

## Supporting Information

### **Near-infrared fluorescent Ag<sub>2</sub>S quantum dots stabilized by penicillamine enantiomers: influence of ligand chirality on linear and nonlinear optical properties and toxicity**

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This supporting information includes the following sections:

- S1.** XRD patterns of prepared Ag<sub>2</sub>S QDs.
- S2.** Absorbance spectra Ag<sub>2</sub>S/Pen QDs under varied synthesis conditions.
- S3.** Emission spectra Ag<sub>2</sub>S/Pen QDs under varied synthesis conditions.
- S4.** Effect of reaction time on optical properties of Ag<sub>2</sub>S/Pen QDs.
- S5.** Time-dependent absorbance and emission spectra of Ag<sub>2</sub>S/Pen QDs.
- S6.** Fluorescence decay times of centrifuged vs. non-centrifuged samples of Ag<sub>2</sub>S/Pen QDs.
- S7.** Comparison of centrifuged QDs and re-centrifuged supernatant.
- S8.** Bi-exponential fitting of fluorescence decay times.
- S9.** Absorbance and normalized emission spectra of Ag<sub>2</sub>S/Pen QDs for optimized synthesis conditions.
- S10.** Detailed information on fluorescence decay times for reactions depending on reaction time and temperature.
- S11.** Fit residuals for the fluorescence lifetime data.

### S1. XRD patterns of prepared $\text{Ag}_2\text{S}$ QDs.

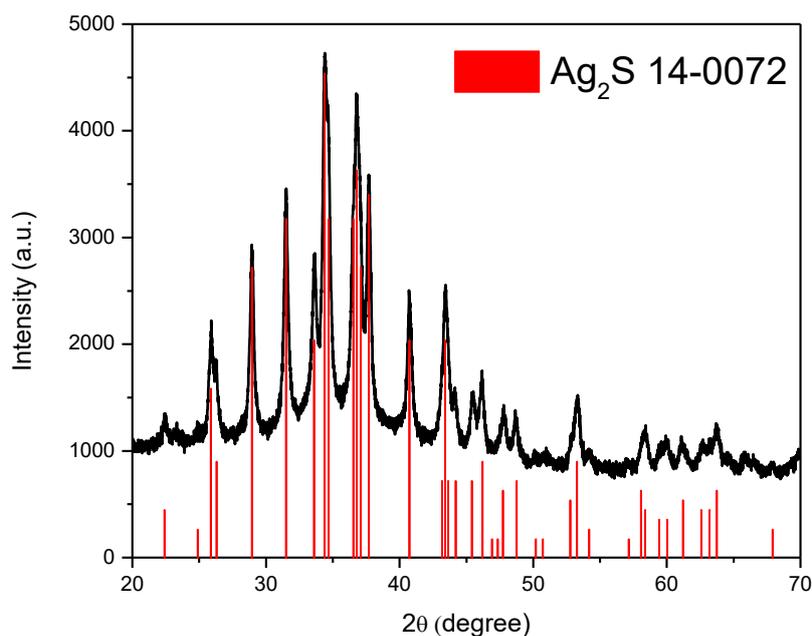


Fig. S1 XRD patterns of water soluble  $\text{Ag}_2\text{S}/\text{D-Pen}$  QDs after drying (black line), ICDD No. 14-0072 ( $\text{Ag}_2\text{S}$ ) (red line)

### S2. Absorbance spectra $\text{Ag}_2\text{S}/\text{Pen}$ QDs under varied synthesis conditions.

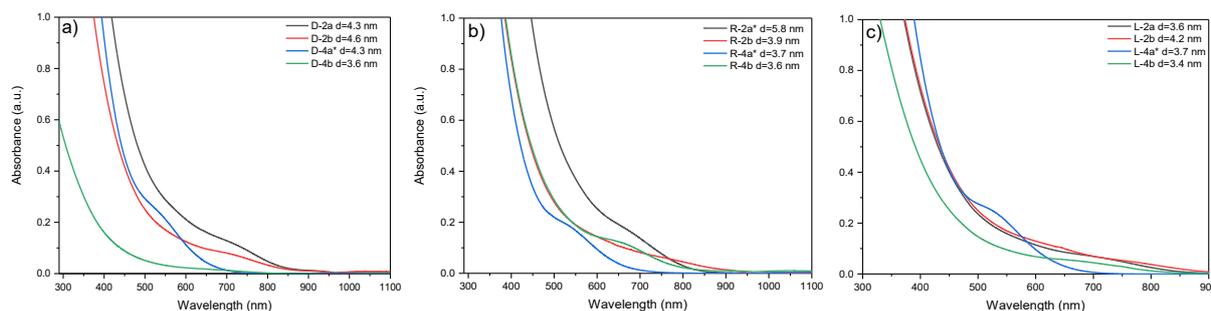


Fig. S2 Absorbance spectra of a)  $\text{Ag}_2\text{S}/\text{D-Pen}$ , b)  $\text{Ag}_2\text{S}/\text{Rac-Pen}$ , c)  $\text{Ag}_2\text{S}/\text{L-Pen}$  QDs samples synthesized at different conditions along with their diameters.

### S3. Emission spectra $\text{Ag}_2\text{S}/\text{Pen}$ QDs under varied synthesis conditions.

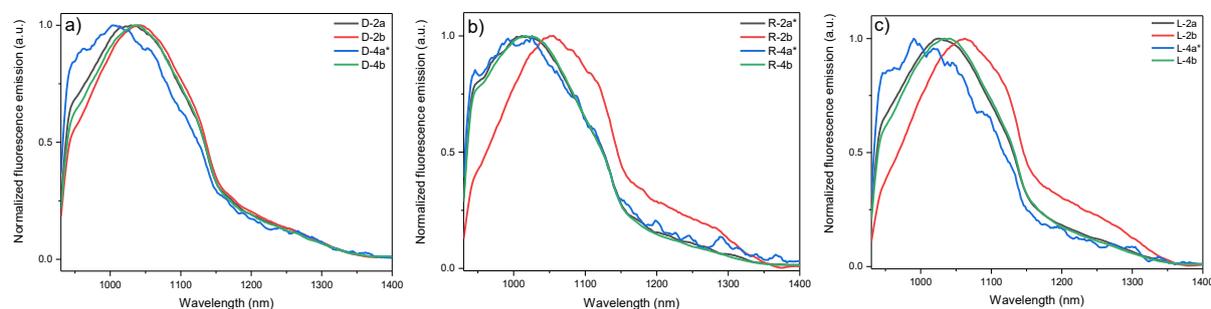


Fig. S3 Normalized fluorescence emission spectra of a)  $\text{Ag}_2\text{S}/\text{D-Pen}$ , b)  $\text{Ag}_2\text{S}/\text{Rac-Pen}$  and c)  $\text{Ag}_2\text{S}/\text{L-Pen}$  QDs excited at 500 nm.

#### S4. Effect of reaction time on optical properties of Ag<sub>2</sub>S/Pen QDs.

| Coating/Rxn time [min] | T [°C] | pH <sub>(after)</sub> | Zeta pot. (mV) | $\tau_{\text{average 3-exponential decay}}$ [ns] | Correlation coefficient $\chi^2_{\text{3-exponential decay}}$ | $\lambda_{\text{em, max}}$ [nm] |
|------------------------|--------|-----------------------|----------------|--|---|---------------------------------|
| D-Pen                  |        |                       |                |  |   |                                 |
| 30                     | 50     | 11.7                  | -9.13          | 31.0   | 1.0190  | 1031                            |
| 60                     | 50     | 11.9                  | -52.69         | <b>73.0</b>                                      | 1.0330  | 1024                            |
| 90                     | 50     | 11.8                  | -79.46         | 69.3   | 1.0460  | 1028                            |
| 150                    | 50     | 11.8                  | -40.35         | 56.3   | 1.0830  | 1036                            |
|                        |        |                       |                |  |   |                                 |
| 30                     | 90     | 12.0                  | -23.05         | <b>38.8</b>                                      | 1.0470  | 1047                            |
| 60                     | 90     | 12.1                  | -17.26         | 30.7   | 1.0460  | 1049                            |
| 90                     | 90     | 12.2                  | -48.01         | 15.0   | 1.0880  | 1055                            |
| 150                    | 90     | 12.2                  | -38.01         | 24.2   | 1.0830  | 1054                            |
| Rac-Pen                |        |                       |                |  |   |                                 |
| 30                     | 50     | 11.8                  | -28.97         | <b>68.2</b>                                      | 1.0550  | 1035                            |
| 60                     | 50     | 11.9                  | -41.12         | 34.0   | 1.0420  | 1036                            |
| 90                     | 50     | 11.9                  | -47.16         | 49.0   | 1.0660  | 1029                            |
| 150                    | 50     | 11.9                  | -52.40         | 34.9   | 1.0330  | 1028                            |
|                        |        |                       |                |  |   |                                 |
| 30                     | 90     | 11.9                  | -55.56         | <b>15.3</b>                                      | 1.0860  | 1050                            |
| 60                     | 90     | 12.0                  | -71.63         | 11.1   | 1.1190  | 1058                            |
| 90                     | 90     | 11.8                  | -42.67         | 9.2  | 1.0870  | 1055                            |
| 150                    | 90     | 11.9                  | -80.07         | 10.0   | 1.1050  | 1070                            |
| L-Pen                  |        |                       |                |  |   |                                 |
| 30                     | 50     | 12.0                  | -35.08         | 27.8   | 1.0230  | 1030                            |
| 60                     | 50     | 12.0                  | -19.19         | <b>31.3</b>                                      | 1.0480  | 1036                            |
| 90                     | 50     | 11.8                  | -9.73          | 27.5   | 1.0690  | 1048                            |
| 150                    | 50     | 11.9                  | -26.27         | 21.7   | 1.0950  | 1054                            |
|                        |        |                       |                |  |   |                                 |
| 30                     | 90     | 11.9                  | -37.66         | 26.4   | 1.0210  | 1032                            |
| 60                     | 90     | 11.9                  | -19.47         | 25.6   | 1.1030  | 1040                            |
| 90                     | 90     | 11.9                  | -22.01         | <b>30.8</b>                                      | 1.0480  | 1037                            |
| 150                    | 90     | 11.6                  | -65.80         | 20.0   | 1.1060  | 1053                            |

Table S1 Effect of reaction time and temperature on the properties of Ag<sub>2</sub>S/Pen QDs.

## S5. Time-dependent absorbance and emission spectra of Ag<sub>2</sub>S/Pen QDs.

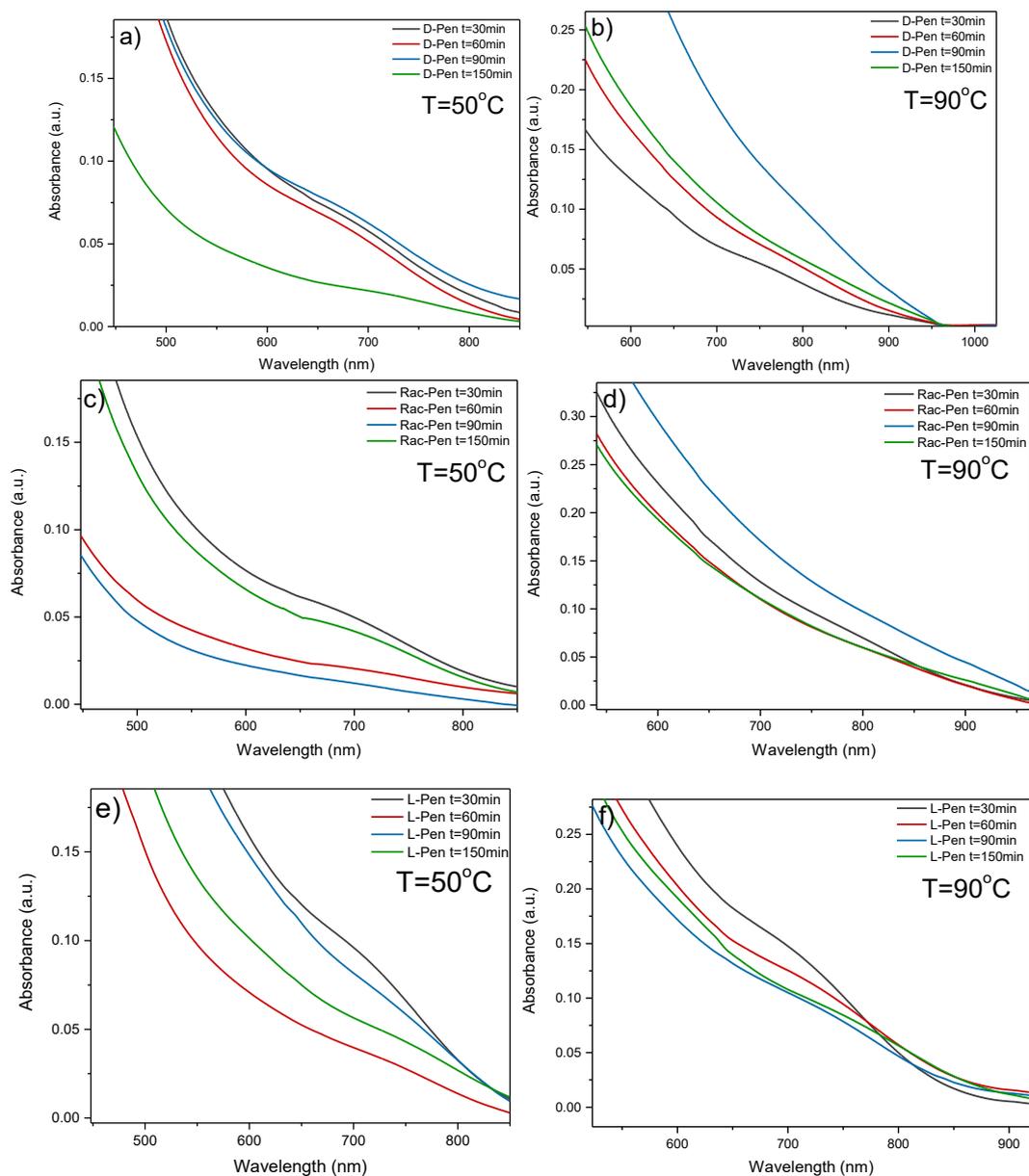


Fig. S4 Absorbance spectra (zoomed on exciton band) of the a, b) Ag<sub>2</sub>S/D-Pen, c, d) Ag<sub>2</sub>S/Rac-Pen and e, f) Ag<sub>2</sub>S/L-Pen QDs during the reaction, with samples taken at intervals ranging from 30 min to 150 min after initiating the reaction.

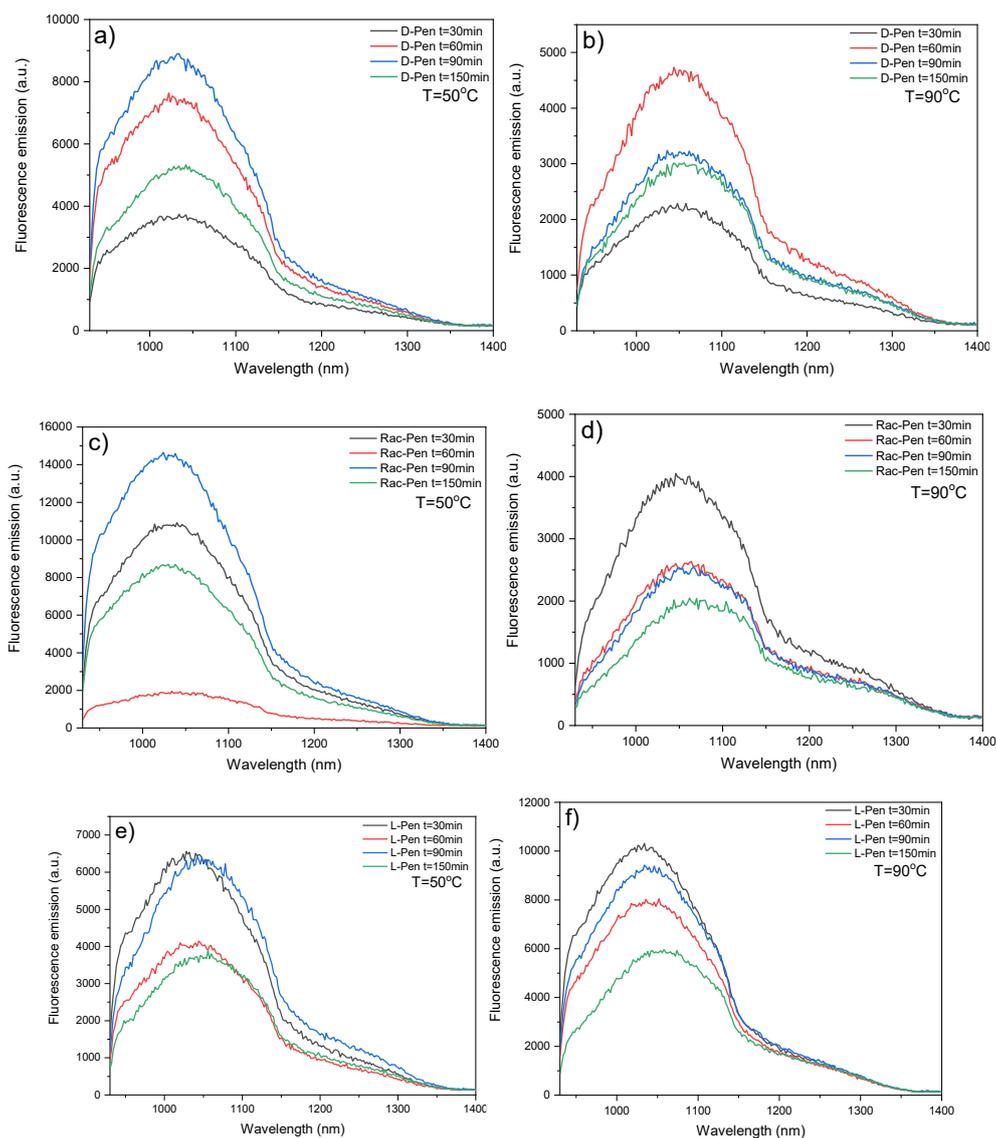


Fig. S5 Emission spectra of the a, b)  $\text{Ag}_2\text{S}/\text{D-Pen}$ , c, d)  $\text{Ag}_2\text{S}/\text{Rac-Pen}$  and e, f)  $\text{Ag}_2\text{S}/\text{L-Pen}$  during the reaction, with samples taken at intervals ranging from 30 min to 150 min after initiating the reaction.

## S6. Fluorescence decay times of centrifuged vs. non-centrifuged samples of $\text{Ag}_2\text{S}/\text{Pen}$ QDs.

| Sample name | $\tau_1$ [ns] | $\tau_2$ [ns] | $\tau_3$ [ns] | A1 [%] | A2 [%] | A3 [%] | $\tau_{\text{average}}$ [ns] | Correlation coefficient $\chi^2$ -exponential decay |
|-------------|---------------|---------------|---------------|--------|--------|--------|------------------------------|---|
| D-2a*       | 31.2          | 10.6          | 3.4           | 25.16  | 52.47  | 22.37  | <b>14.1</b>                  | 1.0450  |
| D-2a        | 106.1         | 38.1          | 11.3          | 31.71  | 54.47  | 13.81  | <b>55.9</b>                  | 1.0670  |
| R-2a*       | 17.5          | 5.8           | 2.0           | 27.50  | 54.33  | 18.18  | <b>8.3</b>                   | 1.1140  |
| R-2a        | 31.0          | 9.6           | 2.8           | 25.09  | 55.13  | 19.77  | <b>13.6</b>                  | 1.1540  |
| L-2a*       | 18.9          | 5.6           | 1.7           | 29.10  | 54.59  | 16.32  | <b>8.8</b>                   | 1.0940  |
| L-2a        | 53.4          | 16.9          | 4.9           | 29.45  | 53.56  | 16.99  | <b>25.6</b>                  | 1.0990  |

Table S2 Fluorescence lifetime components ( $\tau$ ) with their average lifetimes and correlation coefficient ( $\chi^2$ ) for  $\text{Ag}_2\text{S}/\text{Pen}$  QDs depending on the purification method.

## S7. Comparison of centrifuged QDs and re-centrifuged supernatant.

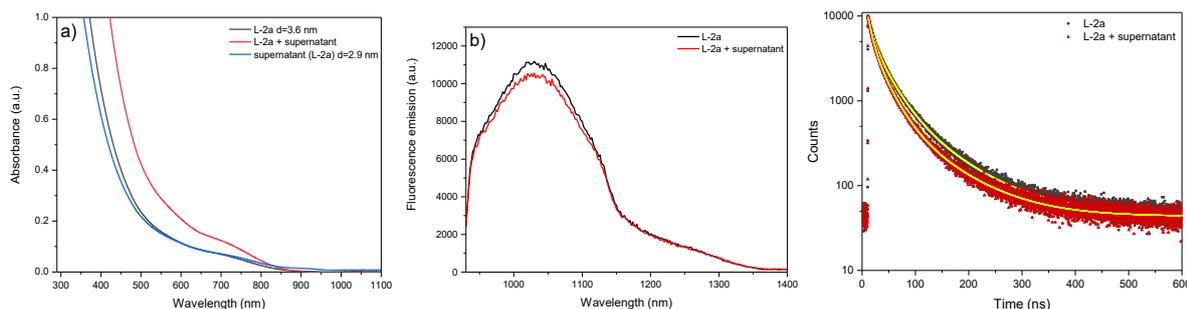


Fig. S6 a) Absorbance, b) emission spectra, and c) fluorescence decays of  $\text{Ag}_2\text{S}/\text{L-Pen}$  QDs (L-2a) and corresponding supernatant.

| Sample name        | $\tau_1$ [ns] | $\tau_2$ [ns] | $\tau_3$ [ns] | A1 [%] | A2 [%] | A3 [%] | $\tau_{\text{average}}$ [ns] | Correlation coefficient $\chi^2_{\text{3-exponential decay}}$ |
|--------------------|---------------|---------------|---------------|--------|--------|--------|------------------------------|---|
| L-2a               | 30.7          | 89.5          | 9.1           | 51.64  | 34.52  | 13.84  | <b>48.0</b>                  | 1.0620  |
| L-2a + supernatant | 85.2          | 26.7          | 8.0           | 31.18  | 51.94  | 16.88  | <b>41.7</b>                  | 1.0500  |

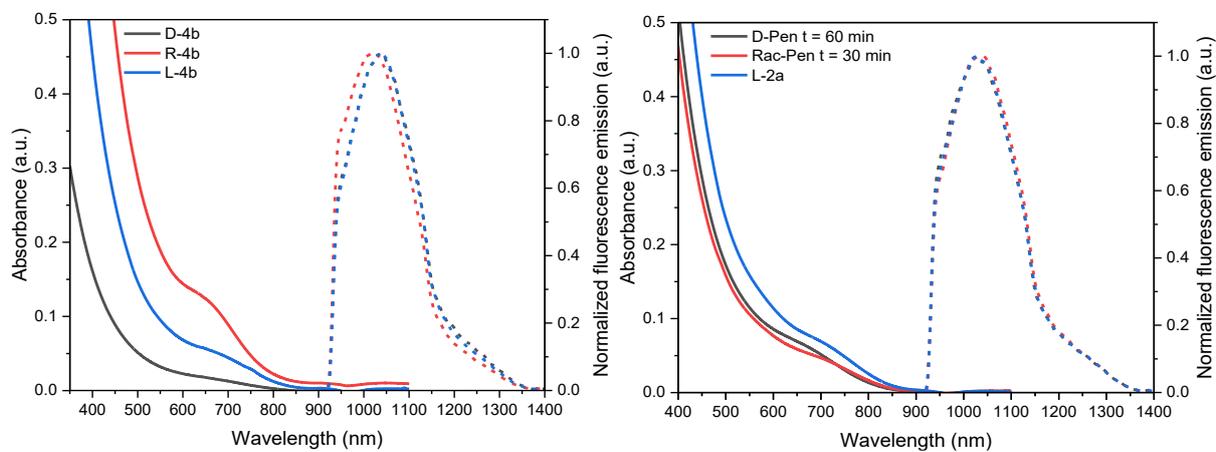
Table S3 Fluorescence lifetime ( $\tau$ ) components, along with their respective amplitudes (A) and the correlation coefficient ( $\chi^2$ ) for  $\text{Ag}_2\text{S}/\text{L-Pen}$  QDs (L-2a) and  $\text{Ag}_2\text{S}/\text{L-Pen}$  + supernatant.

## S8. Bi-exponential fitting of fluorescence decay times.

| Coating/sample number | $\tau_1$ [ns] | $\tau_2$ [ns] | A1 [%] | A2 [%] | $\tau_{\text{average}}$ [ns] | Correlation coefficient $\chi^2_{\text{2-exponential decay}}$ |
|-----------------------|---------------|---------------|--------|--------|------------------------------|---|
| <b>D-Pen</b>          |               |               |        |        |                              |   |
| D-2a                  | 45.4          | 10.7          | 51.37  | 48.63  | 28.6                         | 1.8590  |
| D-2b                  | 75.1          | 20.1          | 58.73  | 41.27  | 52.4                         | 1.4640  |
| D-4a*                 | 16.6          | 3.8           | 53.21  | 46.79  | 10.6                         | 2.1010  |
| D-4b                  | 95.5          | 23.8          | 59.49  | 40.51  | 66.4                         | 1.5710  |
| D-5*                  | 14.0          | 2.8           | 52.55  | 47.45  | 8.7                          | 2.3370  |
| <b>Rac-Pen</b>        |               |               |        |        |                              |   |
| R-2a*                 | 20.8          | 5.8           | 48.77  | 51.23  | 13.2                         | 1.4750  |
| R-2b                  | 21.0          | 5.1           | 48.36  | 51.64  | 12.8                         | 1.9490  |
| R-4a*                 | 12.8          | 2.9           | 54.55  | 45.45  | 8.3                          | 2.2050  |
| R-4b                  | 88.4          | 22.1          | 58.31  | 41.69  | 60.8                         | 1.6060  |
| <b>L-Pen</b>          |               |               |        |        |                              |   |
| L-2a                  | 67.3          | 17.1          | 56.48  | 43.52  | 45.4                         | 1.6040  |
| L-2b                  | 36.8          | 8.8           | 53.32  | 46.68  | 23.7                         | 1.8270  |
| L-4a*                 | 16.7          | 3.7           | 52.12  | 47.88  | 10.5                         | 2.3860  |
| L-4b                  | 26.5          | 109.3         | 37.60  | 62.40  | 78.2                         | 1.6090  |

Table S4 Fluorescence lifetime ( $\tau$ ) components, along with their respective amplitudes (A) and the correlation coefficient ( $\chi^2$ ) using bi-exponential function for  $\text{Ag}_2\text{S}/\text{Pen}$  QDs.

**S9.** Absorption and normalized emission spectra of Ag<sub>2</sub>S/Pen QDs for optimized synthesis conditions.



*Fig. S7 UV-Vis absorption and normalized fluorescence spectra of Ag<sub>2</sub>S/Pen QDs for optimized synthesis conditions, excited at  $\lambda = 500$  nm.*

**S10.** Detailed information on fluorescence decay times for reactions depending on reaction time and temperature.

| Coating/<br>Rxn time<br>[min] | T<br>[°C] | $\tau_1$ [ns] | $\tau_2$ [ns] | $\tau_3$ [ns] | A1 [%]       | A2 [%]       | A3 [%]       | $\tau_{\text{average}}$<br>[ns] | Correlation<br>coefficient<br>$\chi^2$ -exponential<br>decay |
|-------------------------------|-----------|---------------|---------------|---------------|--------------|--------------|--------------|---------------------------------|--|
| D-Pen                         |           |               |               |               |              |              |              |                                 |  |
| 30                            | 50        | 64.4          | 21.8          | 6.7           | 28.61        | 51.47        | 19.92        | 31.0                            | 1.0190   |
| <b>60</b>                     | <b>50</b> | <b>44.2</b>   | <b>131.9</b>  | <b>12.4</b>   | <b>50.97</b> | <b>37.28</b> | <b>11.75</b> | <b>73.0</b>                     | <b>1.0330</b>  |
| <b>90</b>                     | <b>50</b> | <b>45.1</b>   | <b>131.1</b>  | <b>13.3</b>   | <b>52.08</b> | <b>34.04</b> | <b>13.88</b> | <b>69.3</b>                     | <b>1.0460</b>  |
| 150                           | 50        | 33.7          | 129.7         | 8.9           | 54.92        | 27.83        | 17.25        | 56.3                            | 1.0830   |
|                               |           |               |               |               |              |              |              |                                 |  |
| <b>30</b>                     | <b>90</b> | <b>82.7</b>   | <b>25.9</b>   | <b>7.6</b>    | <b>28.36</b> | <b>53.97</b> | <b>17.67</b> | <b>38.8</b>                     | <b>1.0470</b>  |
| 60                            | 90        | 64.8          | 19.3          | 5.8           | 30.36        | 51.42        | 18.22        | 30.7                            | 1.0460   |
| 90                            | 90        | 36.3          | 11.3          | 3.7           | 21.86        | 54.84        | 23.30        | 15.0                            | 1.0880   |
| 150                           | 90        | 57.7          | 16.5          | 4.9           | 25.00        | 51.72        | 23.28        | 24.2                            | 1.0830   |
| Rac-Pen                       |           |               |               |               |              |              |              |                                 |  |
| <b>30</b>                     | <b>50</b> | <b>132.8</b>  | <b>45.7</b>   | <b>13.3</b>   | <b>31.50</b> | <b>53.20</b> | <b>15.30</b> | <b>68.2</b>                     | <b>1.0550</b>  |
| 60                            | 50        | 68.7          | 23.0          | 7.1           | 29.97        | 52.83        | 17.20        | 34.0                            | 1.0420   |
| 90                            | 50        | 32.8          | 96.1          | 9.9           | 52.39        | 31.69        | 15.92        | 49.0                            | 1.0660   |
| 150                           | 50        | 23.7          | 7.2           | 73.9          | 52.22        | 19.28        | 28.50        | 34.9                            | 1.0330   |
|                               |           |               |               |               |              |              |              |                                 |  |
| <b>30</b>                     | <b>90</b> | <b>34.6</b>   | <b>11.5</b>   | <b>3.8</b>    | <b>23.50</b> | <b>55.92</b> | <b>20.58</b> | <b>15.3</b>                     | <b>1.0860</b>  |
| 60                            | 90        | 25.4          | 9.1           | 3.2           | 20.58        | 57.31        | 22.11        | 11.1                            | 1.1190   |
| 90                            | 90        | 19.0          | 7.0           | 2.6           | 24.94        | 56.98        | 18.08        | 9.2                             | 1.0870   |
| 150                           | 90        | 20.9          | 7.5           | 2.7           | 25.70        | 54.36        | 19.94        | 10.0                            | 1.1050   |
| L-Pen                         |           |               |               |               |              |              |              |                                 |  |
| 30                            | 50        | 61.4          | 19.5          | 6.1           | 26.33        | 53.06        | 20.61        | 27.8                            | 1.0230   |
| <b>60</b>                     | <b>50</b> | <b>22.3</b>   | <b>69.8</b>   | <b>7.0</b>    | <b>53.53</b> | <b>26.00</b> | <b>20.47</b> | <b>31.3</b>                     | <b>1.0480</b>  |
| 90                            | 50        | 56.6          | 18.8          | 5.8           | 29.08        | 53.39        | 17.53        | 27.5                            | 1.0690   |
| 150                           | 50        | 47.5          | 16.00         | 5.2           | 24.20        | 56.80        | 19.00        | 21.7                            | 1.0950   |
|                               |           |               |               |               |              |              |              |                                 |  |
| 30                            | 90        | 5.9           | 58.0          | 18.9          | 20.94        | 25.89        | 53.17        | 26.4                            | 1.0210   |
| 60                            | 90        | 18.3          | 57.6          | 5.6           | 54.10        | 25.37        | 20.53        | 25.6                            | 1.1030   |
| <b>90</b>                     | <b>90</b> | <b>65.2</b>   | <b>21.1</b>   | <b>6.3</b>    | <b>28.56</b> | <b>52.42</b> | <b>19.03</b> | <b>30.8</b>                     | <b>1.0480</b>  |
| 150                           | 90        | 41.5          | 13.8          | 4.3           | 28.50        | 54.03        | 17.47        | 20.1                            | 1.1060   |

Table S5 Fluorescence lifetime ( $\tau$ ) components, along with their respective amplitudes (A) and the correlation coefficient ( $\chi^2$ ) for Ag<sub>2</sub>S/Pen QDs depending on the reaction time and temperature.

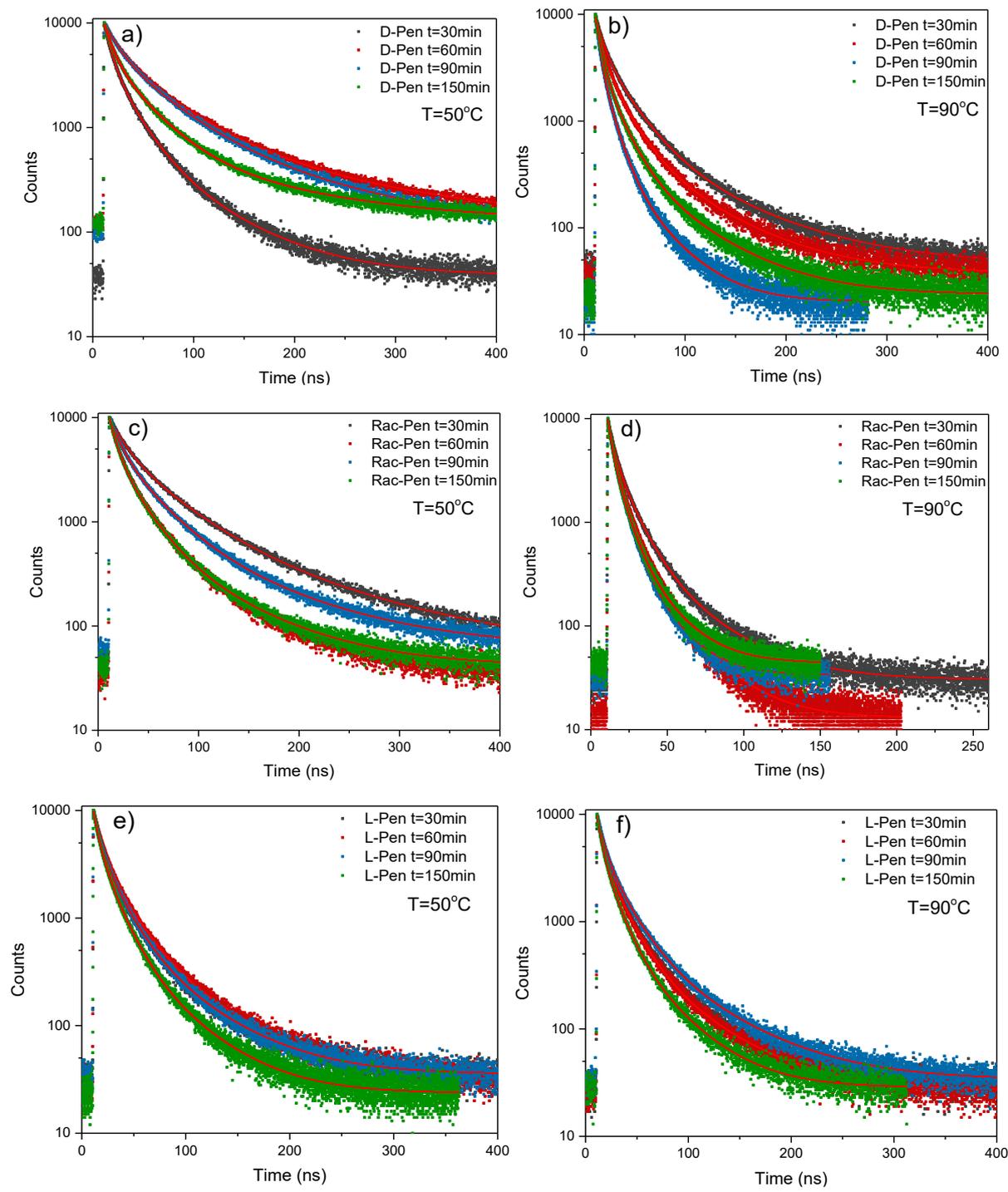


Fig. S8 The fluorescence decays of colloidal solutions of Ag<sub>2</sub>S/Pen QDs depending on the reaction time and temperature.

## S11. Fit residuals for the fluorescence lifetime data.

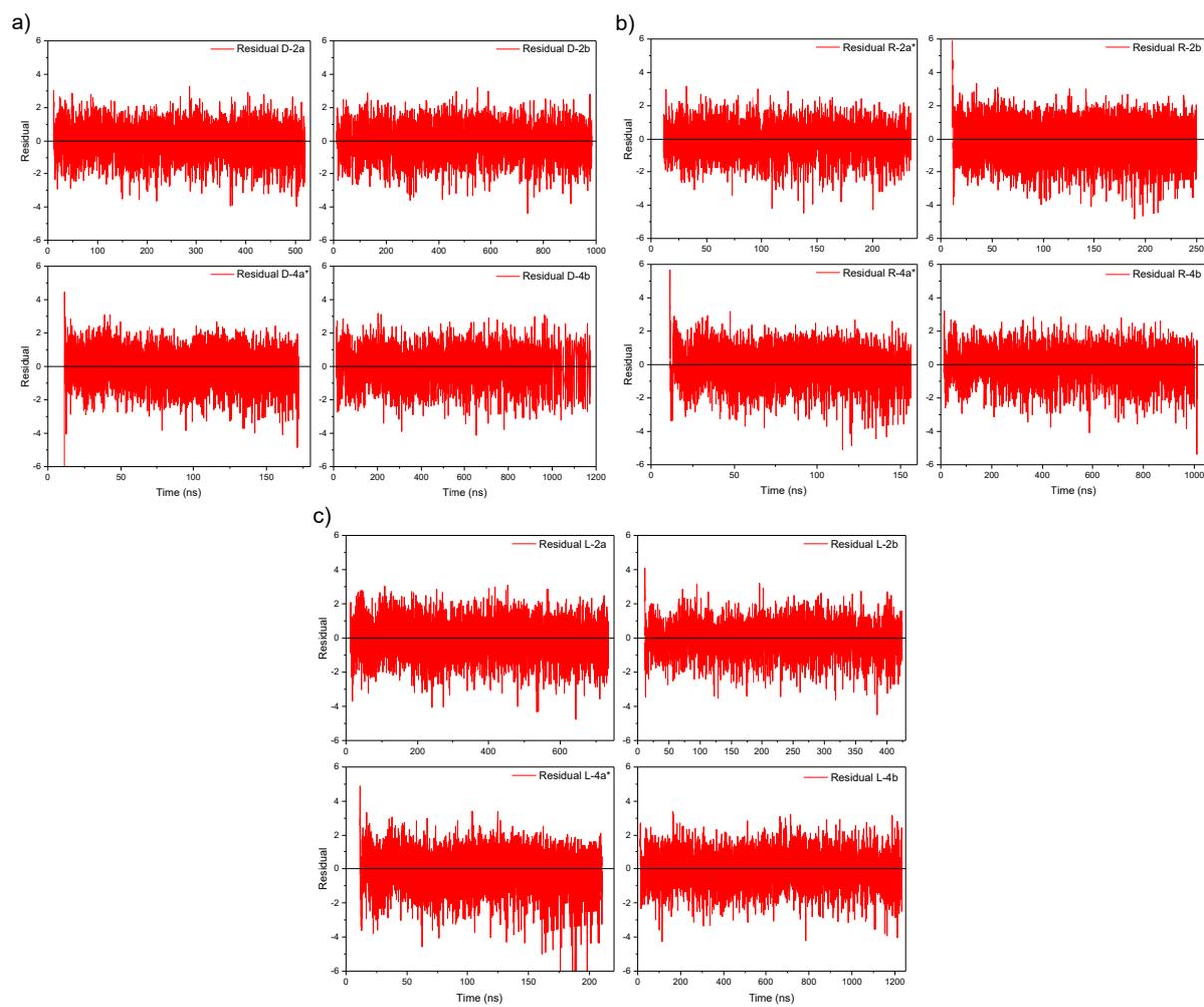


Fig. S9 Fit residuals (3-exponential fit) for the fluorescence lifetime data presented in Table 2 of the main text.