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Thermoresponsive silver/polymer nanohybrids with switchable metal enhanced fluorescence[†]

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In this communication we describe a new approach to the fabrication of fluorescent silver/polymer nanohybrids with thermoswitchable metal enhanced fluorescence (MEF). By manipulating a soft polymer spacer between the silver nanoparticles and the fluorophores a tunable MEF was achieved.

Fluorescence is a promising tool for biological labeling and sensing.¹ Since Kümmerlen *et al.*² confirmed that fluorescent intensity can be enhanced by silver island films, many studies have been conducted on methodologies to achieve enhanced fluorescence, including metal-enhanced fluorescence (MEF) techniques. MEF phenomena have been observed with varied plasmonic nanostructured materials such as silver,^{3,4} copper,⁵ gold,⁶ aluminium,⁷ zinc⁸ and chromium.⁹ Using these metals, fabrication of a variety of fluorescent functional nanoparticles and nanobioconjugates has been reported.

MEF usually results from the interaction between fluorophores in an excited state and the surface plasmon resonance of metal particles. The distance between the fluorophore and the metal surface is critical to achieve optimal MEF. It is noteworthy that the optimal distance for obtaining maximal MEF depends on the nature of both the metal surface and the fluorophore. Accordingly, the reported distances vary from 5 to 75 nm.^{2,4,7,10} Nanoparticles with metallic cores and various semiconducting shells *e.g.* polyelectrolytes,⁴ biomolecules,¹¹ and silica^{10,12} are suitable for designing systems with a tunable MEF.

Metal nanoparticles can be endowed with tailored compatibility and versatile functionality upon modification with various functional groups such as thiol,¹³ pyridine,¹⁴ and carboxylic acids.¹⁵ Dithioester or trithiocarbonate terminal moieties have also been employed to graft homo- or co-polymer chains onto metal nanoparticles *via* metal–sulfur coordination.¹⁶ Poly-(*N*-isopropylamide) (PNIPAM) is a thermoresponsive polymer

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that can undergo thermo-triggered morphology transition behavior, during which the polymer chain conformation changes at lower critical solution temperature (LCST).¹⁷ The thermoresponsive properties of PNIPAM can be exploited to design fluorescent nanohybrids with a soft polymer spacer between the silver nanoparticle (AgNP) and a fluorophore to achieve thermo-controlled MEF.

As illustrated in Scheme S1 (ESI⁺) the preparation of fluorescent nanohybrids was achieved in three steps: first, synthesis of AgNPs and a block copolymer of PNIPAM with polyacrylic acid (PAA), PNIPAM-b-PAA; second, the attachment of PNIPAM-b-PAA onto AgNPs via Ag-sulfur coordination, leaving the PAA block sitting on the outer surface of the particle: third, covalent attachment of rhodamine B (RB) on the particle surface in the presence of N, N'-dicyclohexyl carbodiimide (DCC) and 4-dimethyl amino pyridine (DMAP). PNIPAM-b-PAA was obtained from the hydrolysis of a block copolymer comprised of PNIPAM and poly(tert-butyl acrylate) (PtBA), PNIPAM-b-PtBA (synthesized via reversible addition fragmentation chain transfer (RAFT) polymerization¹⁸), in the presence of trifluoroacetic acid. The successful synthesis of PNIPAM-b-PtBA and PNIPAMb-PAA was evidenced by 1HNMR (Fig. S2, ESI[†]). The living radical RAFT mechanism preserves high end-group integrity with trithiocarbonate end groups left intact for attaching chains onto AgNPs, leaving PAA at the outer surface available for covalent coupling with the fluorophore, RB (Fig. 1). RB was first tailored with hydroxyl groups to facilitate esterification coupling with PAA (Fig. S1, ESI[†]).

The successful modification of AgNPs with PNIPAM-*b*-PAA and RB was evidenced by TEM and polarization microscopy. As shown in Fig. 2a the polymer corona can be clearly observed



Fig. 1 A schematic showing a fluorescent silver nanohybrid with thermoresponsive PNIPAM spacer, exhibiting thermo-controlled MEF.

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Fig. 2 Transmission electron microscopy (TEM) image (a) and polarization microscopy (b) of the fluorescent silver nanohybrids (phosphotungsten acid was used as contrast agent for TEM imaging).

around the particles (with the assistance of phosphotungsten acid contrast agent). The polarization microscopy showed a red corona around the particles, evidencing the successful attachment of the RB fluorophore (Fig. 2b). It is noteworthy that the polarization microscopy cannot visualize nano-sized particles and the observed are mostly particle aggregates.

We designed a flexible PNIPAM spacer between the fluorophores and AgNPs knowing that PNIPAM is a thermosensitive polymer with a LCST in water of ca. 32 °C. The critical transition can be exploited to vary the distance between AgNP and RB, leading to a variable MEF. As shown in Fig. 3 the nanohybrids fabricated with a PNIPAM spacer (having a degree of polymerization (DP) 300) exhibited enhanced fluorescence (with a MEF factor of 3.7) at temperatures below the LCST. Furthermore, a reversible MEF phenomenon was observed when the solution temperature was cycled below and above the LCST (Fig. 3 inset). We also investigated the influence of molecular weight of PNIPAM on the MEF while maintaining other experimental conditions constant. As shown in Fig. 4 when the PNIPAM was designed with a DP of 300, the highest MEF factor was achieved. The fluorescent nanohybrids tailored with PNIPAM spacers with either higher or lower DP exhibited sub-optimal MEF values.

It is well-known that polymeric chains are flexible in solution and a geometrical length is difficult to define. Dynamic light scattering can be used to analyze particle sizes and was therefore exploited to analyze the fluorescent nanohybrids. As shown in Fig. S3 (ESI[†]) a diameter difference of 30 nm was revealed for the



Fig. 3 Fluorescent emission spectra of the rhodamine B modified AgNPs (DP = 300) at 20 and 40 °C in an aqueous medium. The inset shows switchable fluorescence behavior upon temperature cycling.



Fig. 4 The MEF factors (ratio of the fluorescence at 20 °C to that at 40 °C) obtained with fluorescent nanohybrids with PNIPAM spacers of different molecular weight (expressed as degree of polymerization on the *x*-axis).

nanohybrids (with PNIPAM of DP 300) in aqueous suspensions below and above the LCST. It is evident that the LCST affects the spacer length thereby inducing MEF variation. If we hypothesize that the theoretical length of PNIPAM (DP = 300) is *ca*. 75 nm the conformation of PNIPAM chains in an aqueous medium is consistent with a coiled morphology (as observed by others).^{17,19} We are currently investigating the dynamic chain conformations of PNIPAM using fluorescent probes.

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Notes and references

- P. Alivisatos, *Nat. Biotechnol.*, 2004, **22**, 47; W. C. W. Chan and S. Nie, *Science*, 1998, **281**, 2016; M. E. Åkerman, W. C. W. Chan, P. Laakkonen, S. N. Bhatia and E. Ruoslahti, *Proc. Natl. Acad. Sci.* U. S. A., 2002, **99**, 12617; Y. He, Z. H. Kang, Q. S. Li, C. H. A. Tsang, C. H. Fan and S. T. Lee, *Angew. Chem.*, 2009, **121**, 134; J. R. Lakowicz, *Anal. Biochem.*, 2001, **298**, 1; F. Ercole, T. P. Davis and R. A. Evans, *Polym. Chem.*, 2010, **1**, 37.
- 2 J. Kümmerlen, A. Leitner, H. Brunner, F. R. Aussenegg and A. Wokaun, *Mol. Phys.*, 1993, 80, 1031.
- 3 W. H. Weber and C. F. Eagen, *Opt. Lett.*, 1979, 4, 236; K. Aslan, Z. Leonenko, J. R. Lakowicz and C. D. Geddes, *J. Phys. Chem. B*, 2005, 109, 3157.
- 4 K. Kim, Y. M. Lee, J. W. Lee and K. S. Shin, *Langmuir*, 2009, **25**, 2641.
- 5 Y. Zhang, K. Aslan, M. J. R. Previte and C. D. Geddes, *Appl. Phys. Lett.*, 2007, **90**, 173116.
- 6 S. Nathali, M. Alexandre, M. Sergey, J. Jean-Claude and N. Igor, *Biopolymers*, 2000, 57, 325.
- 7 K. Ray, M. H. Chowdhury and J. R. Lakowicz, *Anal. Chem.*, 2007, **79**, 6480.
- 8 K. Aslan, M. J. R. Previte, Y. Zhang and C. D. Geddes, J. Phys. Chem. C, 2008, 112, 18368.
- 9 R. Pribik, K. Aslan, Y. Zhang and C. D. Geddes, J. Phys. Chem. C, 2008, 112, 17969.
- 10 K. Aslan, M. Wu, J. R. Lakowicz and C. D. Geddes, *J. Am. Chem. Soc.*, 2007, **129**, 1524; M. Lessard-Viger, M. Rioux, L. Rainville and D. Boudreau, *Nano Lett.*, 2009, **9**, 3066; L. Guo, A. Guan, X. Lin, C. Zhang and G. Chen, *Talanta*, 2010, **82**, 1696; D. Cheng and Q. H. Xu, *Chem. Commun.*, 2007, 248.
- 11 K. Aslan, J. Huang, G. M. Wilson and C. D. Geddes, J. Am. Chem. Soc., 2006, 128, 4206.
- 12 K. Aslan, J. R. Lakowicz, H. Szmacinski and C. D. Geddes, J. Fluoresc., 2004, 14, 677.

- 13 C. J. Sandroff, S. Garoff and K. P. Leung, *Phys. Lett.*, 1983, 22, 547.
- 14 J. A. Creighton, Surf. Sci., 1983, 124, 209.
- 15 M. Moskovits and J. S. Suh, J. Am. Chem. Soc., 1985, 107, 6826.
- 16 A.-S. Duwez, P. Guillet, C. Colard, J.-F. Gohy and C.-A. Fustin, *Macromolecules*, 2006, **39**, 2729; C. Boyer, M. R. Whittaker, C. Nouvel and T. P. Davis, *Macromolecules*, 2010, **43**, 1792;

J. Liu, E. Setijadi, Y. Liu, M. R. Whittaker, C. Boyer and T. P. Davis, Aust. J. Chem., 2010, 63, 1245.

- 17 F. M. Winnik, Polymer, 1990, 31, 2125.
- 18 C. Boyer, V. Bulmus, T. P. Davis, V. Ladmiral, J. Liu and S. Perrier, *Chem. Rev.*, 2009, **109**, 5402.
- 19 C. Boyer, M. H. Stenzel and T. P. Davis, *J. Polym. Sci., Part A: Polym. Chem.*, 2010, **49**, 551; H. Mao, C. Li, Y. Zhang, D. E. Bergbreiter and P. S. Cremer, *J. Am. Chem. Soc.*, 2003, **125**, 2850.