

Supplementary Information

S.1. PS DNA Stabilized AuNCs

Small thiolated compounds have a strong affinity for both neutral and ionic gold atoms, and have been widely used as reducing agents and stabilizers in the synthesis of AuNCs [1]. In comparison to DNA however, thiol stabilizers lack the 3D structure that allows greater control over size distribution and the ability to modulate emission through variations in base sequence. Here, we expect that PS modifications may provide new coordination chemistry in DNA for preparing new fluorescent AuNCs. Our previous work indicates that shorter DNA produces stronger fluorescence [2]. To investigate the utility of PS DNA in AuNC synthesis, A₅, T₅, C₅ and G₅ templates (Table S1), both without and with full PS modification were screened using conditions based on those previously employed.

Table S1. DNA sequences used as templates in AuNC synthesis (from 5'-terminus).

DNA Name	Sequence and Modifications
A ₅ -PO	AAAAA
A ₅ -PS	A*A*A*A*A
T ₅ -PO	TTTTT
T ₅ -PS	T*T*T*T*T
C ₅ -PO	CCCCC
C ₅ -PS	C*C*C*C*C
G ₅ -PO	GGGGG
G ₅ -PS	G*G*G*G*G

* = PS modification

In a typical synthesis, 65 μ M of DNA (see Table 1) was dissolved in ultrapure water. H₂AuCl₄ was added to give a Au³⁺:base ratio of 1:1.3, and the mixture was vortexed. Then, citrate buffer was added to give a final concentration of approximately 50 mM, the sample was again vortexed, and incubated in the dark for a minimum of 8 hours or overnight.

Following our previous work [2,3], fluorescent AuNCs were produced using both A₅-PO and A₅-PS templates using a pH 6 citrate solution as a buffer and reducing agent. A₅-PO and A₅-PS produced emission bands at 465 nm and 429 nm respectively as seen in Figure S1A. Although successful, the overall emission intensity of the A₅-PS template clusters was approximately half that of its PO counterpart. PS modification of the A₅ template also induced a red-shift in excitation wavelength (300 nm \rightarrow 353 nm) and a blue-shift in emission wavelength (465 nm \rightarrow 429 nm), resulting in a significantly reduced Stokes shift.

Next, we tested C₅ DNA using citrate as both buffer and reducing agent. Previous work indicates that lower pH works best for poly-C DNA templated AuNCs, and here we also found that fluorescence was produced with the PO-DNA at lower pH (Figure S1B). Although a small hump was observed for the C₅-PS template, it is significantly weaker than the C₅-PO, pH 3 emission band. At neutral pH, the emission was poor for both PO and PS C₅ DNA (data not shown).

When T₅ and G₅ were tested, no strong emission was observed for either sample (data not shown). Therefore, overall, PS modification did not enhance the emission property of DNA templated AuNCs, although fluorescent AuNCs can still be produced with unmodified poly-A and poly-C DNA.

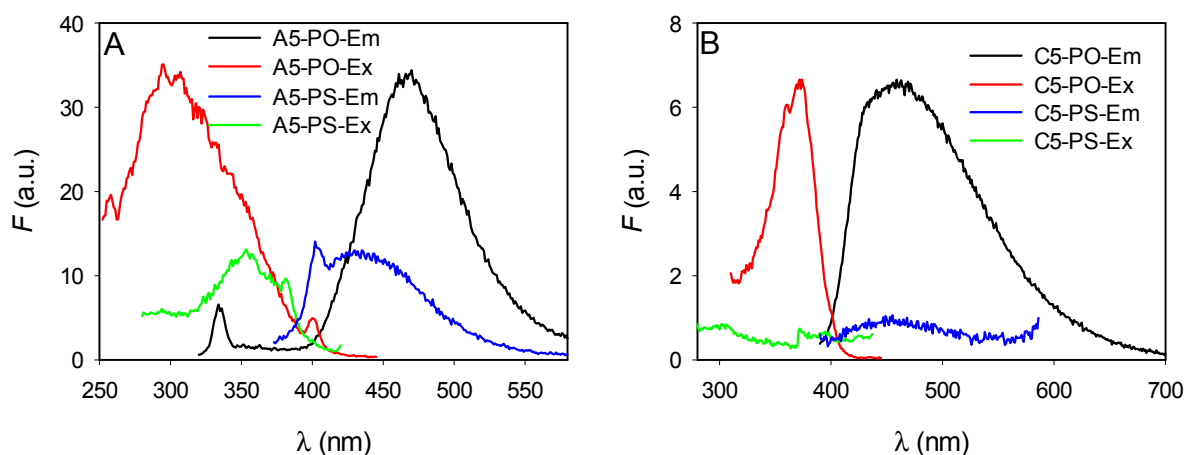


Figure S1. Fluorescence excitation and emission spectra of the (A) A₅ DNA at pH 6 (PO and PS) and (B) C₅ DNA at pH 3 (PO and PS) stabilized fluorescent AuNCs. The excitation and emission wavelengths are at the corresponding peak positions. Spectra were acquired after 8 hours dark incubation, on 1:2.5 dilutions in ultrapure water. The synthesis was carried out in citrate buffer with 65 μ M DNA and 250 μ M HAuCl₄. The small peak at approximately 400 nm (Figure S1A) can be attributed to water Raman scattering.

S.2. PS DNA Stabilized AgNCs

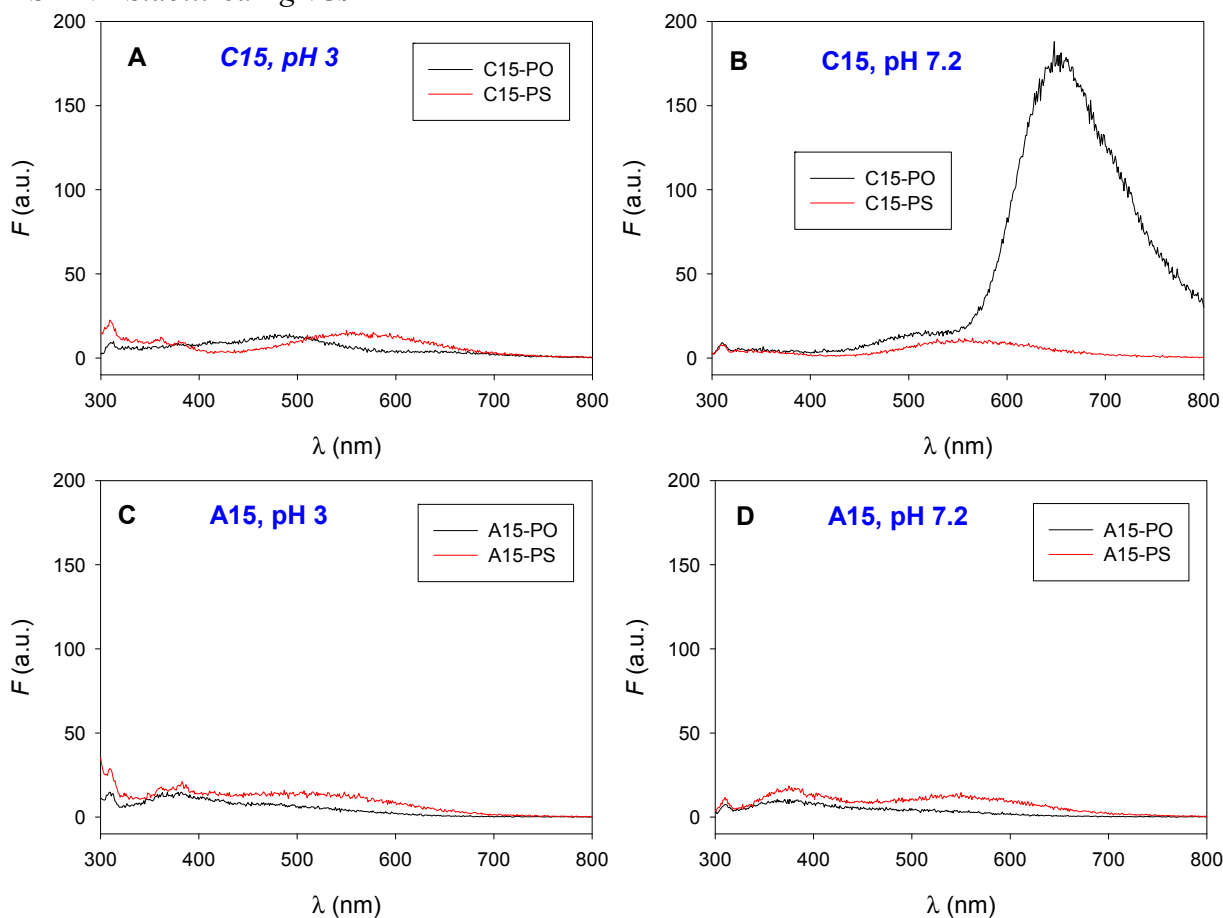


Figure S2. Cont.

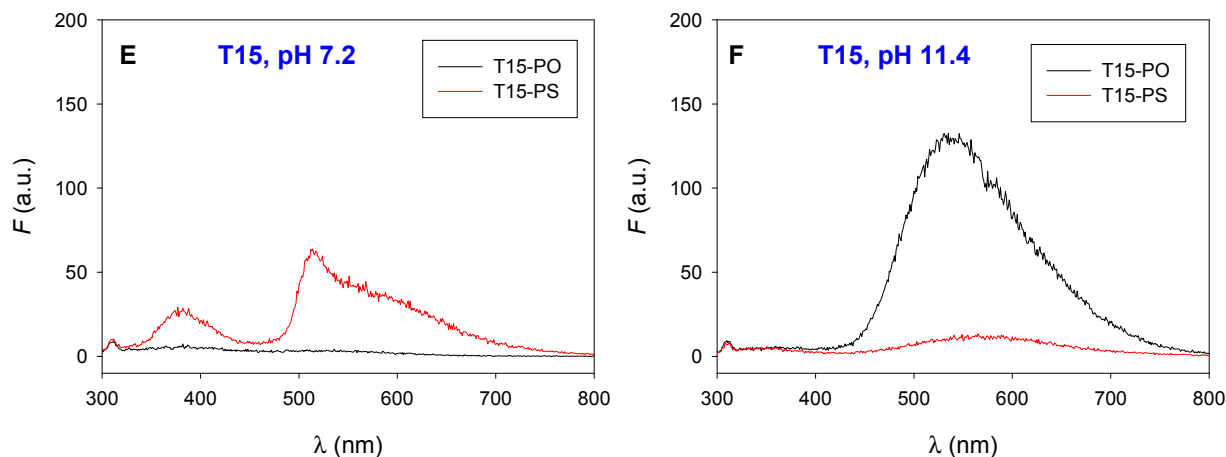


Figure S2. Emission spectra (λ_{EX} 280 nm) of PO- and PS-modified (A) C₁₅ at pH 3; (B) C₁₅ at pH 7.2; (C) A₁₅ at pH 3; (D) A₁₅ at pH 7.2; (E) T₁₅ at pH 7.2; and (F) T₁₅ at pH 11.4. Samples were prepared using 15 μM DNA, 120 μM AgNO₃, 120 μM NaBH₄, and 25 mM pH 7.2 phosphate buffer. Spectra were recorded on undiluted samples following 2 h dark incubation followed by exposure to hand held short wavelength UV light for 5 min.

References

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2. Lopez, A.; Liu, J. DNA templated fluorescent gold nanoclusters reduced by Good's buffer: From blue emitting seeds to red and near infrared emitters. *Can. J. Chem.* **2015**, doi:10.1139/cjc-2014-0600.
3. Kennedy, T.A.C.; MacLean, J.L.; Liu, J. Blue emitting gold nanoclusters templated by poly-cytosine DNA at low pH and poly-adenine DNA at neutral pH. *Chem. Commun.* **2012**, *48*, 6845–6847.

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