Supporting Information:

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

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Table of Content

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

1.1 Synthesis of 8-(3-bromopropoxy)-2-methylquinoline (PQ):\(^1\) A mixture of 8-hydroxyquinaldine (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. \(^1\)H NMR (500 MHz, CDCl\(_3\), (CH\(_3\))\(_4\)Si): \(\delta\) (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). \(^1^3\)C NMR (125MHz, CDCl\(_3\), (CH\(_3\))\(_4\)Si)): \(\delta\) (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 (\(\upsilon_{max}\)): 3349, 3051, 2925, 1642, 1503, 1428, 1378, 1325, 1259, 1109, 826, 754, 664, 609 cm\(^{-1}\). MS: FAB [M\(^{+}\)] 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. $^1$H NMR (500 MHz, CDCl$_3$, (CH$_3$)$_4$Si): $\delta$ (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). $^{13}$C NMR (125MHz, CDCl$_3$, (CH$_3$)$_4$Si): $\delta$ (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 (v$_{\text{max}}$): 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 (HAuCl$_4$ XH$_2$O) (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 NaBH$_4$, the HAuCl$_4$ 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 (v$_{\text{max}}$): 3095, 2909, 2859, 1730, 1669, 1603, 1540, 1438, 1360, 1240, 1089, 831,
713, 684 cm$^{-1}$. 

S3
3. TEM Image of AuDQT

![TEM Image of AuDQT nanoparticles](image)

**Figure S1.** TEM image of AuDQT nanoparticles

4. TEM images of AuPQT

![TEM images of AuPQT in (A) neutral and (B) protonated form](image)

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

5. Absorption spectra of PQSS on protonation

![Absorption spectra of PQSS on protonation](image)
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**

![Excitation spectra of PQSS and AuPQT](image)

**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 $\varepsilon = \frac{A}{C \lambda}$

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 = $7.9 \times 10^{-6}$ g/L.

Concentration of Au in AuPQT = $0.04019 \times 10^{-6}$ M.

Therefore, $\varepsilon = 1.9 \times 10^6$ M$^{-1}$cm$^{-1}$. 
10. Gold core removal via cyanide etching

The dissolution of gold was started by adding a stock solution (400 μl; 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 PQSS concentration in AuPQT nanoparticles

Stock solution of cyanide = 26.1 mM
Total volume of cyanide used for etching = 400 μL
Concentration of cyanide used for etching = 3.13 mM
Volume of AuPQT taken = 10 μL
Optical density of \( \lambda_{\text{max}} \) (251nm) after cyanide etching (A) = 1.44
Extinction coefficient of PQSS (\( \varepsilon \)) = \( 4.71 \times 10^4 \) mol\(^{-1}\) cm\(^{-1}\)
Scattering contribution of Au nanoparticles (%) = 28%

Concentration of PQSS in 10 μL AuPQT (C)

\[ A = \varepsilon C \]

Therefore, C=30.48 μM
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.

<table>
<thead>
<tr>
<th>TFA Conc.</th>
<th>PQSS Concentration</th>
<th>( \tau_1 ) (ns)</th>
<th>( \tau_2 ) (ns)</th>
<th>( \tau_3 ) (ns)</th>
<th>( \chi^2 )</th>
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<tbody>
<tr>
<td>0 mM</td>
<td>10^{-5}</td>
<td>1.0 (65%)</td>
<td>4.1 (17%)</td>
<td>16.3 (18%)</td>
<td>1.06</td>
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<tr>
<td></td>
<td>10^{-6}</td>
<td>1.0 (47%)</td>
<td>4.1 (20%)</td>
<td>17.1 (33%)</td>
<td>1.01</td>
</tr>
<tr>
<td></td>
<td>10^{-7}</td>
<td>0.9 (61%)</td>
<td>3.8 (23%)</td>
<td>17.8 (18%)</td>
<td>1.15</td>
</tr>
<tr>
<td>0.15 mM</td>
<td>10^{-5}</td>
<td>1.1 (22%)</td>
<td>4.9 (12%)</td>
<td>16.5 (66%)</td>
<td>1.03</td>
</tr>
<tr>
<td></td>
<td>10^{-6}</td>
<td>1.1 (12%)</td>
<td>4.1 (15%)</td>
<td>17.3 (73%)</td>
<td>1.06</td>
</tr>
<tr>
<td></td>
<td>10^{-7}</td>
<td>1.1 (10%)</td>
<td>4.3 (5%)</td>
<td>17.6 (85%)</td>
<td>1.04</td>
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**13. References**

