



Tuning of the perylene probe excimer emission with silver nanoparticles

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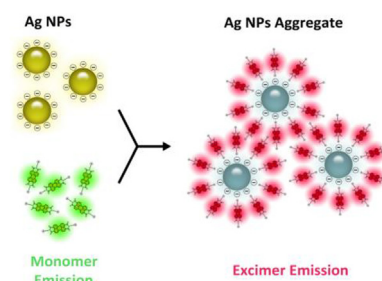
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HIGHLIGHTS

- Silver nanoparticles (Ag NPs) enhanced perylene probe excimer emission is reported for the first time.
- A remarkable emission enhancement of over 1000 fold was obtained compared to anionic polymers and other nanoparticles.
- The excimer emission can be finely tuned by the size of the Ag nanoparticles and the functionalities of the perylene probe.
- A facile ratiometric H₂O₂ fluorescence assay method is demonstrated based on the excimer-monomer emission transition.

GRAPHICAL ABSTRACT



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ABSTRACT

Silver nanoparticles (Ag NPs) enhanced perylene probe excimer emission is reported for the first time. It was observed that strong interactions between the perylene probe and the Ag NPs induced co-aggregation. As a result, a new in situ generated plasmonic absorption band of the Ag NPs at longer wavelength emerged. The monomer emission of the perylene probe was efficiently quenched, and dramatically enhanced probe excimer emission was observed. A remarkable emission enhancement of over 1000 fold was obtained compared to anionic polymers and other nanoparticles. The excimer emission intensity could be finely modulated by the size of the Ag NPs and the functionalities of the perylene probe. The observed Ag NPs enhanced perylene probe excimer emission shows good potential for the development of novel sensing techniques for various bioanalytical applications.

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1. Introduction

Fine tuning of plasmonic interactions of metallic nanostructures has been widely used in sensing. The aggregation of metallic

nanoparticles could create “hot spots” which could enhance the Raman scattering intensity of the adsorbed Raman reporter molecules by many orders of magnitude. And this effect has been used for the development of many sensing techniques [1–5]. The aggregation of metallic nanoparticles (e.g. gold nanoparticles) can cause strong UV–vis absorption spectral changes as a result of the strong plasmon coupling. The assay solution shows clear color changes, and because of the very high molar extinction coefficient (about three orders of magnitude higher than that of organic dye molecules), the colorimetric assay is quite sensitive. Numerous colorimetric sensing strategies based on this principle have been reported [6–10]. In addition, novel applications based on metal enhanced fluorescence, metal enhanced infrared absorption, etc., have all drawn increasing attentions [11–13].

Fluorescence based detection is one of the most commonly used sensing techniques in biotechnology, medical diagnostics, and life science. The enhancement of fluorescence intensity of fluorophores is therefore of great importance for the improvement of detection sensitivity and achieving lower detection limit [14]. Numerous fluorescence based sensing techniques have been developed in recent years. One unique class of fluorescence based assay is to use excimer fluorescence for sensing applications. In many cases when fluorophores are brought into close proximity, the fluorescence of the fluorophore decreases significantly due to the concentration quenching effect. To overcome this problem, two techniques have been developed. One is to use the AIE (aggregation induced emission) effect. Because of the restriction of intramolecular rotations, enhanced fluorescence emission is observed upon fluorophore aggregation [15,16]. The other method relies on excimer emission. When certain types of planar aromatic fluorophores aggregate, the monomer fluorescence emission shows dramatic decrease, and a new excimer emission band at longer wavelength is observed. The excimer emission shows much increased Stokes shift, and has found many applications in various sensing areas [17,18].

Perylene diimide (PDI) derivatives have attracted significant interest in dye and pigment research for a long history due to their outstanding optical and electronic properties [19–21]. They have low-lying LUMO orbitals, prominent photochemical stability, excellent chemical inertness, and high fluorescence quantum yield. In addition, the π -stacked PDI derivatives have strong electronic communications among the individual chromophores in close proximity in both their ground and excited states [22,23]. They have been utilized in organic field-effect transistors, organic photovoltaic materials, organic solar cells, and new fluorescent nanoparticles fabrication [24–27]. Growing number of reports have utilized PDI derivatives as fluorescence probes for tracking, bio-labeling, base-mismatch detection, biomolecule sensing, and bio-imaging [28–32]. An the synergetic effect between the functionalized perylene and nanoparticles has been utilized to improve the sensitivity and selectivity of the sensor [33].

The stacked perylene derivatives can form excimers as a result of the delocalization of excitation energy over multiple chromophores [34–36]. The formation and the emission properties of the perylene excimers have been extensively investigated [37–39]. The excimer states depend strongly on π -stacking distance, transverse and longitudinal displacement among individual chromophores, and the degree of aggregation of the chromophores [40–42]. The excimer emission has distinct large Stokes shift which could substantially reduce the background fluorescence at the detection wavelength, and it can be finely tuned. Nevertheless, few reports have used perylene probe excimer emission for sensing applications [43,44]. The emission intensity is usually quite weak in an aqueous environment, and high concentrations of probe molecules are needed to get the detectable signal, which seriously limits its applications.

In this study, we investigated the interactions between the Ag NPs of different size and a positively charged perylene probe (Probe 1). It was observed that Ag NPs could induce significant excimer emission of Probe 1 (Scheme 1). The intensity of the excimer emission was found to be strongly dependent on the size of the Ag NPs and the functionalities of the perylene probe. A remarkable emission enhancement of over 1000 fold was obtained compared to the anionic polymers and other types of nanoparticles. The Ag NPs tuned perylene probe excimer fluorescence provides a new strategy for the construction of novel fluorescence sensors.

2. Experimental section

2.1. Reagents

3,4:9,10-perylenetetracarboxylic dianhydride (PTCDA) was obtained from Acros (Shanghai, China). *N,N*-dimethyl-1,3-propanediamine, imidazole and 3-propanolamine were purchased from Alfa Aesar (Shanghai, China). Silver nitrate (AgNO_3), 30% hydrogen peroxide (H_2O_2) and methyl iodide (CH_3I) were purchased from Shanghai Chemical Reagent Co. Ltd. (Shanghai, China). Trisodium citrate dihydrate ($\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$) and $\text{NH}_3 \cdot \text{H}_2\text{O}$ were obtained from Beijing Chemical Reagent (Beijing, China). Sodium borohydride (NaBH_4), poly(acrylic acid, sodium salt) (PAAS, average MW 5100) and poly(vinylsulfonic acid, sodium salt) (PVSA, 25 wt % in H_2O , average MW 6115) were purchased from Sigma-Aldrich (Shanghai, China). Sodium dodecyl benzene sulfonate (SDBS) was purchased from Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China). Tetraethyl orthosilicate (TEOS) was obtained from Aladdin (Shanghai, China). $\text{FeS} \cdot \text{O}_4 \cdot 4\text{H}_2\text{O}$ was purchased from Beijing Yili Chemical Reagent (Beijing, China). Probes 1 and 2 were synthesized according to literature procedures [31,43]. All reagents were of analytical grade and used as received. All sample solutions were prepared using water purified with a Millipore Milli-Q A10 filtration system (Billerica, MA, USA). The concentration of the anionic polymers was calculated as the concentration of the repeating unit.

2.2. Instrumentation

UV–vis absorption spectra were obtained with a Cary 50 Bio Spectrophotometer (Varian Inc. CA, USA). Fluorescence spectra were recorded using a Fluoromax-4 spectrofluorometer (Horiba Jobin Yvon Inc. USA). The excitation and emission spectra were both recorded with slit of 5 nm, and with an excitation wavelength of 495 nm. All optical measurements were taken using quartz cuvettes with 10 mm path length at 25 °C. Emission spectra were corrected against the PMT response. Transmission electron microscopy (TEM) images were taken using a JEM-2100F high resolution transmission electron microscope (Philips, the Netherlands) operated at 200 kV. Dynamic light scattering and Zeta potential measurements were performed with a Zetasizer NanoZS (Malvern Instruments, USA). ^1H NMR spectra were obtained with a Bruker AVANCE 600 (600 MHz) Fourier transform NMR spectrometer with chemical shifts reported in parts per million (ppm) relative to tetramethylsilane. Splitting patterns are reported as s (singlet), d (doublet), t (triplet), and m (multiplet). The fluorescence decay curves were obtained with LifeSpec II (Edinburgh Instruments, UK).

2.3. Synthesis of Probe 3

The synthetic route for Probe 3 is shown in Scheme 2 [45,46].

Synthesis of Compound 1: Perylene tetracarboxylic dianhydride (PTCDA, 3.00 g, 7.65 mmol) was added to 5% (w/v) KOH solution (35.0 mL) in a 100 mL three-neck flask and heated at 90 °C for 4 h

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