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Tetraphenylethene and Maltoheptaose Conjugate with Aggregation-Induced Emission (AIE) Characteristic for Temperature Sensor

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The amphiphilic maltoheptaose-tetraphenylethylene (Mal-TPE) conjugate can assemble in aqueous medium and the aggregrates exhibit aggregation-induced emission (AIE) effect. The sizes of Mal-TPE aggregrates decrease with the increase in temperature, resulting in temperature-dependent fluorescence property.

Fluorescent thermometers have attracted increasing attention in clinical, biomedical, industrial and environmental applications.¹⁻⁴ They allow "remote" sensing of temperature based on various fluorescent parameters, including fluorescence intensity, lifetime and anisotropy, quantum yield, and peak wavelength.⁵⁻⁷ Among these characteristics, monitoring of changes in the relative fluorescence intensity has been commonly used due to its visually readable signal and simple instrumental setup.⁵ To date, a wide variety of luminophores, including metal-ligand complexes,⁸ organic and inorganic fluorophores,⁹⁻¹¹ conjugated polymers,¹² metal organic frameworks,¹³ nanoclusters,¹⁴ quantum dots,¹⁵ and upconversion nanoparticles,¹⁶ have been used to construct the fluorescent thermometers.

Aggregation-Induced Emission (AIE) is an exotic photophysical phenomenon and have an exactly opposite property of earlier aggregation-caused quenching (ACQ) effect. The compound with AIE effect is non-emissive in the soluble state but emits strong fluorescence in the aggregated state.¹⁷ Since Tang et al. first reported the AIE phenomenon of silole compound in 2001,¹⁸ various AIE luminogens (AIEgens) have been

prepared for applications in sensors,^{19,20} disease theranostics,²¹ bioimaging²²⁻²⁵ and opto-electronic systems.²⁶ Tetraphenylethylene (TPE), a propeller-like molecule bearing four peripheral phenyl rings around a central C=C bond, is a classical AIEgens.²⁰ Free rotation of the four phenyl rings in the soluble state could serve as a nonradiative relaxation pathway for the excited electrons, resulting in no or weak fluorescence emission. However, the restricted intramolecular rotation of these phenyl rings in the aggregated state could prevent the nonradiative relaxation, leading to strong fluorescence enhancement.^{20,27,28} The solubility, phase and selfassembly behaviors, intermicellar interactions, and surface forces of non-ionic surfactants display effects.²⁹ temperature-dependent Since TPE is hydrophobic and insoluble in aqueous media, its conjugation with a hydrophilic component would lead to the formation of amphiphilic surfactant with thermoresponsive properties. The light-up characteristic of TPE derivative could be modulated by lowering temperature and used to monitor the change of temperature. As far as we know, this is the first report on the construction of fluorescent thermometer based on the amphiphilic AIE luminogen.

In this work, the azide-containing TPE was conjugated with hydrophilic alkyne-terminated maltoheptaose via copper(I)-catalyzed azide-alkyne cycloaddition (CuAAC) reaction (Figure 1). Maltoheptaose was obtained by a ring-opening reaction of β -cyclodextrin, followed by functionalization at the distal end with alkyne group. Hydroxyl group in TPE-OH was methanesulfonated to convert into azide moiety via azidation. The intermediate products, Mal-alkyne and TPE-N₃ were reacted in the presence of copper catalyst to form the Mal-TPE conjugate. The final products were successfully synthesized, as demonstrated by ¹H NMR (Figure S1, ESI) and mass (Figure S2, ESI) spectroscopy.

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Figure 1. Schematic illustration for the synthesis of Mal-TPE conjugate.

The UV-visible absorption spectra of Mal-TPE in phosphate-buffered saline (PBS) solution and N,Ndimethylformamide (DMF) (Figure 2a) exhibit absorption peaks at about 300 and 305 nm, respectively. The absorption band of Mal-TPE in DMF is red-shifted by ca. 5 nm, which may be attributed to the change in solvation or interactions between Mal-TPE and solvents. Due to the good solubility of Mal-TPE in DMF, its solution emits almost negligible fluorescence under UV light irradiation. However, a strong blue fluorescence is observed in the PBS solution of Mal-TPE at the same condition (Inset of Figure 2b). This phenomenon may be

arising from the trigger of AIE characteristic upon the aggregation of Mal-TPE in aqueous medium. The aggregation of Mal-TPE in aqueous medium was verified by ¹H NMR spectroscopy. As shown in Figure S3 (ESI), the ¹H NMR spectrum of Mal-TPE in D₂O only shows partial proton signals of Mal segment. The shield of proton signals of TPE segment suggests it has been assembled within the interior of aggregates. The aggregation of Mel-TPE in aqueous medium was further confirmed by transmission electron microscopy (TEM) image. As shown in Figure S4 (ESI), the Mal-TPE aggregates possess irregular spherical shape and broad size distribution.



Figure 2. (a) UV-visible adsorption spectra of Mal-TPE (40 μ M) in PBS solution and DMF; (b) fluorescence spectra of Mal-TPE (40 µM) in PBS-DMF mixtures (0-100% for DMF fraction) with an excitation wavelength of 350 nm; (c) fluorescence spectra of Mal-TPE in water at different pH; (d) pH-dependent maximum fluorescence intensity of Mal-TPE in water.

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Figure 3. (a) Fluorescence spectra of Mal-TPE (40 μ M) in PBS solution at different temperatures with an excitation wavelength of 350 nm; (b) temperature-dependent maximum fluorescent intensity of Mal-TPE at different concentrations (20 and 40 μ M); (c) changes in the maximum fluorescence intensity of Mal-TPE (40 μ M) during repeated heating and cooling processes.

Figure 2b shows the fluorescence spectra of Mal-TPE in PBS-DMF mixtures. The fluorescence intensity centered at about 466 nm increases with the increase in the aqueous fraction, clearly indicating the AIE characteristic of Mal-TPE. The absolute quantum yields (ϕ) of Mal-TPE in PBS solution and DMF are determined to be 0.354 and 0.007, respectively. The lifetime of Mal-TPE in PBS solution is evaluated to be 4.5 ns (Figure S5, ESI). The effect of pH value on the fluorescence characteristic of Mal-TPE in water was then investigated. As shown in Figure 2c and 2d, the fluorescence intensity of Mal-TPE aqueous solution increases with the increase in pH value in the range from 1 to 7, and decreases with the further increase. A maximum fluorescence intensity is achieved at neutral pH. The changes in fluorescence intensity of Mal-TPE at alkaline (or acidic) pH may be attributed to the dissociation (or protonation) of hydroxyl groups in Mal-TPE, increasing the solubility of Mal-TPE and weakening its AIE characteristic. To eliminate the influence of pH, the temperaturedependent fluorescence behavior of Mal-TPE was studied in buffer solution.

Figure 3a and Figure S6 (ESI) represent the temperature-dependent fluorescence spectra of Mal-TPE in PBS solution at concentrations of 40 and 20 µM, respectively, at different temperatures ranging from 20 - 65 °C. It is evident that the maximum fluorescence intensity of Mal-TPE decreases with the increase in temperature. This tread is more pronounced for Mal-TPE at a high concentration (Figure 3b). Upon heating from 20 to 65 °C, the corresponding maximum fluorescence intensity is decreased by 90% and 86%, respectively, for Mal-TPE at concentrations of 20 and 40 μ M. Figure 3c shows the changes of maximum fluorescence intensity of Mal-TPE when temperature changes repeatedly between 20 and 55 °C. The result clearly shows the PBS solution of Mal-TPE exhibits reversible fluorescence intensity changes upon alternative heating and cooling processes. This indicates that the aggregates of Mal-TPE in aqueous medium undergo smooth morphological change in response to temperature, thereby allowing the "turn-on/turn-off" model of AIE characteristic.

Dynamic light scattering (DLS) analysis was used to examine the sizes of Mal-TPE aggregates in PBS solution

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at different temperature. As shown in Figure 4a, the size distribution of Mal-TPE is relatively broad at 20 °C. When the temperatures increase to 40 and 60 °C, their size distributions become narrow and particle sizes become small. A schematic illustration of the change in particle sizes during the heating and cooling process is provided in Figure 4b. This phenomenon may be due to the hydrogen bonding interaction within oligosaccharide in Mal-TPE is sensitive to temperature, leading to the increased solubility of amphiphilic Mal-TPE conjugate at high temperature. The Mal-TPE aggregates could be partially dissociated during the heating process. Therefore, the reduced particle sizes of Mal-TPE aggregates weaken their AIE effect, resulting in the decreased fluorescence intensity at high temperature.



Figure 4. (a) DLS measurements of Mal-TPE in PBS solution at 20, 40 and 60 °C; (b) schematic illustration of the size change of Mal-TPE aggregates during heating and cooling process.

In conclusion, a simple amphiphilic AlEgen with thermo-responsive property was presented. The resulting Mal-TPE conjugate emits weak fluorescence in good solvent, and emits strong blue fluorescence in aqueous media, due to its aggregation. The aggregates of amphiphilic Mal-TPE exhibit thermo-responsive behavior, and their sizes decrease with the increase in temperature. The decreased sizes of Mal-TPE aggregates can influence their AIE effect, resulting in temperature-dependent fluorescence intensities. This study provides a new perspective for the construction of fluorescent thermometers based on amphiphilic AlEgens.

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Conflicts of interest

There are no conflicts to declare.

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Amphiphilic maltoheptaose-tetraphenylethene conjugate exhibits AIE effect in aqueous medium and its