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Broadening AIEgen application: rapid and portable sensing of foodstuff hazards in deep-frying oil†

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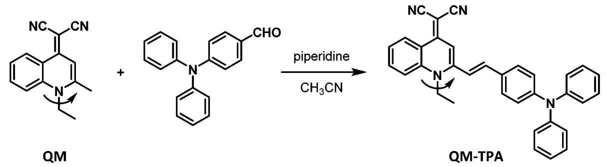
Development of fluorescent probes that can monitor foodstuff hazards is highly desirable. Herein we report the first example of an AIEgen probe (QM-TPA), conjugated by a quinoline–malononitrile (QM) scaffold and triphenylamine unit, for direct sensing of triacylglycerol polymers in frying oil, enabling a rapid probing, on-site analysis, and portable operation in food inspection applications.

As a mainstream in food science, frying is a chemically complex process.[1] Numerous complicated reactions take place during frying roughly, which involve hydrolysis, oxidation, isomerization, and polymerization, thereby resulting in acids, alcohols, aldehydes, ketones, lactones, and polymer products.[2] Among these types of hazards, triacylglycerol (TAG)-based polymers are associated with various diseases, such as digestive and cardiovascular disorders, and act as an important indicator to evaluate food safety.[3] For instance, when the content range of polymers is beyond 10–16%, it has been proposed to determine the rejection of the used frying oil.[3a] Thus, the level quantification of polymers in deep-frying oil is urgently needed.

Up to now, chromatography-based technologies, such as gas chromatography (GC), high performance liquid chromatography (HPLC), GC- or HPLC-mass spectroscopy, have been the current gold standard in food analysis, and the concentration of TAG-based polymers has been also determined by HPLC. Unfortunately, this method suffers from bulky and expensive instruments, complicated pretreatments, and time-consuming procedures, which are inaccessible to the public.[4] Therefore, there is a strong motivation to exploit a novel sensing tool with a rapid and convenient feature for hazards in the field of food safety.

A better alternative strategy to simplify the sensing process is to use a fluorescence technique with high sensitivity since it has revolutionized the way of visualization at nanoscopic levels, along with having broad utility in biotechnology and engineering.[5,6] Notably, aggregation-induced emission luminogens (AIEgens), which can be induced to emit efficiently by aggregate formation, are identified as a type of rising star materials with promising optical-related applications.[7,8] Moreover, the significant characteristic of AIEgens is that their fluorescence intensity has an apparently positive correlation with the degree of aggregation, making them suitable for measurement of viscosity.[7a,9] Nevertheless, AIE-active probes used in frying oil or even foodstuffs have been scarcely reported.

With this in mind, we envisioned that AIEgens may be an ideal candidate to monitor the total levels of polymers in deep-frying oil because the viscosity of this system is enhanced with the increased content of polymers.[1,3a] In this study, we present an AIE probe QM-TPA, and evaluate its sensing performance for hazards (TAG-based polymers) in deep-frying oil. QM-TPA is composed of an AIE-active quinoline–malononitrile (QM)[10] chromophore and an extending π conjugation triphenylamine donor that is used for red-shifting wavelengths (Scheme 1). The response of TAG-based polymers to QM-TPA relies on the alteration ability of viscosity to modulate the optical properties. Specifically, in accordance with the results obtained from HPLC analysis, emission of QM-TPA is switched on during the



QM

QM-TPA

Scheme 1 Synthetic route of AIE-active probe QM-TPA.

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formation of nanoaggregates in deep-frying, indicative of its versatile capabilities and applicability to detection of TAG-based polymers in foodstuff.

The AIE property of QM-TPA was investigated in tetrahydrofuran (THF)/water mixtures with different water fractions (f_w), in which THF is a good solvent and water is a poor solvent for QM-TPA. As shown in Fig. 1a, absorption spectra of QM-TPA were slightly changed with the increase in f_w from 0% to 60%. However, when the f_w was beyond 70%, the absorbance dropped dramatically at 430 nm, which is attributed to the scattering effect of *in situ* generated nanoaggregates. Meanwhile, in agreement with its absorption spectra, QM-TPA is non-emissive in solutions with the f_w ranging from 0% to 60%, while the fluorescence intensity rocketed sharply by about 180-fold from pure THF to the f_w = 90% mixed solution (Fig. 1b and c). *In situ* formation of AIEgen nanoaggregates was measured and confirmed by dynamic light scattering (DLS) and scanning electron microscope (SEM) characterization. At f_w = 90%, the average hydrodynamic diameter of the obtained nanoaggregates was estimated to be *ca.* 160 nm (Fig. 1d) and the SEM image further verified the nanoparticle with corresponding average diameter (Fig. 1e). Furthermore, in the solid state, QM-TPA showed an intensive fluorescence emission under UV light irradiation (Fig. 1f) and about 40 nm red shift in maximum emission from solution to solid powder (Fig. S1 and Table S1, ESI†), which is caused by the fact that QM-TPA aggregated more tightly in solid than solution. All these results demonstrate that probe QM-TPA possesses a typical AIE nature both in aqueous and solid state. Moreover, although the absorption of QM-TPA was not sensitive to solvent polarity, the fluorescence emission showed a significant blue shift with decreasing polarity in that QM-TPA is a typical donor–π–acceptor system (Fig. S2 and S3, ESI†).

Having established the AIE effects of QM-TPA, we turned our attention to its response to the viscosity. We proposed that the restriction of intramolecular motions of the AIEgen in high viscosity solution may hamper its nonradiative decay channels, thus making it highly emissive. By increasing the glycerol to ethanol ratio, the viscosity of the solution increased from 1.2 cP (0 vol% glycerol) to 625 cP (90 vol% glycerol). As expected, the fluorescence intensity of QM-TPA (10 μM) showed a quick and steady enhancement at 610 nm in a viscosity-dependent fashion, and an approximately 26-fold higher fluorescence intensity was observed in the 90 vol% glycerol system than that in the pure ethanol solution (Fig. 2a). Meanwhile, the fluorescence lifetime showed a *ca.* 3.3-fold increase with viscosity increasing from 1.2 to 625 cP (Fig. S4, ESI†). Significantly, we found that the fluorescence intensity has an apparent linear relationship with the solvent viscosity by using the Förster–Hoffmann equation fitting (R^2 = 0.975, Fig. 2b),[11] manifesting that AIE probe QM-TPA is capable of quantitatively sensing the viscosity of the targeted solution.

Encouraged by the desirable fluorescence response of QM-TPA to the high viscosity, we next examined its ability for rapid and portable sensing of the levels of TAG-based polymers in deep-frying oil. The oxidized triacylglycerol monomer (ox-TGM) was formed from the oxidation reaction, and which produced triacylglycerol dimer and oligomer *via* polymerization (Fig. 3a).[3a] Initially, according to Matthäus' frying procedure,[12] 3000 g palm oil was filled into the fryer and then the oil was heated up to 180 °C. 200 g pre-fried potatoes were fried for 180 s, which is defined as one time frying. Twenty operations were carried out

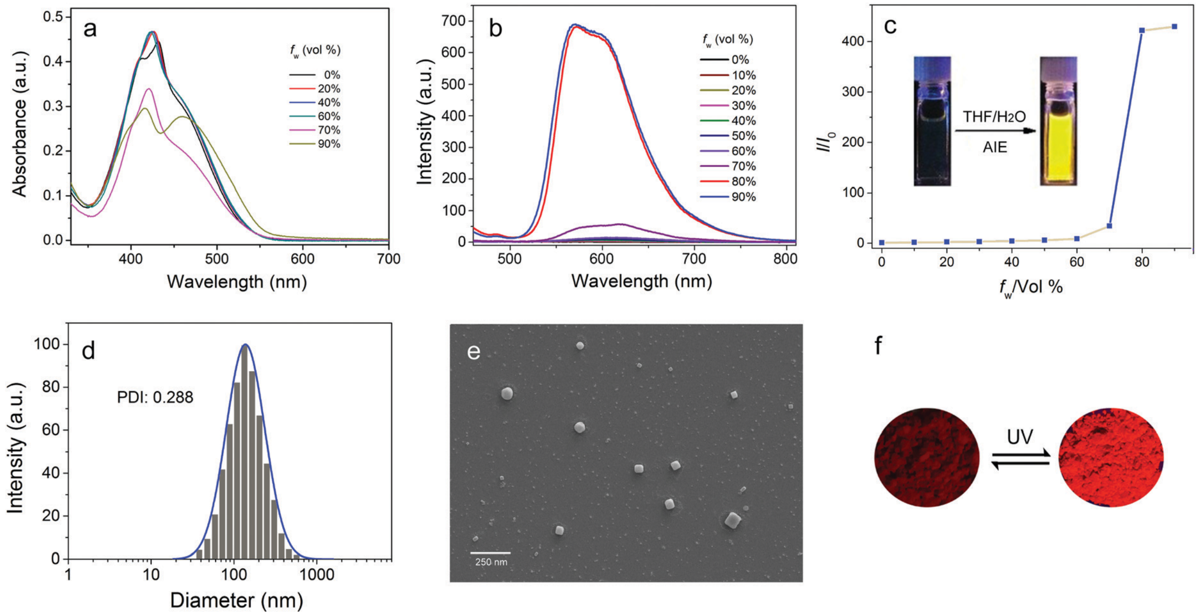

Fig. 1 (a) Absorption and (b) fluorescence spectra of QM-TPA (10 μM) in H_2O/THF mixtures with different water fractions (f_w), λ_{ex} = 430 nm. (c) Plot of relative emission intensity as a function of f_w, λ_{ex} = 430 nm. Inset: Fluorescence photos in pure THF solution and f_w = 90% H_2O/THF mixture of QM-TPA under 365 nm illumination. (d) DLS data and (e) SEM image of nanoaggregates obtained from QM-TPA suspension (f_w = 90%). (f) Photos of QM-TPA (solid powder) under normal light (left) and 365 nm illumination (right), red fluorescence appeared under UV lamp illumination.

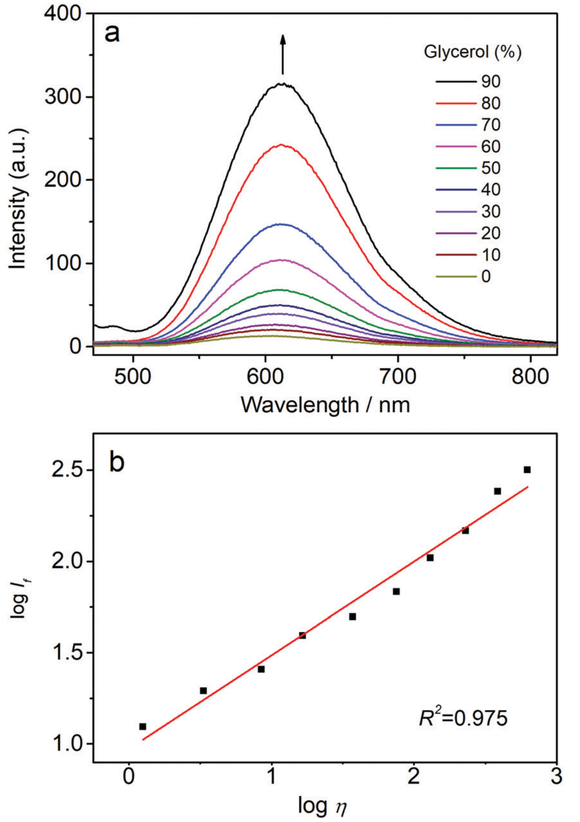

Fig. 2 (a) Fluorescence spectra of QM-TPA (10 μM) with the variation of solution viscosity (glycerol/ethanol mixture), glycerol ratio from 0 to 90 vol%. (b) Linear relationship of $\log I_f$ and $\log \eta$, Förster–Hoffmann equation: $\log I_{614\text{nm}} = C + \log \eta$ (η is the viscosity, I_f is the emission intensity, C is a constant).

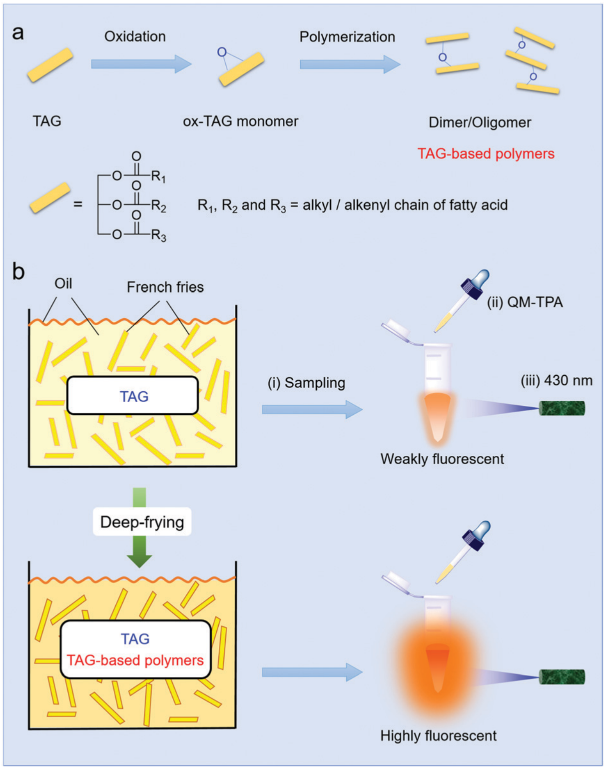

Fig. 3 (a) Chemical reactions in deep frying: TAG first oxidized into oxidized triglycerol monomer, then transformed into TAG-based polymers (dimer or oligomer). (b) Schematic of fluorescence sensing for TAG-based polymers in deep-frying oil with AIEgen probe QM-TPA.

each day with 200 g pre-fried potatoes, keeping the thermal load of the oil at 8 h per day. And the experiment was successively repeated for 5 days. At the end of each day, the oil was cooled down, filtrated and 2 mL of oil were taken for the characterization with the AIEgen probe (Fig. 3b).

Increasing frying times from 0 to 100 times, the maximum fluorescence intensity showed an obvious enhancement in the mixture of oil/ethanol (1/1, v/v) within 1 min, suggesting a rapid response of QM-TPA to oil with different cycle times. Also, the maximum fluorescence intensity increased with the increase in frying frequency (Fig. S5, ESI†). Additionally, the content of TAG-based polymers and viscosity in oil with different frying frequencies were confirmed by HPLC and viscometer measurements, respectively. Both the level of polymers and viscosity became enhanced with the increase in frying frequency, and showed a superior linear relationship as a function of frying frequency (Fig. 4a). With the accumulation of polymers in deep frying, the viscosity of the system increases, leading to the aggregation of probe QM-TPA and yielding highly fluorescent signals. Clearly, the degree of TAG-based polymers was calculated to be 3.5, 6.01, 7.59, 9.27, 11.75, and 13.65% at 0, 20, 40, 60, 80, and 100 frying times, respectively, and correlated linearly with the fluorescence intensity of QM-TPA (Fig. 4b), indicating that the optical intensity could directly reflect the concentration of TAG-based polymers in edible oil. Therefore, AIE-active probe QM-TPA as a portable tool enables rapid sensing of foodstuff hazards, such as TAG-based polymers, in deep-frying oil.

In summary, we have presented an AIEgen probe, QM-TPA, for detection of TAG-based polymers *via* a viscosity-mediated mechanism in frying oil. QM-TPA features a fast fluorescence-enhanced response to TAG-based polymers in deep-frying oil because the increasing viscosity and the interactions between polymers and the AIE-active probe can restrict the intramolecular motion. Superior to the conventional chromatography-based technology, this technique shows rapid response, real-time sensing, and portable operation. Furthermore, our results from the AIEgen probe are well consistent with that of HPLC analysis, the current gold standard in the food industry, indicating the feasibility of QM-TPA in food inspection applications.

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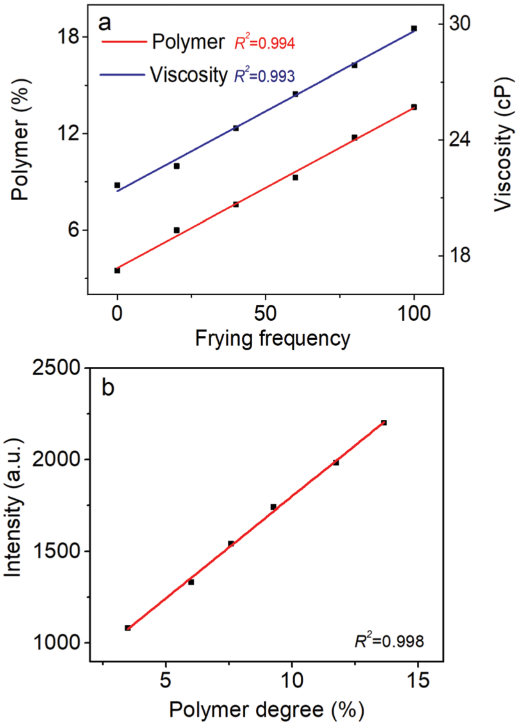

Fig. 4 (a) The degree of polymers and viscosity as a function of frying frequency employed by HPLC and viscometer measurements, respectively. The testing standard of polymers was in accordance with the AOCS method Cd 22-91. (b) Plot of linear relationship between fluorescence intensity at 500 nm and the degree of polymers.

Conflicts of interest

There are no conflicts to declare.

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