peaked at 516 nm emerged and gradually rose as time went by. Such a remarkable ratiometric response clearly demonstrated that the DMTPS-p-DCV readily reacted with Cys via Michael addition, which disrupted the conjugation between the DMTPS core and the substituents, diminishing the ICT effect (Scheme S1). The shortened conjugation together with the weakened ICT effect blue shifted the fluorescence spectra. Furthermore, the multiple intermolecular hydrogen-bonding between the amino and carboxylic groups aid the reaction product to form aggregates and thereby results in lower solubility. Accordingly, the transparent detection system turned turbid, enabling direct visual observation. Meanwhile, the aggregation of reaction products activated the RIM process and aroused the AIE effect of DMTPS, leading to the enhancement in the emission at 516 nm. When the probe was added to the Hcy solution, the intense fluorescence at 602 nm of DMTPS-p-DCV immediately started to drop but the decrease amplitude was a bit smaller as compared to that in Cys solution (Fig. 4b). The emission band with a maximum at around 516 nm also appeared but the intensity of which did not increase much. It means that the addition reaction between Hcy and DMTPS-p-DCV indeed occurred, but their product is more soluble in the detection
medium than the product of Cys and DMTPS-p-DCV, hence resulting in a smaller augmentation of fluorescence at 516 nm. Interestingly, when incubated with GSH, DMTPS-p-DCV behaved distinctively from when it was incubated with either Cys or Hcy. During the observation course of 300 min, the fluorescence intensity merely decreased slightly without any change in the peak shape and position (Fig. 4c). It suggested that the thiol group in GSH probably could not efficiently interact with DMTPS-p-DCV or the solubility of their reaction product is good. The significant ratiometric responses in the fluorescence of DMTPS-p-DCV to Cys and Hcy are clearly illustrated by the plots of $I_{516}/I_{602}$ versus time shown in Fig. 4d. The value of $I_{516}/I_{602}$ was 0.076 for Cys and DMTPS-p-DCV at 1 min and it rapidly grew to 2.17 at 97 min, displaying a 28.6-fold enhancement in the ratiometric ratio. For Hcy and DMTPS-p-DCV, the $I_{516}/I_{602}$ value changed from 0.27 to 2.06 with time extending from 1 to 267 min. In sharp contrast, the $I_{516}/I_{602}$-time plot for DMTPS-p-DCV coexisting with GSH is a straight line parallel to the abscissa with the $I_{516}/I_{602}$ value of ca. 0.05. Therefore, it can be concluded that DMTPS-p-DCV could discriminate Cys and Hcy from GSH with the aid of distinguish kinetics.

As mentioned above, the ICT effect and intramolecular motions made DMTPS-m-DCV in the mixture of DMSO/H$_2$O (6/4, v/v) only moderately fluoresced. When it coexisted with 2 mM Cys in the detection medium, the responses took place in an instant at room temperature. The yellow fluorescence peaked at 550 nm decreased very quickly, and in the meantime, the new emission band arose with a peak at 490 nm (Fig. 5a). Similar but even faster responses were observed when DMTPS-m-DCV existed with Hcy in the DMSO/H$_2$O (6/4, v/v) solution (Fig. 5b). Such responses could be interpreted as follows. The Michael addition between DMTPS-m-DCV and Cys or Hcy cleaved the double bond, broke the overall conjugation and eliminated the ICT effect as well, bringing about the hypsochromic shift in fluorescence. The lower solubility of the reaction product compared to the probe originating from the multiple hydrogen bonds between the amino and carboxyl groups assisted the aggregation, which restricted the intramolecular motions, blocked the nonradiative pathway, and resulted in the enhanced cyan emission. The aggregate formation could be witnessed visually because the detection system changed from transparent to turbid during the probing course. Different from its para isomer, DMTPS-m-DCV was able to respond to GSH (Fig. 5c), although the responses are not as pronounced as that to Cys and Hcy. It probably could be ascribed to the weaker conjugation between the DMTPS skeleton and the meta-positioned DCV groups, which renders the electron cloud density of ethylene unit lower than that in the DMTPS-p-DCV, making it easier to be attacked by the thiol species. The quantitative evaluations of the variations in the fluorescence intensity and peak wavelength of the detection systems as time went by are displayed in Fig. 5d. With an initial $I_{490}/I_{550}$ value of approximate 0.29, the ratiometric response of DMTPS-m-DCV to Cys reached the plateau ($I_{490}/I_{550} \approx 1.90$) in 90 min, while the dynamic curve of DMTPS-m-DCV to Hcy arrived to the inflection point in about 30 min with the $I_{490}/I_{550}$ value increasing from 0.38 to about 1.50. The smallest change in the $I_{490}/I_{550}$ value of the detection system is suggestive of the lowest reactivity of GSH to DMTPS-m-DCV. It is worth mentioning that generally DMTPS-m-DCV showed faster responses but smaller signal-to-noise ratio in comparison to its para isomer. The faster responses might stem from the higher reactivity contributed by the weaker conjugation of meta-substitution, and the smaller increment in the $I_{490}/I_{550}$ value might be due to the larger spectral overlap between DMTPS-m-DCV and its reaction product with thiols.

Fig. 4. Time dependent fluorescence (FL) spectra when DMTPS-p-DCV was added to a) Cys, b) Hcy or c) GSH in the DMSO/H$_2$O (6/4, v/v) solution; (d) Plots showing the changes in FL intensity for a), b), and c). [DMTPS-p-DCV] = 10 μM, [analyte] = 2.0 mM.
The sensitivity of DMTPS-\textit{p}-DCV or DMTPS-\textit{m}-DCV to Cys was assessed by the fluorescence spectroscopic titration experiments. The changes in the fluorescence intensity with Cys concentration in DMSO/H\textsubscript{2}O (6/4, v/v) mixture are depicted in Fig. 6. In general, the fluorescence was gradually intensified and blue-shifted with the Cys concentration varying from 0 to 2000 μM (Fig. 6a and c). The plots of $I/I_0$ versus Cys concentration exhibited in Fig. 6b and d provided more detailed information. For DMTPS-\textit{p}-DCV, the value of $I/I_0$ fluctuated below zero with no regularity in the Cys concentration range of 0.5−250 μM, and showed an approximately linear growth afterwards ([Cys] > 250 μM). Whereas, when DMTPS-\textit{m}-DCV was used as the probe, even 0.5 μM Cys will cause obvious spectral changes with the value of $I/I_0$ of 0.51, evidently suggesting the high sensitivity of DMTPS-\textit{m}-DCV. Moreover, the fluorescence enhancement ($I/I_0$) steadily increased and was almost linearly correlated with the Cys concentration in the range of 0.5−2000 μM, which would be beneficial to the quantification of Cys level in the biological systems. The higher sensitivity of DMTPS-\textit{m}-DCV in contrast to its \textit{para} isomer should be attributed to the synergies of AIE, ICT effect, and the weaker conjugation between DMTPS and DCV moieties, which for one thing, ensures the minimal background interference, and for another, assures the high reactivity.

The specificity is another crucial parameter to a probe besides sensitivity. To evaluate the specificity of DMTPS-\textit{p}-DCV and DMTPS-\textit{m}-DCV to thiols, their responses to various other amino acids were investigated under parallel conditions. As displayed in Figs. 7 and S11 (ESI), for both DMTPS-\textit{p}-DCV and DMTPS-\textit{m}-DCV, Cys gave the most significant fluorescence responses in 1 h. To be more specific, in the presence of 2 mM Cys, the fluorescence enhancement of the detection system with DMTPS-\textit{p}-DCV as a probe is 1.57 (Fig. 7a). Most of the other analytes blue shifted and slightly decreased the emission while the asparagic acid (Asp) and glutamic acid (Glu) red shifted and enhanced the fluorescence to some extent. Despite this, DMTPS-\textit{p}-DCV could specifically show blue-shifted and greatly enhanced fluorescence response to Cys. As can be seen from Fig. 7b, DMTPS-\textit{m}-DCV also enjoyed a high specificity to thiols (mainly Cys and Hcy). Among all the other analytes, only lysine (Lys) exhibited a moderate enhancement in the blue emission due to its dual amino groups. Furthermore, the fluorescence spectrum of DMTPS-\textit{m}-DCV with Lys is distinct from that with Cys or Hcy (Fig. S11b, ESI). It is noteworthy that DMTPS-\textit{m}-DCV exhibited a larger fluorescence enhancement in comparison with DMTPS-\textit{p}-DCV owing to its AIE feature and the stronger ICT effect.

3.4.2. Detecting thiols on the TLC plates

Hereinbefore, thiols could be assayed by recording the changes in the fluorescence signals (intensity and color) of the probes with the analyte concentrations in the solution state (e.g., DMSO/water mixture with $f_\text{w} = 40$ vol%) by means of a spectrofluorimeter. However, performing thiol assays on solid matrices should be preferable for its no demand for complex/expensive equipment, large amount of probe, and tedious sample preparation[20g,22]. In other words, it is simple, fast and convenient. The thorny ACQ problem always encountered by traditional luminophores limited the exploration of probes for thiol detection in the solid state. It is because once loaded on the solid supports, the luminescence of the probe and its reaction resultant with the analyte would be weakened or even completely quenched, which usually exert negative influences on the detection performances. It can be anticipated that

![Fig. 5. Time dependent fluorescence (FL) spectra when DMTPS-m-DCV was added to a) Cys, b) Hcy or c) GSH in the DMSO/H\textsubscript{2}O (6/4, v/v) solution; (d) Plots showing the changes in FL intensity for a), b), and c). [DMTPS-m-DCV] = 10 μM, [analyte] = 2.0 mM.](image-url)
the AEE-active DMTPS-\textit{p}-DCV and AIE-active DMTPS-\textit{m}-DCV would work as efficient solid-state fluorescent probes for the detection of thiols.

TLC plates were selected as the solid matrices for the probing system, considering that TLC has been extensively employed as a handy tool in chemical research, especially for monitoring the progress of chemical transformations. The probe strips based on TLC plates were prepared by dropping small aliquots of the DCM solution of DMTPS-\textit{p}-DCV or DMTPS-\textit{m}-DCV (0.1 mM) onto the TLC plates with capillary glass tubes. The reactivity or responsiveness of these silole derivatives to Cys were first tested by individually dipping the TLC plates loaded with DMTPS-\textit{p}-DCV and DMTPS-\textit{m}-DCV into the DMSO solution of Cys for a certain period of time. After being taken out, the residual DMSO was removed by the warm air from a hand-held electronic blow drier. The TLC plates were afterwards checked by a hand-held UV lamp and taken photographs under the UV illumination at 365 nm. The fluorescent photographs of the test strips soaked in Cys solution for different time ranges were exhibited in Figs. S12 and S13 (ESI†). The DMTPS-\textit{p}-DCV spot on the TLC plate before dipping into the Cys solution showed intense orange red emission. The test strip of DMTPS-\textit{p}-DCV responded to Cys within 1 min with the fluorescence turned yellowish green, indicative of a quicker response as compared to solution detection. As the immersion period prolonged, the fluorescence became greener and brighter, reaching the maximum at 8 min (Fig. S12, ESI†). Meanwhile, the orange yellow spot of DMTPS-\textit{p}-DCV on the TLC plate observable under daylight disappeared within about 5 min in the Cys solution, suggestive of the complete transformation from probe to a less-conjugated resultant. The luminescence became weaker with too long soak. It might be because that the reaction product on the TLC plates could be partially soaked out and dispersed into the DMSO solution, decreasing the amount of luminescent species residing on the strip and resulting in the weakening of fluorescence. The responses of DMTPS-\textit{m}-DCV on the TLC plates to Cys are even faster and more
significant (Fig. S13, ESI†). Intense blue fluorescence emerged in 1 min and reached the culmination at 4 min. The marked responses could be maintained by 8 min. The luminescence of test strip dipped into Cys for more than 8 min decreased dramatically, further evidencing that the reaction resultant of probe and Cys could be taken away from the TLC plates by long-time immersion. The faster responses of DMT-PS-m-DCV to Cys in contrast to its para isomer verified its higher reactivity for a second time. According to the time dependence of the fluorescent responses, 8 min was set as the standard soak period for the following tests.

With this simple and handy assay approach, the responsiveness of DMT-PS-p-DCV and DMT-PS-m-DCV to other thiol species was also defined by dipping their TLC strips into different thiol solutions (2.48 mM) for 8 min. As shown in Fig. 8, when dipped into blank DMSO solution for 8 min, the DMT-PS-p-DCV spot on the TLC plate merely showed moderate orange yellow fluorescence (Fig. 8), which was slightly blue-shifted and greatly weakened compared to the un-soaked one. This is probably because the good solubility of DMT-PS-p-DCV in DMSO enabled its dissociation from TLC plate. This para isomer responded to the chosen thiols to a varying degree in a ratiometric fashion. The overall order of the response degree is Cys, Hcy, GSH > N-acetyl-L-Cys > 3-mercaptopropionic acid, 16-mercaptopentadecanoic acid > p-thiocresol > BSA, methyl-3-mercaptopropionate. The intense green fluorescence from the strips immersed in Cys, Hcy and GSH originated from the Michael addition reactions, which destroyed the conjugation between the substituents and DMT-PS core and generated products with lower solubility that could aggregate more closely and emit more efficiently owing to the AIE nature of DMT-PS. As shown in Scheme S1, the most significant responses of DMT-PS-p-DCV to Cys/Hcy/GSH probably can be attributed to the following two aspects: (1) The products of these three biothiols and DMT-PS-p-DCV may possess lowest solubility owing to their numerous hydrogen-bonding interactions between the amino and carboxyl groups, the aggregation of which could not only drive the reaction equilibrium to the right but also intensify the AIE effect. (2) The nucleophilicity of these three amino thiols might be the best among the thiols presented here, rendering the highest extent of reaction in a certain period of time.

With respect to DMT-PS-m-DCV, before dipping into the DMSO solution, its test strip shows a weak orange fluorescence owing to the ICT effect and the loose packing in the aggregated state (Fig. 9). Whereas that soaked in the blank DMSO solution exhibited weak fluorescence under UV light. The test strips immersed in the DMSO solutions of various thiols displayed varying extents of changes in the fluorescence intensity and color. Similar to its para isomer, DMT-PS-m-DCV showed a response order as Cys, Hcy, GSH > N-acetyl-L-Cys, 3-mercaptopropionic acid >16-mercaptopentadecanoic acid > BSA, methyl-3-mercaptopropionate > p-thiocresol. Thanks to the minimal background and the remarkable AIE effect, the fluorescence responses of DMT-PS-m-DCV to Cys, Hcy, GSH, N-acetyl-L-Cys, 3-mercaptopropionic acid and 16-mercaptopentadecanoic acid were displayed in a turn-on mode (see Fig. 9). These results further proved that the response performances of these silole derivatives to thiols relied on the molecular structure of probes, the reactivity of both probe and thiol species, and the solubility of the reaction resultant.

Similar to the solution detection, the test strips of both DMT-PS-p-DCV and DMT-PS-m-DCV showed a good specificity to Cys and Hcy, as indicated by the fluorescent photographs shown in Figs. 10 and 11. Specifically speaking, after being treated by the Cys or Hcy solution for 8 min, the fluorescence from the spots on the TLC plates loaded with DMT-PS-p-DCV turned from orange red to bright green (Fig. 10). Although the immersion of test strip into Lys solution also brought about green light, the brightness was much lower. The DMT-PS-p-DCV spots on the test strips treated with the other amino acids without thiol group merely faintly luminesced or exhibited intensified orange fluorescence (Asp and Glu), indicating that DMT-PS-p-DCV could distinguish biothiols from the other biomolecules in the solid state. For DMT-PS-m-DCV, only the test strips soaked in Cys and Hcy solutions exhibited significantly enhanced cyan fluorescence (Fig. 11). The fluorescence from Lys-treated test

![Fig. 8. The responses of DMT-PS-p-DCV to thiols. (a) Cys, (b) Hcy, (c) GSH, (d) BSA, (e) N-acetyl-L-Cys, (f) methyl-3-mercaptopropionate, (g) 3-mercaptopropionic acid, (h) 16-mercaptopentadecanoic acid, (i) p-thiocresol and (j) blank. Photographs were taken under illuminations of 365 nm UV light after the TLC plates had been dipped into the DMSO solutions of thiols (2.48 mM) for 8 min.](image)

![Fig. 9. The responses of DMT-PS-m-DCV to thiols. (a) Cys, (b) Hcy, (c) GSH, (d) BSA, (e) N-acetyl-L-Cys, (f) methyl-3-mercaptopropionate, (g) 3-mercaptopropionic acid, (h) 16-mercaptopentadecanoic acid, (i) p-thiocresol and (j) blank. Photographs were taken under illuminations of 365 nm UV light after the TLC plates had been dipped into the DMSO solutions of thiols (2.48 mM) for 8 min.](image)

![Fig. 10. The specificity of DMT-PS-p-DCV to aminothiols. Photographs were taken under illuminations of 365 nm UV light after the TLC plates had been dipped into the DMSO solutions of amino acids (2.48 mM) for 8 min.](image)

![Fig. 11. The specificity of DMT-PS-m-DCV to aminothiols. Photographs were taken under illuminations of 365 nm UV light after the TLC plates had been dipped into the DMSO solutions of amino acids (2.48 mM) for 8 min.](image)
A reduction in the Cys concentration to 2.48 mM gave rise to yellowish luminescence. Further studies were performed with Cys in water at a concentration of 2.48 mM via the same procedures as discussed in Figs. S12 and S13 (ESI†). Different from the results obtained by using DMSO solution of Cys, the TLC plate of DMTPS-p-DCV still displayed quite brilliant orange yellow fluorescence after being dipped into the aqueous solution of Cys for 10 min. The fluorescence began to change at 30 min and evident change could not be observed after 12 h (upper panel of Fig. S14, ESI†). It means that DMTPS-p-DCV on the TLC plate could react with Cys in aqueous solution; however, owing to the strong hydrophobicity of the para-substituted DMTPS derivative, the DMTPS-p-DCV molecules need a long time to fully interact with the cysteine molecules to initiate the reaction. Very interestingly, DMTPS-m-DCV loaded on the TLC plate still possesses the capability of readily reacting with Cys in water (lower panel of Fig. S14, ESI†). The reaction between the probe and Cys under this condition probably could complete in 6 min since the intense blue fluorescence arrived at the apogee at 6 min and remained unchanged afterwards. The different response behaviors of DMTPS-p-DCV and DMTPS-m-DCV addressed the following issues: (1) DMTPS-p-DCV is more hydrophobic than DMTPS-m-DCV because of its more extended \( \pi \)-conjugation and aromatic framework; (2) DMTPS-p-DCV and DMTPS-m-DCV could not be dissolved in water and neither could their thiolated products; (3) DMTPS-p-DCV and DMTPS-m-DCV are soluble in DMSO and their thiolated resultants might be partially soluble. In addition to the rapid response, the test strips of DMTPS-m-DCV are also sensitive to the Cys in water. The fluorescent photographs of TLC plates loaded with DMTPS-m-DCV after being immersed in the aqueous solutions of Cys with different concentrations for 6 min are displayed in Fig. S15 (ESI†). Clear fluorescence response was observable at a Cys concentration of 24.8 \( \mu \)M. When the Cys level in water is as low as 2.48 \( \mu \)M, although the fluorescence of the spot on TLC plate is somewhat weak, it is still discernable, implying that DMTPS-m-DCV holds a great potential to be used for real-sample detection.

4. Conclusion

Attaching electron-withdrawing DCV moieties to the meta-positions of the 2,5-phenyl groups on the silole core via simple Knoevenagel condensation afforded the novel polar silole DMTPS-m-DCV. Systematic and comparative studies on the structures, properties and application in the thiol detection of DMTPS-m-DCV and its para-isomer DMTPS-p-DCV have been carried out and discussed in details with an emphasis on the structure-property relationships. Owing to the similarity in structure and constitution, these two isomers share some common features. For example, the multiple rotatory moieties and non-planar 3D configurations endow them with AEE/AIE properties. Their A-D-A type electronic structures account for the strong ICT effect. The reactive DCV units make them capable of detecting thiols via the Michael addition. However, the minor variation in the substitution position of DCV units gives rise to a number of differences in their structure, properties and thus detection performances. For instance, a more extended molecular structure, DMTPS-p-DCV possesses larger \( \pi \)-conjugation and intense molecular packing, hence showing more efficient orange red aggregated-state emission and higher thermal stability, while DMTPS-m-DCV merely exhibits moderate yellow fluorescence in the aggregated state. Because of the weaker conjugation between the DMTPS skeleton and the

![Fig. 11. The specificity of DMTPS-m-DCV to aminothiols. Photographs were taken under illuminations of 365 nm UV light after the TLC plates had been dipped into the DMSO solutions of amino acids (2.48 mM) for 8 min.](image)

![Fig. 12. The concentration dependence of (a) DMTPS-p-DCV and (b) DMTPS-m-DCV to cysteine in DMSO for 8 min.](image)
meta-situated DCV groups, DMTPS-m-DCV holds stronger ICT effect, more significant solvatochromism, and higher reactivity to thiol species. As for the detection performances, each of these two isomers has its own merits. With larger spectral difference between the probe and its thiolated product, the ratiometric response of DMTPS-p-DCV is more profound in comparison with its meta-isomer. The marked AIE, stronger ICT effect and higher reactivity make DMTPS-m-DCV a turn-on type ratiometric probe with higher sensitivity and faster response. This work shed light on the relationship between the structure and property of DCV-functionalized DMTPS derivatives, and perfectly corroborated the general opinion that “structure determines property”.

It is noteworthy that this work also provides guidance on the molecular design of probes. The AIE/AEE plus ICT features enabled specific thiol detection with low background, remarkable blue-shift in fluorescence, large fluorescence enhancement and thus high signal-to-noise ratio. Intriguingly, DMTPS-p-DCV could differentiate Cys and Hcy from GSH with the help of distinct kinetics. DMTPS-m-DCV has pretty high sensitivity to Cys with a detection limit lower than 0.5 μM. Simple and handy test strips of these two isomers have been developed using TLC plates as solid supports. The practicability of the TLC plates loaded with DMTPS-m-DCV was confirmed by the fast and sensitive response to Cys in water. In addition, the distinguishable response behavior exhibited by the test strips of both DMTPS-p-DCV and DMTPS-m-DCV to various thiol species have demonstrated that the response performance depends on the molecular structure of probe, the reactivity of both probe and thiol species, and the solubility of the thiolated product, offering new clues to the follow-up research works.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2017.02.039.

References


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