

Supporting Information:

Metal Induced Fluorescence Lifetime Enhancement of Quinaldine Chromophore on Gold Nanoparticle Surface

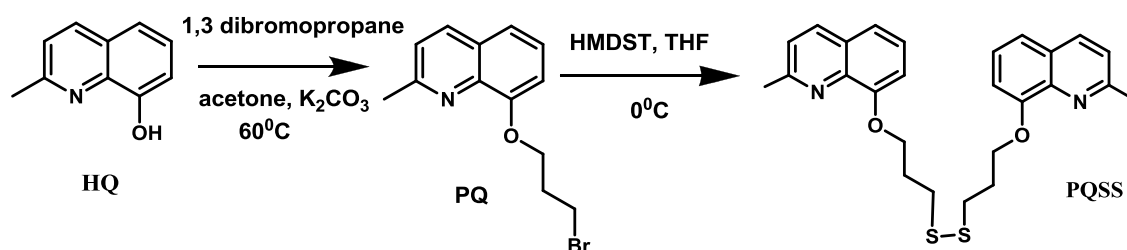
Jisha Babu, Jino George and Ramavarma Luxmi Varma*

Chemical Sciences and Technology Division, National Institute for Interdisciplinary Science and Technology (NIIST), CSIR, Thiruvananthapuram, 695 019, India

lux_varma@rediffmail.com

Table of Content	Page No.
1. Synthesis of capping agent	S2
2. Synthesis of AuDQT	S3
3. TEM image of AuDQT	S4
4. TEM images of AuPQT	S4
5. Absorption spectra of PQSS on protonation	S4
6. Absorption and emission spectra of AuPQT and AuDQT on protonation	S5
7. Differential absorption spectra of AuPQT on protonation	S5
8. Excitation spectra of PQSS and AuPQT	S6
9. Calculation of extinction coefficient of AuPQT	S6
10. Gold core removal via cyanide etching	S7
11. Calculation of PQSS concentration in AuPQT nanoparticles	S7
12. Concentration dependent study of PQSS on AuPQT	S8
13. References	S9

1. Synthesis of capping agent (PQSS)



1.1 Synthesis of 8-(3-bromopropoxy)-2-methylquinoline (PQ):¹ A mixture of 8-hydroxyquinoline (2 gm, 0.0125 mol), 1,3-dibromopropane (5.07 gm, 0.025 mol), and potassium carbonate (3.45 gm, 0.025 mol) in dry acetone (30 ml) was refluxed for 24 h. The reaction mixture was stirred at this temperature until the reaction was complete as indicated by TLC (24 h). Potassium carbonate was filtered off and solvent was removed under reduced pressure. After removing the solvent, the remaining residue was extracted 3 times with chloroform. The combined organic layer was washed with saturated brine and finally the resulting organic layer was dried over anhydrous sodium sulphate. The organic layer was evaporated and the compound was purified by column chromatography using ethyl acetate-hexane (10%) to give 1.35 gm of final product in 38.4% yield. ¹H NMR (500 MHz, CDCl₃, (CH₃)₄Si): δ (ppm) 8.01 (d, 1H), 7.41 (m, 2H), 7.31 (d, 1H), 4.40 (t, 2H), 3.75-3.71(t, 2H), 2.76 (s, 3H), 2.59 (m, 2H). ¹³C NMR (125MHz, CDCl₃, (CH₃)₄Si): δ (ppm) 158.8, 153.9, 136.3, 127.7, 125.5, 122.5, 119.9, 109.9, 67.0, 32.1, 30.4, 25. IR (ν_{max}): 3349, 3051, 2925, 1642, 1503, 1428, 1378, 1325, 1259, 1109, 826, 754, 664, 609 cm⁻¹. MS: FAB [M⁺²] 284.62 (calculated-284.62)

1.2 Synthesis of 1,2 bis (3-2-methyl quinolin-8-yloxy)propyl) disulfide (PQSS):² A mixture of tetrabutyl ammonium fluoride (3 g) and hexamethyl disilathiane (4.8 g) in THF (20 ml) was added to compound PQ (2.6 g) in THF(10 mL) kept at -10°C. The mixture was

allowed to warm at room temperature, while being stirred and further stirred at room temperature for 12 h. The reaction mixture was concentrated to remove THF and diluted with dichloromethane and then washed with saturated ammonium chloride solution. The organic layer was concentrated and column chromatographed over alumina using 10% ethyl acetate/hexane as eluent to give 1 g of **PQSS**. **¹H NMR** (500 MHz, CDCl₃, (CH₃)₄Si): δ (ppm) 7.99 (d, 1H), 7.38 (m, 2H), 7.31 (d, 1H), 7.02 (d, 1H) 4.33 (t, 2H), 3.01(t, 2H), 2.76 (s, 3H), 2.44 (m, 2H). **¹³C NMR** (125MHz, CDCl₃, (CH₃)₄Si): δ (ppm) 158.1, 154.1, 139.9, 136.1, 127.7, 125.6, 122.5, 119.9, 109.4, 67.1, 35.1, 28.4, 25.6. **IR** (ν_{\max}): 3054, 2922, 2853, 1727, 1662 (C=N), 1603, 1532, 1430, 1381, 1326, 1259, 1107, 831, 752, 664, 609 cm⁻¹. **MS**: FAB [M⁺] 465.58 (calculated- 465.16).

2. Synthesis of 1,2 bis (3-2-methyl quinolin-8-yloxy)decyl) disulfide (DQSS) functionalized gold nanoparticles (AuDQT)

45mg (0.115 mmol) of tetrachloroauric acid (HAuCl₄ XH₂O) (99%) and 75 mg (0.115 mmol) of **DQSS** were added to a mixture of 30 ml MeOH (HPLC grade) and 5 ml of acetic acid in a 250 ml flask and stirred for 5 min, which gave a clear yellow solution. Subsequently, a solution of sodium borohydride (45 mg, 1.2 mmol) dissolved in 5.0 ml of MeOH was added dropwise into the above solution with rapid stirring. On addition of the first drop of NaBH₄, the HAuCl₄ solution immediately turned to dark brown from yellow and rapid stirring was continued for 2 h. The hybrid nanoparticles formed were purified by repeated precipitation and filtration using ether. Purified nanoparticles were re-dispersed in methanol. **IR** (ν_{\max}): 3095, 2909, 2859, 1730, 1669, 1603, 1540, 1438, 1360, 1240, 1089, 831, 713, 684 cm⁻¹.

3. TEM Image of AuDQT

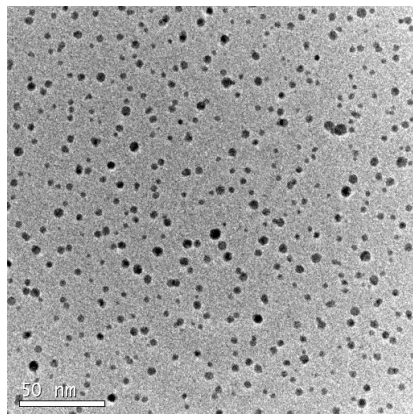


Figure S1. TEM image of AuDQT nanoparticles

4. TEM images of AuPQT

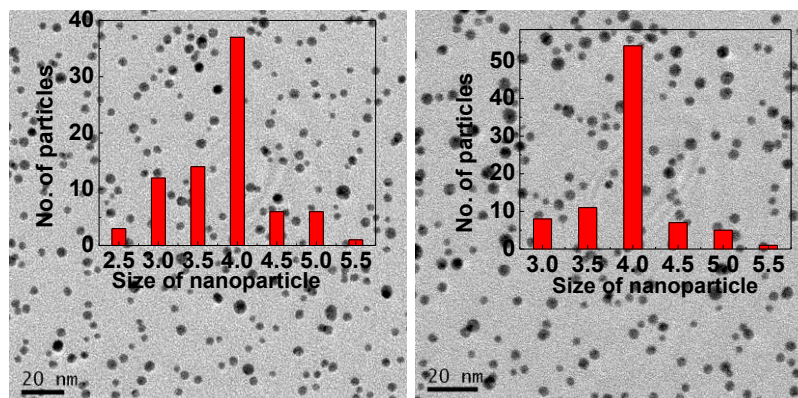


Figure S2. TEM images of AuPQT in (A) neutral and (B) protonated form.

5. Absorption spectra of PQSS on protonation

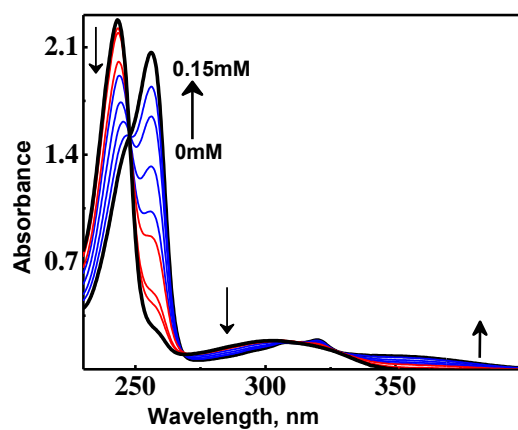


Figure S3. Absorption spectra of PQSS (0.14 mM) in methanol on varying the concentration of TFA (0 to 0.15 mM).

6. Absorption and Emission spectra of AuPQT and AuDQT on protonation

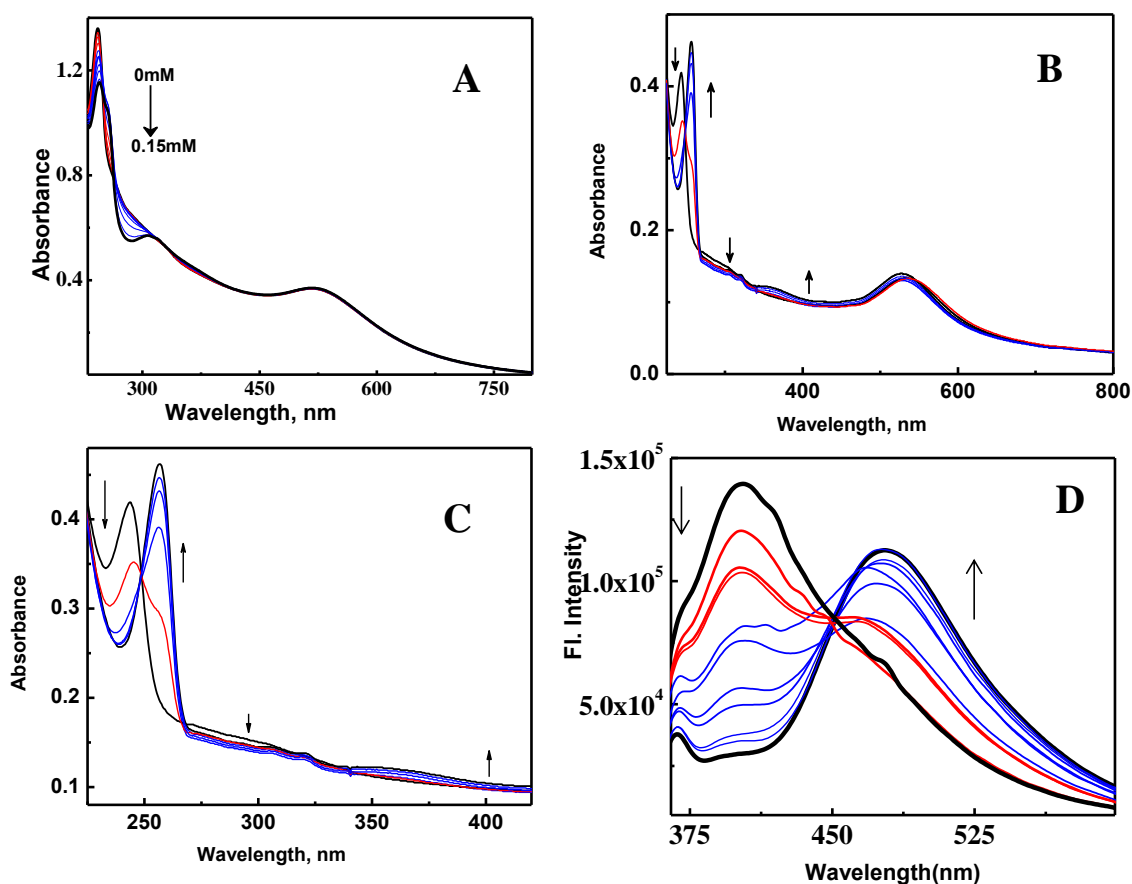


Figure S4. Absorption spectra of (A) AuPQT (40 nM), (B) AuDQT in methanol on varying the concentration of TFA (0 to 0.15 mM), (C) Absorption spectra of AuDQT in methanol in the wavelength range 200-400 nm.; (D) Emission spectra of AuDQT in methanol on varying the concentration of TFA (0 to 0.15 mM).

7. Differential absorption spectra of AuPQT on protonation

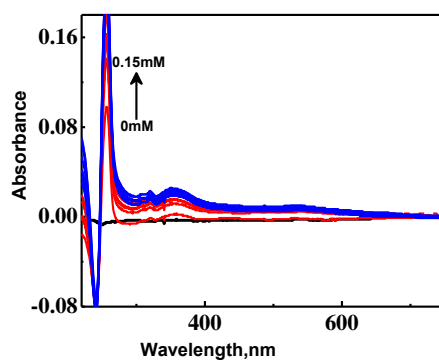


Figure S5. Differential absorption spectra of **AuPQT** (40 nM) in methanol on varying the concentration of TFA (0 to 0.15 mM).

8. Excitation spectra of PQSS and AuPQT

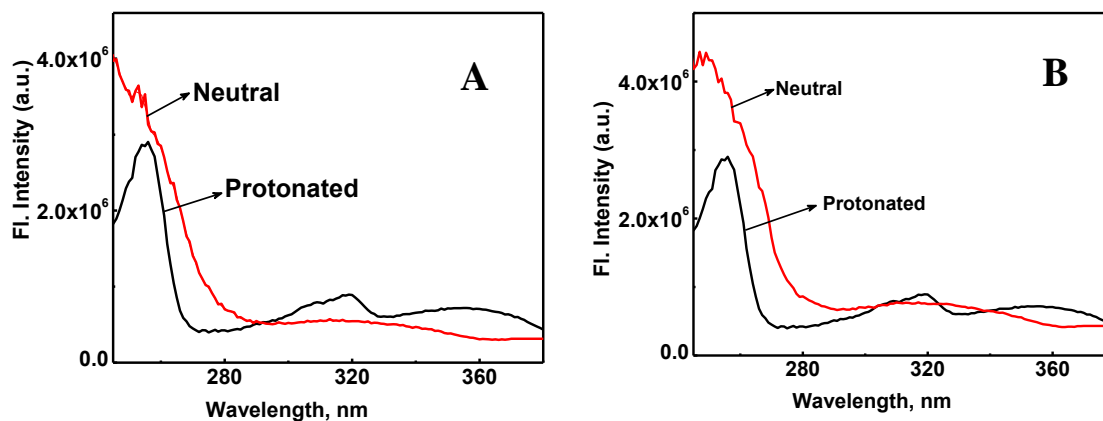


Figure S6. Excitation spectra of (A) **PQSS** and (B) **AuPQT** (40 nM) in the neutral and protonated states .

9. Calculation of extinction coefficient of AuPQT

Extinction coefficient $\epsilon = A/Cl$

Optical density of **AuPQT** in 3ml methanol (A) = 0.076.

Concentration of Au in **AuPQT** solution (C) = Au content / Molecular weight of Au

Au content as per ICP analysis in **AuPQT** solution = 7.9×10^{-6} g/L.

Concentration of Au in **AuPQT** = 0.04019×10^{-6} M.

Therefore, $\epsilon = 1.9 \times 10^6 \text{ M}^{-1}\text{cm}^{-1}$.

10. Gold core removal via cyanide etching ⁴

The dissolution of gold was started by adding a stock solution (400 μ l; 26 mM) of KCN in water into a cuvette containing particle suspension to a final concentration of 3 mM (KCN). The evolution of the UV-Vis absorption spectra was followed in time.

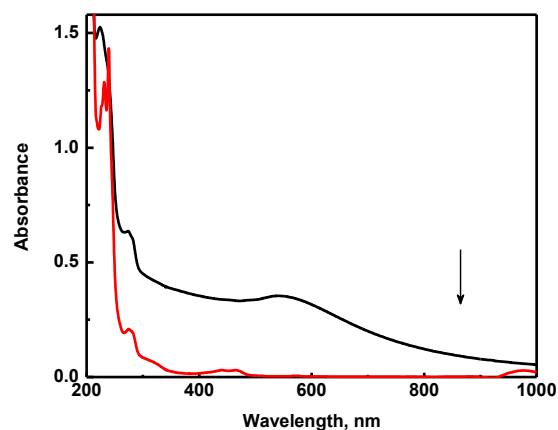


Figure S7. Evolution of the absorption spectrum of a solution of **AuPQT** in methanol upon addition of 3 mM KCN. The complete disappearance of the gold nanocore occurs after 24 h.

11. Calculation of POSS concentration in AuPQT nanoparticles

Stock solution of cyanide = 26.1 mM

Total volume of cyanide used for etching = 400 μ L

Concentration of cyanide used for etching = 3.13 mM

Volume of **AuPQT** taken = 10 μ L

Optical density of λ_{\max} (251nm) after cyanide etching (A) = 1.44

Extinction coefficient of **PQSS** (ϵ) = $4.71 \times 10^4 \text{ mol}^{-1} \text{ cm}^{-1}$

Scattering contribution of Au nanoparticles (%) = 28%

Concentration of **PQSS** in 10 μ L **AuPQT** (C)

$$A = \epsilon Cl$$

Therefore, C = 30.48 μ M

Concentration of **PQSS** in 10 ml stock solution of **AuPQT** = 9 mM

Theoretical value (from synthesis) of the concentration of **PQSS** in **AuPQT** stock solution = 14 mM.

12. Concentration dependent study of **PQSS** on **AuPQT**

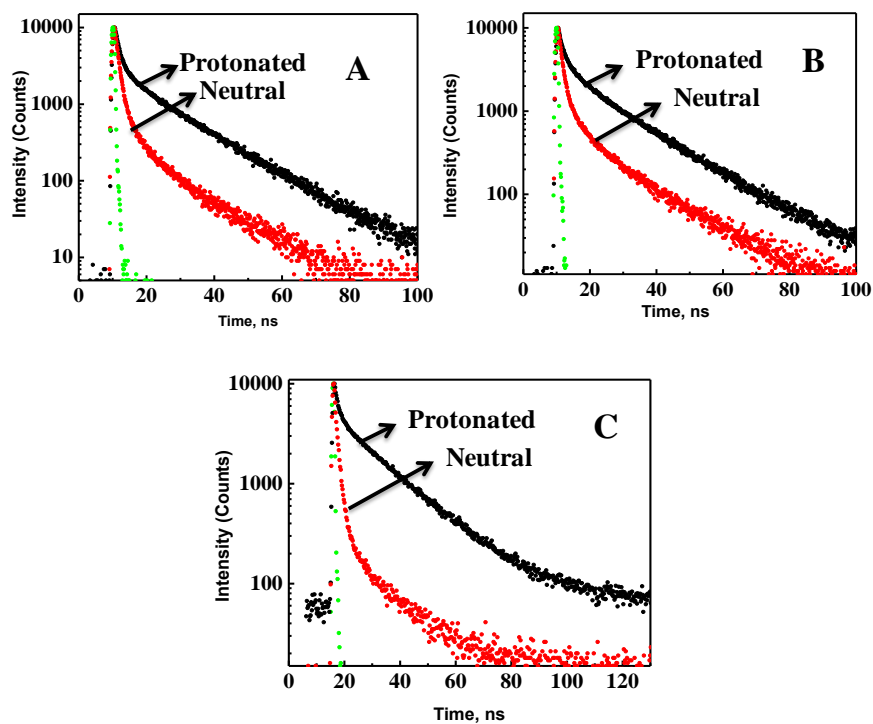


Figure S8. Fluorescence lifetime spectrum of **AuPQT** (40 nM) at A) 10^{-5} M, B) 10^{-6} M and C) 10^{-7} M concentrations of **PQSS** in methanol on varying the concentration of TFA (0 to 0.15 mM).

Table S1. Measured fluorescence lifetime values of **AuPQT** nanoparticles on different concentrations of **PQSS**.

TFA Conc.	PQSS Concentration											
	10^{-5}				10^{-6}				10^{-7}			
	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	χ^2	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	χ^2	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	χ^2
0 mM	1.0 (65%)	4.1 (17%)	16.3 (18%)	1.06	1.0 (47%)	4.1 (20%)	17.1 (33%)	1.01	0.9 (61%)	3.8 (23%)	17.8 (16%)	1.15
0.15 mM	1.1 (22%)	4.9 (12%)	16.5 (66%)	1.03	1.1 (12%)	4.1 (15%)	17.3 (73%)	1.06	1.1 (10%)	4.3 (5%)	17.6 (85%)	1.04

13. References

1. L. Praveen, V. B. Ganga, R. Thirumalai, T. Sreeja, M. L. P. Reddy and R. Luxmi Varma, *Inorg. Chem*, 2007, **46**, 6277.
2. A. C. Templeton, , J. J. Pietron, R. W. Murray and P. Mulvaney, *J. Phys. Chem. B*, 2000, **104**, 564.
3. G. Schneider and G. Decher, *Nano Lett*, 2006, **6**, 530.