Aqueous self-assembly of amphiphilic nanocrystallo-polymers and their surface-active properties

Kwang-Suk Jang,†[a] Hyun Jin Lee,†[a] Hee-Man Yang,[a] Eun Jung An,[a] Tae-Hwan Kim,[b] Sung-Min Choi[b] and Jong-Duk Kim*[a]

[a] *Department of Chemical and Biomolecular Engineering (BK21 Graduate Program), Korea Advanced Institute of Science and Technology, Daejeon 305-701, Republic of Korea. E-mail: jdkim@kaist.ac.kr*

[b] *Department of Nuclear and Quantum Engineering, Korea Advanced Institute of Science and Technology, Daejeon 305-701, Republic of Korea.*

† These authors contributed equally to this work.

ESI 1. Confirmation of synthesis of polymers.

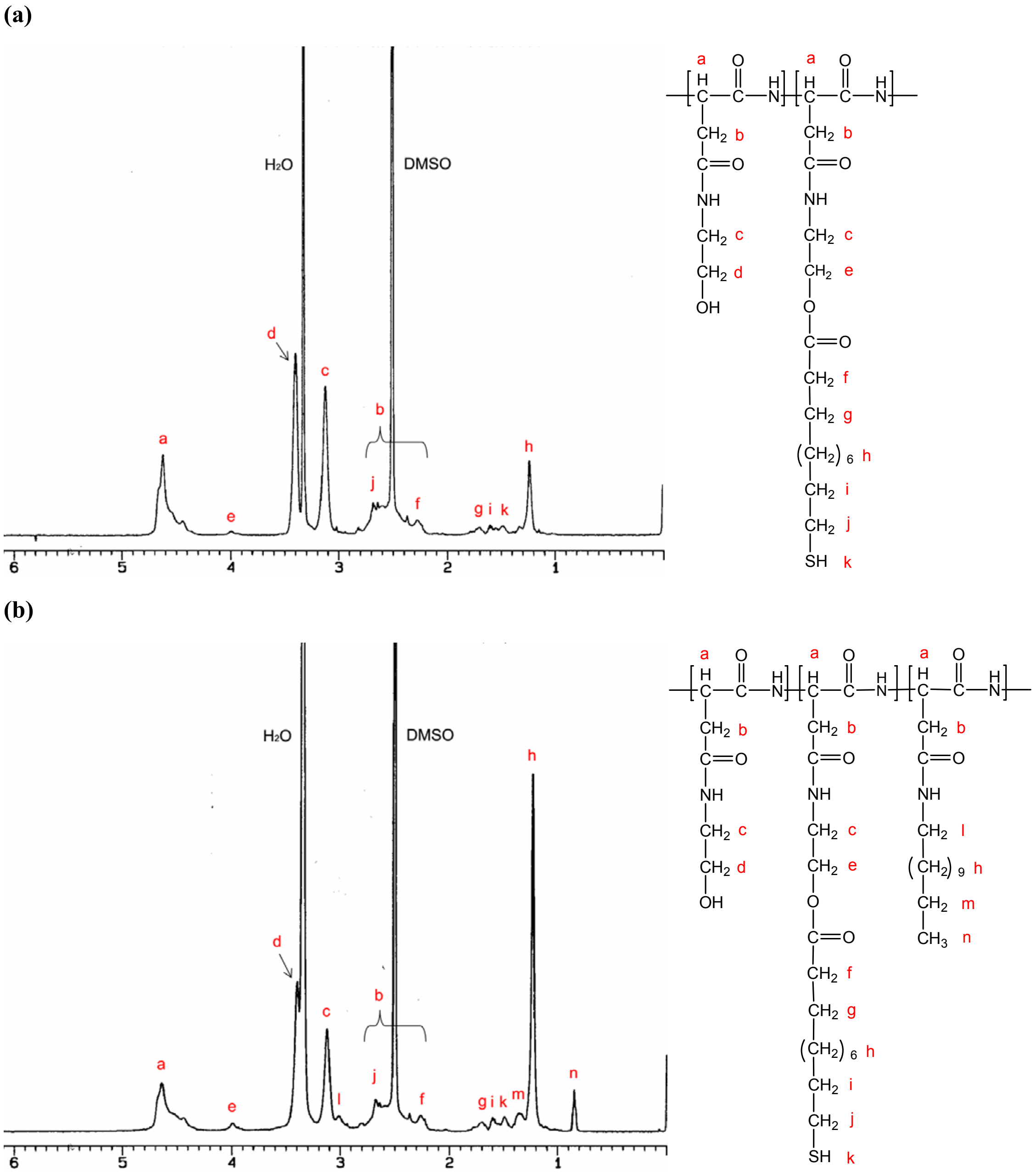


Fig. 1S. ^{1}H NMR spectra of (a) P-*g*-C_{11}SH and (b) P-*g*-C_{12}-C_{11}SH 1.

ESI 2. Synthesis of Dodecanethiolate-Protected Au Nanocrystals. Au nanocrystals were synthesized as follows.[1-3] 0.31g of $HAuCl_4$ was added to a solution of 1.5g of tetraoctylammonium bromide in 80 mL of toluene. After vigorous stirring, 0.092g of dodecanethiol was added. The solution was vigorously stirred for 10 min and 0.38g of sodium borohydride in 25 mL of DDI water was then added immediately. After stirring for 3 hr, upper organic phase was collected and the solvent was removed by rotary evaporation. Finally, samples were washed with ethanol and acetone 3-4 times.

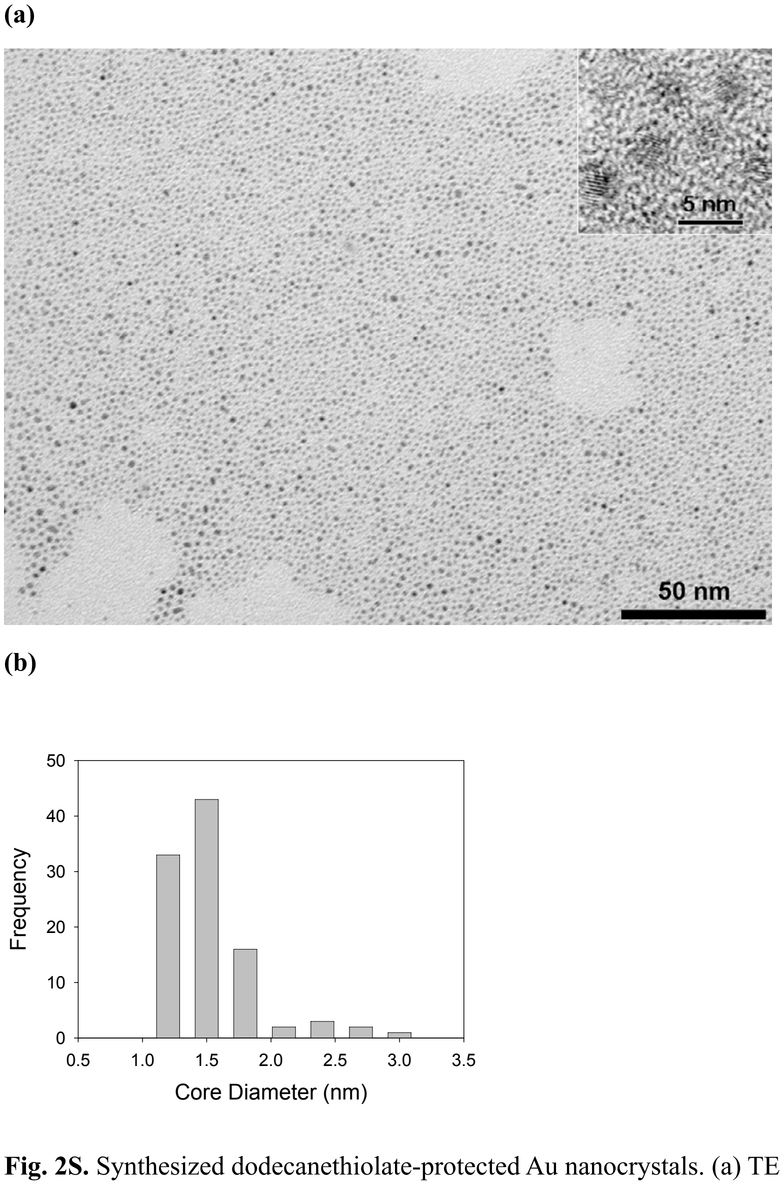


Fig. 2S. Synthesized dodecanethiolate-protected Au nanocrystals. (a) TEM images. (b) Size histogram.

ESI 3. Small-angle XRD pattern of spherical aggregates self-assembled from P-*g*-Au NC. Uniformly close-packed nanocrystals in the core of spherical aggregates were confirmed by small-angle XRD measurement. After the sample was prepared as dry powder form by lyophilization of aggregate solution, small-angle XRD measurement was performed by using a RIGAKU D/MAX-2500 with CuK$_\alpha$ radiation (λ=0.154 nm).

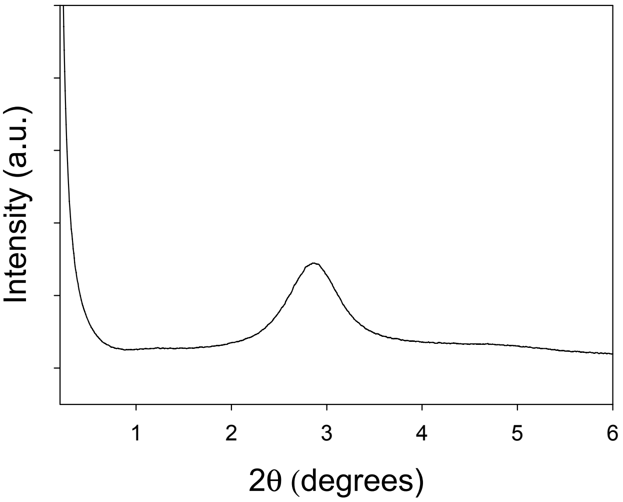


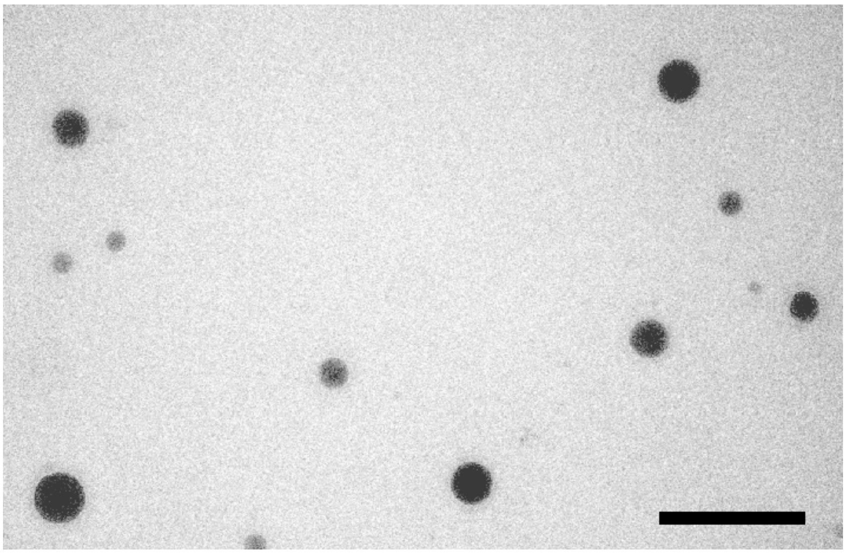
Fig. 3S. Small-angle XRD pattern of spherical aggregates self-assembled from P-*g*-Au NC.

ESI 4. Self-assembly of PHEA-*g*-CdSe/ZnS QDs with surface-active properties. In order to study the surface-active properties of nanocrystallo-polymers, we prepared another type of nanocrystallo-polymer, PHEA grafted with hydrophobic quantum dots (QDs). QDs are semiconductor nanocrystals having discrete energy levels. QDs have been extensively studied during the past decade due to their unique optical properties and their applicability to a numerous areas including biological field.[4,5] Compared to traditional organic dyes, QDs have significant advantages in terms of optical properties. QDs have high quantum yield, broad absorption and narrow, tunable, symmetric emission, and high resistance to photobleaching and chemical degradation.[4,5] For the QD conjugation, CdSe/ZnS QDs were purchased from Evident Technologies (Troy, NY). These QDs have an emission peak around 490 nm and a crystal diameter of approximately 1.9 nm. Because the QDs are coated with trioctylphosphine oxide (TOPO), they have hydrophobic surface property. Thiolated ligands can be easily attached to the surface of CdSe/ZnS QDs by ligand place-exchange,[4-8] and thus P-*g*-C_{11}SH was also used for the preparation of PHEA grafted with TOPO-protected CdSe/ZnS QDs (P-*g*-QD).

The prepared QD-grafted polymers are also amphiphiles and have surface-active properties. Fig. 4S shows TEM images of spherical aggregates self-assembled from P-*g*-QD in aqueous solution. Hydrophobic CdSe/ZnS QDs are tightly packed inside a self-aggregate, forming a core. The D_h of the aggregates measured by DLS is 138.2 nm. This is larger than the diameter of spherical aggregates of Au nanocrystallo-polymers. This is due to the larger size of the hydrophobic component. In addition to morphological similarities, the prepared amphiphilic QD-grafted polymers also show surfactant-like properties. After addition of oil to an aqueous solution of the aggregate and vigorous stirring, they form a liquid mixture without phase separation. Added oil should be located in the hydrophobic core of the aggregates, swelling the core in a manner similar to microemulsions. Fig. 5Sa shows the hydrodynamic mean diameters of self-aggregates from P-*g*-QD swollen by chloroform. The concentration of P-*g*-QD was fixed at 5 mg/mL, and 0, 1, 2, 3 weight % of chloroform was added and vigorously stirred. As the added amount of chloroform is increased, the diameter of the self-aggregates increases.

The core swelling was also verified by fluorescence measurement (Fig. 5Sb). The self-aggregates without chloroform have very low fluorescence emission intensity around a wavelength of 490 nm. The gradually reduced fluorescence emission is due to the fluorescence self-quenching of the QDs.[9-11] Fluorescence self-quenching is a special case of static quenching where fluorephores within a critical distance of each other act as perfect traps. In the core of the self-aggregates, QDs with hydrophobic surfaces are close-packed due to the hydrophobic effect, as shown in Fig. 4S. In a mixture of THF and ethanol, P-*g*-QD cannot form self-aggregates and exhibit high fluorescence emission intensity around a wavelength of 490 nm without fluorescence quenching. However, the arrangement of QDs and their optical interactions were controlled by oil addition (Fig. 5Sc). The fluorescence intensities around a wavelength of 490 nm gradually increase as the amount of added chloroform is increased (Fig. 5Sb). The reduced self-quenching should be due to the increased inter-QD distance by the core swelling. When adding more than 4 weight % of chloroform, they form a milky suspension and the fluorescence intensity decreases sharply because of light scattering. This is indicative of dynamic self-assembling and surface-active properties of the amphiphilic nanocrystallo-polymers.

(a)



(b)

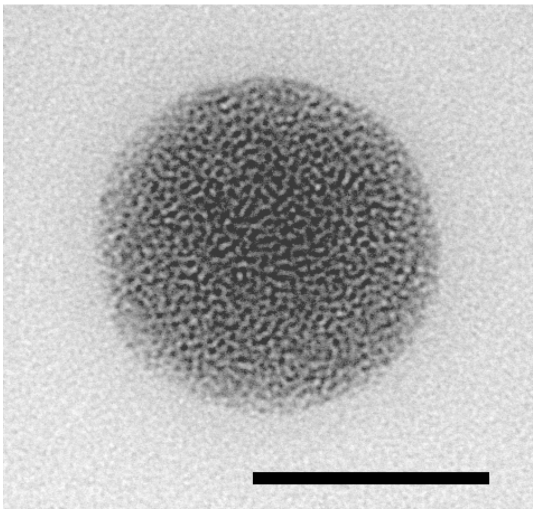


Fig. 4S. TEM images of spherical aggregates self-assembled from P-*g*-QD. Scale bars: (a) 200 nm; (b) 80 nm.

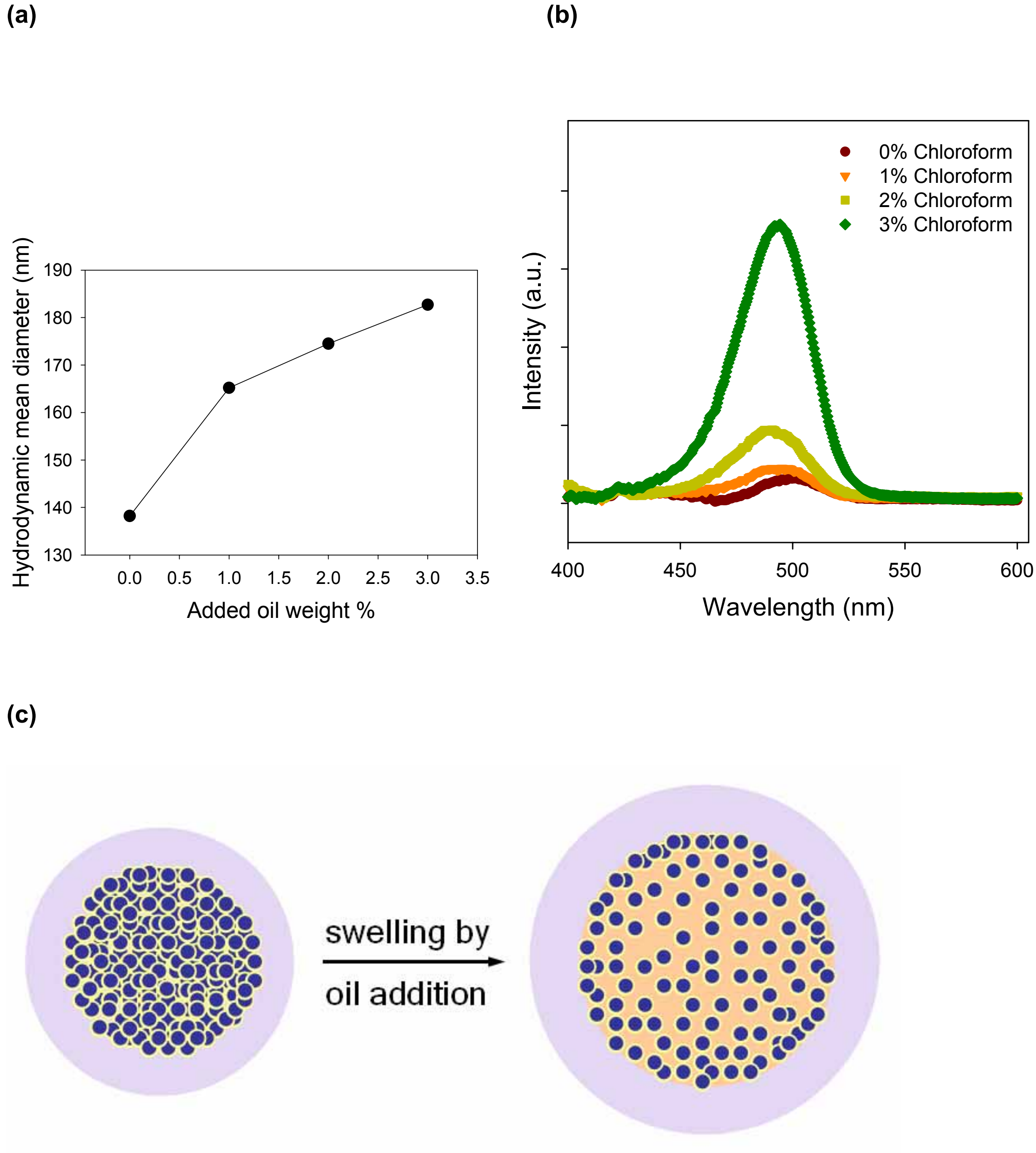


Fig. 5S. Self-assembly of PHEA-*g*-CdSe/ZnS QDs with surface-active properties. (a) Hydrodynamic mean diameters of self-aggregates from P-*g*-QD swollen by chloroform. (b) Fluorescence emission spectra of aqueous solutions of P-*g*-QD swollen by chloroform. (c) Schematic diagram of the core swelling.

ESI 5. AFM images of spherical aggregates from P-*g*-Au NC-C_{12} 1. Spherical shape of the self-aggregates were confirmed by AFM measurement. After the aggregate solution was dried at room temperature on a Si-wafer, AFM measurement was performed by using a PSIA XE-100.

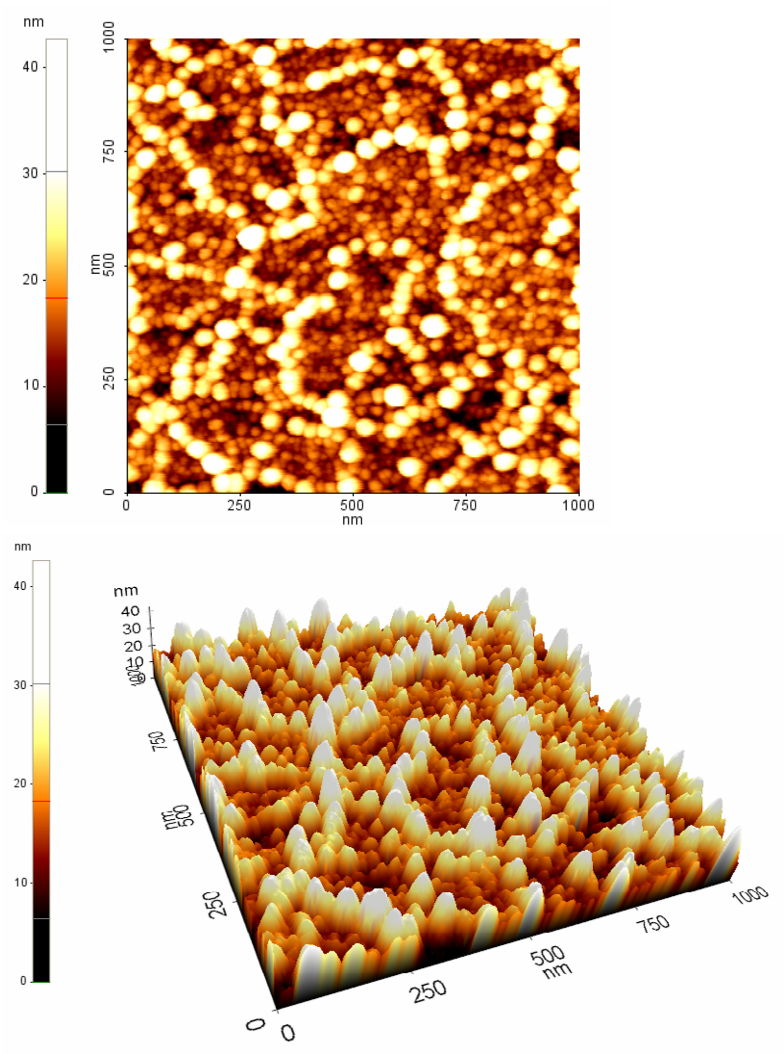


Fig. 6S. AFM images of self-aggregates from P-*g*-Au NC-C_{12} 1.

References

1. M. Brust, M. Walker, D. Bethell, D. J. Schiffrin and R. J. Whyman, *J. Chem. Soc., Chem. Commun.*, 1994, 801-802.

2. M. Brust, J. Fink, D. Bethell, D. J. Schiffrin and C. J. Kiely, *J. Chem. Soc., Chem. Commun.*, 1995, 1655-1656.

3.M. J. Hostetler, J. E. Wingate, C. J. Zhong, J. E. Harris, R. W. Vachet, M. R. Clark, J. D. Londono, S. J. Green, J. J. Stokes, G. D. Wignall, G. L. Glish, M. D. Porter, N. D. Evans and R. W. Murray, *Langmuir*, 1998, **14**, 17-30.

4. X. Michalet, F. F. Pinaud, L. A. Bentolila, J. M. Tsay, S. Doose, J. J. Li, G. Sudaresan, A. M. Wu, S. S. Gambhir and S. Weiss, *Science*, 2005, **307**, 538-544.

5. I. L. Medintz, H. T. Uyeda, E. R. Goldman, H. Mattoussi, *Nat. Mater.*, 2005, **4**, 435-446.

6. W. C. W. Chan, S. M. Nie, *Sceince*, 1998, **281**, 2016-2018.

7. G. P. Mitchell, C. A. Mirkin, R. L. Letsinger, *J. Am. Chem. Soc.*, 2000, **122**, 12142-12150.

8. H. T. Uyeda, I. L. Medintz, J. K. Jaiswal, S. M. Simon, H. Mattoussi, *J. Am. Chem. Soc.*, 2005, **127**, 3870-3878.

9. Z. Tang, Z. Zhang, Y. Wang, S. C. Glotzer, N. A. Kotov, *Science*, 2006, **314**, 274-278.

10. C. R. Kagan, C. B. Murray, M. Nirmal, M. G. Bawendi, *Phys. Rev. Lett.*, 1996, **76**, 1517-1520.

11. S. A. Crooker, J. A. Hollingsworth, S. Tretiak, V. I. Klimov, *Phys. Rev. Lett.*, 2002, **89**, 186802.