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COMMUNICATION

Tuning of Polyarylene Ether Nitrile Emission Profile by using Red-emitting Gold Nanoclusters via Fluorescence Resonance Energy Transfer

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

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Fluorescence resonance energy transfer (FRET) between blue fluorescent polyarylene ether nitrile (PEN) and red-emitting gold nanoclusters (Au NCs) has been firstly reported in this work. Consequently, the emission profile of PEN can be readily tuned depending on the loading content of Au NCs.

During the past decades, fluorescent polymers have witnessed ongoing development due to their potential applications in the organic light-emitting diodes,^{1,2} plastic lasers,³ chemical sensors and bioprobes.^{4,5} Compared to the widely used organic fluorescent dyes, the polymeric fluorescent materials are advantageous in the practical device applications, mainly due to their better photo-stability and film-forming capacity. Fluorescent polymer can be roughly classified as two groups: the fluorophore-doped luminescent polymer and intrinsic fluorescent polymeric materials.⁶ The former one is normally synthesized via conjugation of small organic dye molecules or their derivatives into polymer backbone and their fluorescent emission is determined by the doped fluorophore, while the intrinsic fluorescent polymer is prepared via the polymerization of the non-fluorescent monomers and their emission wavelength is usually located in 400 to 500 nm under ultraviolet excitation. Polyarylene ether nitrile (PEN) is one type of special engineering thermoplastic polymer with outstanding thermo-stability (glass transition temperature of ~260 °C), mechanical and dielectric properties.^{7,8} PEN can be synthesized from the nucleophilic substitution polymerization using 2, 6-dichlorobenzonitrile (DCBN) and different aromatic diphenols. Very recently, we have developed a series of intrinsic fluorescent PEN copolymer containing pendant carboxyl group by using phenolphthalein and phenolphthalin (PPL) as the aromatic diphenols.⁹ However, the emission wavelength of the obtained PEN is basically limited in the violet-blue range of 400 nm to 430 nm, which would hinder their practical applications. Therefore, it is of great importance to expand the emission wavelength range of the fluorescent PEN.

Fluorescence resonance energy transfer (FRET) is a well-known photophysical process established between an energy donor and an energy acceptor, where the fluorescent emission profile of this FRET pair can be readily modulated via non-radiative dipole-dipole coupling.¹⁰ The FRET efficiency is strongly dependent on the distance and orientation between donor and acceptor (i.e. inversely proportional with six power of distance), thus any minute changes of distance or relative orientation can be probed by monitoring the fluorescent emission, leading to the widespread application of FRET in biological and chemical research.^{11,12} On the other hand, metal nanoclusters, the emerging nanoparticles in the dimensional range between atoms and nanocrystals, have attracted increasing interests both in basic and applied research mainly due to their molecular like properties, such as quantized charging and luminescence.^{13,14} Particularly, thiolated-protected gold nanocluster is one of the most typical and intensively researched metal nanoclusters due to their ultrafine size, low toxicity, tunable fluorescent emission and good biocompatibility. The thiolated ligand of Au NCs plays an important role in determining their luminescent properties,¹⁵ actually the fundamental principle of the strong luminescence emission of these thiolated-protected Au NCs is the aggregation-induced emission (AIE) of thiolated ligand.¹⁶ Recently, the red-emitting Au NCs with precise structure of Au₂₂(SR)₁₈ was identified and their strong luminescence (quantum yield of 8 %) was attributed to the controlled aggregation of longer thiolated-Au(I) motifs (two RS-[Au-SR]₃ and two RS-[Au-SR]₄) on the surface of prolate Au(0) core (Au₈).¹⁷

In this work, the red-emitting gold nanoclusters (Au NCs), stabilized with the most abundant plasma protein bovine serum albumin (BSA), was synthesised and employed to accept the energy from blue fluorescent PEN in the solution thanks to their good spectral overlap, thus the photoluminescence of Au NCs/PEN complex can be readily tuned by the fluorescent resonance energy transfer (FRET) between PEN and Au NCs.

As shown in Figure 1a, the PEN was synthesized via the condensation polymerization of 2, 6-dichlorobenzonitrile (DCBN)

and bisphenol A (BPA)/phenolphthalin (PPL) (1:1, molar ratio). In a typical synthesis, DCBN (44 g, 0.26 mol), BPA (29 g, 0.13 mol), PPL (41 g, 0.13 mol), anhydrous K_2CO_3 (70 g, 0.5 mol) were dissolved in *N*-methyl-2-pyrrolidone (NMP) solvent (170 mL) supplemented with 75 mL toluene in a 250 mL three-neck round bottom flask equipped with a Dean-Stark trap, condenser, mechanical stirrer and thermometer. The water produced during the reaction was removed by heating mixture at 140-150 °C via azeotropic distillation with toluene (35 mL), and then the mixture was heated at ~200 °C with continuous stirring for 5 h, followed by pouring the mixture solution into ethanol to precipitate the copolymer. Further, the raw product was crushed, acidified with hydrochloric acid, washed with boiling water and dried in a vacuum oven overnight to finally obtain purified white powder (yield: 80%). The chemical structures of copolymer (see Figure 1b) was then characterized with FTIR (2969 cm^{-1} : stretching vibration of $-CH_3$, 2231 cm^{-1} : symmetrical stretching vibration of $-CN$, 1243 cm^{-1} : phenylene ether stretching vibration) and NMR (1H NMR, DMSO- d_6 , δ =12.98 ppm: carboxyl proton in PPL, δ =6.71 ppm: proton linked to the tertiary carbon, δ =1.67 ppm: methyl protons in BPA section). The weight average molecular weight (M_w), number average molecular weight (M_n) and polydispersity index (M_w/M_n) of resulted PEN were measured with gel permeation chromatography (GPC) using polystyrene as standard to be 11904, 28337 and 2.38, respectively. The obtained PEN was dissolved in the *N,N*-dimethylformamide (DMF) solvent (1.5 mg/mL) for the fluorescent measurement. The sub-nanometer sized red-emitting Au NCs were prepared according to the published work¹⁸ using the gold precursors ($HAuCl_4$, 5 mL, 10 mM) in the presence of BSA protein (5 mL, 50 mg/mL) and sodium hydroxide (NaOH, 0.5 mL, 1 M) aqueous solution. The obtained red-emitting Au NCs are characterized with high resolution TEM imaging (see Figure 1c), confirming their ultrafine size in the sub-nanometer range. Interestingly, the DMF solution of PEN is compatible to the aqueous solution of Au NCs, as the mixture solution of equal volume ratio is quite homogenous without any aggregation observed and the UV-Vis absorption spectra are nearly identical at least for five days (see Figure S1 in the ESI). This solution compatibility is attributed to the miscibility of DMF solvent/ H_2O , ultrafine size of Au NCs and slight hydrophilicity of PEN containing pendant carboxyl groups.

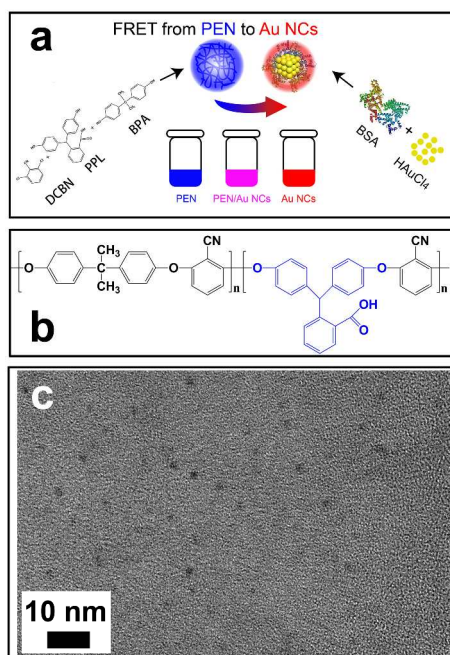


Figure 1. The illustration of FRET from donor blue PEN to acceptor red-emitting Au NCs (a), chemical structure of PEN (b) and high resolution TEM imaging of synthesised Au NCs (c). DCBN is 2, 6-dichlorobenzonitrile, PPL is phenolphthalin, BPA is bisphenol A, and BSA is bovine serum albumin.

The fluorescent excitation spectra and emission spectra of obtained PEN and Au NCs in solution were recorded using a fluorescence spectrophotometer (F-4600, Hitachi). As shown in Figure 2a, the maximum excitation wavelength of PEN is detected at 365 nm, while the excitation spectra of Au nanoclusters show the maximum fluorescent intensity at 502 nm. When these two solutions are excited at 365 nm, the maximum emission wavelength of PEN and Au NCs is 431 nm and 675 nm, respectively (Figure 2b). Besides, a small fluorescent peak around 460 nm is detected from Au NCs aqueous solution, which is attributed to the weak fluorescence of BSA protein on the surface of Au NCs. As a photo-physical process involving non-radiative energy transfer between two neighbour fluorophore, fluorescence resonance energy transfer (FRET) can be employed to fine-tune the fluorescence emission profile.^{10, 12} The good overlap between emission spectrum of PEN and excitation spectrum of Au NCs therefore enables the effective FRET from PEN to Au NCs.

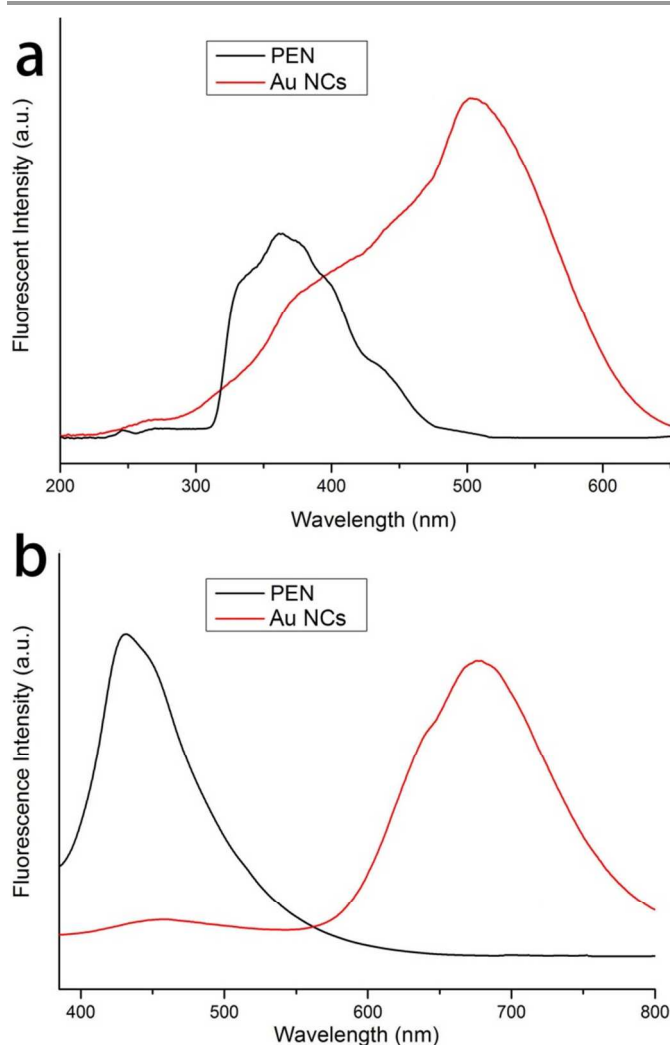


Figure 2. The fluorescent excitation spectra (a) and emission spectra (b) of the PEN polymer solution in DMF and Au NCs aqueous solution, the excitation wavelength for the fluorescent emission measurement was 365 nm.

Next, the photoluminescence spectra of PEN/Au NCs mixture solution with different relative concentration ratios were recorded to confirm the FRET between PEN and Au NCs. It should be noted that the BSA protein on the surface of Au NCs also exhibited weak blue fluorescence under the same excitation condition (see Figure 2b), and different solvents of DMF and H₂O were involved in the PEN and Au NCs solution, respectively, thus the influence of H₂O and BSA to the fluorescence of PEN should be determined. As shown in Figure S2 in the electronic supplementary information (ESI), the fluorescent spectra of PEN polymer in DMF solution is nearly independent of the presence of H₂O, while the enhanced and blue shifted PEN fluorescence emission is observed in the presence of low content of BSA protein. In addition, the maximum emission wavelength of PEN solution in DMF can be readily modulated in the range of 400 to 460 nm in the presence of different concentrations of BSA: blue shifted with a lower BSA concentration while red shifted with a higher BSA concentration (see Figure S3 in the ESI). These complex fluorescent modulations could be resulted from the potential non-covalent interactions (electrostatic, hydrogen bond, etc.) between BSA and carboxylated PEN in the solution phase, the research work concerning the exact mechanism is currently in progress and the details would be reported in the future.

Given the fact that the BSA influence on the PEN fluorescence was declined for a higher BSA concentration (*i.e.* larger Au NCs/PEN volume ratio), the FRET experiments were conducted by adding different volume (0.5 mL, 1 mL, 1.5 mL, 2 mL) of PEN solution into 2 mL of Au NCs solution to minimize the interference from BSA. As shown in Figure 3, the Au NCs, Au NCs/PEN (7:3, volume ratio), Au NCs/PEN (5:5, volume ratio) and PEN polymer solution show intense red, rose, pink and blue color under the 365 nm UV-light irradiation, indicating that the relative fluorescent intensity of Au NCs and PEN polymer can be readily modulated via the energy transfer process in the solution phase.

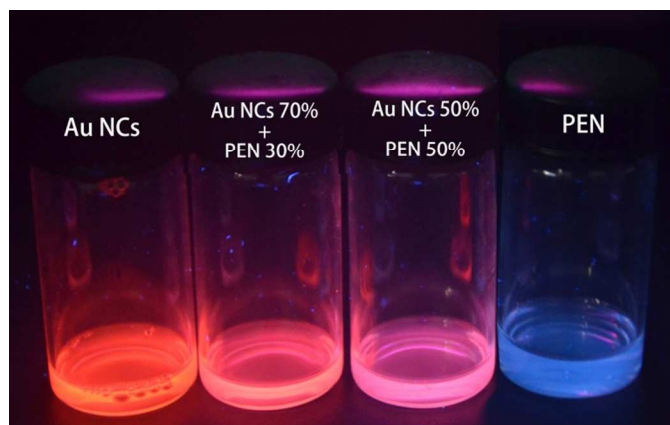


Figure 3. The digital photo of Au NCs, Au NCs/PEN (7:3, volume ratio), Au NCs/PEN (5:5, volume ratio) and PEN polymer solution under the 365 nm UV light irradiation.

The fluorescent emission spectra of the Au NCs, Au NCs/PEN mixtures with different compositions and PEN

polymer solutions were recorded under the excitation wavelength of 365 nm. As shown in Figure 4, the as-synthesized Au NCs show a broad fluorescent peak centred at 675 nm, while a sharper fluorescent emission peak at 432 nm is detected for PEN polymer. Interestingly, as the PEN polymer donor concentration increases, the fluorescent intensity of Au NCs is obviously increased due to the enhanced radiationless intermolecular energy transfer between PEN and Au NCs. For instance, the fluorescent intensity of 2 mL PEN solution at 430 nm is 240 a.u., while the intensity is sharply decreased to 40 a.u. in the presence of same quantity of Au NCs (2 mL PEN + 2 mL Au NCs), which indicates that part of energy is transferred from excited PEN macromolecular to Au NCs, leading to three times enhancement of Au NCs fluorescence at 675 nm in the PEN/Au NCs complex when compared to the pure Au NCs solution. Since the relatively low concentration of BSA has strong influences on the PEN fluorescence, the FRET experiments using lower Au NCs/PEN concentration ratios have been conducted as well, from the results shown in Figure S4 in the ESI, the fluorescent emission of Au NCs in the PEN/Au NCs complex is always proportionally enhanced when the relative Au NCs volume concentration is higher than 30%, indicating that the energy transfer is gradually saturated at this threshold value, after which the totally different fluorescence spectra of Au NCs/PEN complex are observed. Although the exact mechanism concerning the interaction of PEN and Au NCs pair is yet unclear, the potential non-covalent intermolecular interactions (e.g. electrostatic interaction, hydrogen bonding, Van der Waals forces) between carboxylated PEN and BSA protein grafted on the surface of Au NCs would be the major reason, because all the fluorescent measurement in this study were conducted by physically mixing the two solutions and immediately tested in a short time scale (less than 1 min) where the covalent interaction is unlikely to be established. On the other hand, the Au NCs aqueous solution is negatively charged (zeta potential of -30.1 mV) due to the presence of BSA protein, thus the electrostatic repulsion between surface protein BSA and carboxylated PEN contributes to the long term stability of the PEN/Au NCs mixtures solution (without any aggregation or variation of UV-Vis spectroscopy as seen from Figure S1 in ESI). Given the surface electrical charge of BSA protein can be readily modulated via pH value, small amount of concentrated hydrochloric acid (10 μ L, 1 M) was added into 2 mL PEN/Au NCs mixture solution (70:30, volume ratio) to further decrease the distance between FRET pair by attenuating their electrostatic repulsion, thus the FRET efficiency can be further enhanced, which finally leads to a brighter color from PEN/Au NCs mixture after addition of HCl (see Figure S5 in the ESI). By combining the results from Figure 3 and Figure 4, it is believed that the rational fluorescence modulation of PEN polymer/Au NCs complex can be realized via the FRET between PEN and Au NCs as long as the relative Au NCs/PEN volume concentration ratio is larger than 30%.

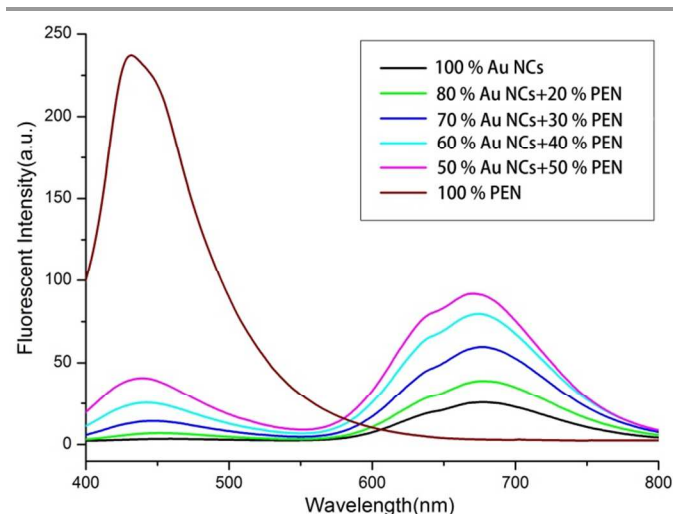


Figure 4. The fluorescent emission spectra of 2 mL Au NCs, four Au/PEN mixtures with different compositions and 2 mL PEN polymer solution. The excitation wavelength is 365 nm.

Conclusions

The blue fluorescent PEN polymer and red-emitting gold nanoclusters were synthesized and the fluorescence resonance energy transfer was established using PEN polymer and Au NCs as the energy donor and acceptor, respectively. Consequently, the fluorescence emission of the PEN/Au NCs complex can be readily modulated in the solution phase depending on their relative concentration. To our best knowledge, this is the first report involving the FRET between intrinsic fluorescent polymer PEN and gold nanoclusters. However, the FRET of PEN/Au NCs complex is only observed at a higher volume concentration of Au NCs ($\geq 30\%$) in the present work, because the PEN polymer fluorescence is dramatically changed in the presence of low concentration of BSA protein on the surface of obtained Au NCs. Therefore, more detailed work will be conducted in the future as follow: the modification the chemical structures of PEN polymer in order to minimize the fluorescence interference from BSA protein, the appropriate covalent chemistry should be employed to finely control the distance and the relative orientation between PEN and Au NCs, which will further improve the FRET efficiency between PEN and Au NCs pair and therefore pave the way for their future sensing applications.

Acknowledgements

The authors gratefully thank the financial support from National Natural Science Foundation of China (Project No. 51173021, No. 51373028, No. 51403029), “863” National Major Program of High Technology (2012AA03A212) and the Fundamental Research Funds for the Central Universities (ZYGX2013J121). The authors also appreciate Dr. Xiao Tong Zhen from KLATM of University of Southwest Jiaotong University for his kind assistance in the TEM characterization.

Notes and references

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Electronic Supplementary Information (ESI) available: [Stability test of UV-Vis absorption of PEN/Au NCs for five days, Fluorescent emission spectra of control samples]. See DOI: 10.1039/c000000x/

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