Electronic Supplementary Information

Mn$^{2+}$-Doped Zn-In-S Quantum Dots with Tunable Bandgaps and High Photoluminescence Properties

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Table S1. Optical Properties of typical Mn$^{2+}$-doped QDs in the reported works

<table>
<thead>
<tr>
<th>QDs</th>
<th>PL QY/(%)</th>
<th>Peak/(nm)</th>
<th>Lifetime/(ms)</th>
<th>Band gap/(eV)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn:ZnS</td>
<td>&gt; 50</td>
<td>590</td>
<td>1.71</td>
<td>~3.7</td>
<td>1</td>
</tr>
<tr>
<td>Mn:ZnS</td>
<td>&gt; 50</td>
<td>585</td>
<td>0.37</td>
<td>~3.7</td>
<td>2</td>
</tr>
<tr>
<td>Mn:CdS</td>
<td>not</td>
<td>580-620,</td>
<td>not mentioned</td>
<td>~2.7</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>mentioned</td>
<td>tunable</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn:ZnSe</td>
<td>35</td>
<td>590</td>
<td>0.38</td>
<td>~2.7</td>
<td>4</td>
</tr>
<tr>
<td>Mn:ZnSSe</td>
<td>~60</td>
<td>~595</td>
<td>not mentioned</td>
<td>~2.9</td>
<td>5</td>
</tr>
<tr>
<td>MnS/ZnS/CdS</td>
<td>68</td>
<td>580</td>
<td>0.68</td>
<td>2.6-3.1, tunable</td>
<td>6</td>
</tr>
<tr>
<td>Mn:ZnCdS</td>
<td>30</td>
<td>580</td>
<td>not mentioned</td>
<td>2.7-3.9, tunable</td>
<td>7</td>
</tr>
<tr>
<td>Mn:CuInZnS</td>
<td>45</td>
<td>600</td>
<td>2.12</td>
<td>~2.7</td>
<td>8</td>
</tr>
<tr>
<td>Mn:CdInS</td>
<td>17</td>
<td>630</td>
<td>1.1</td>
<td>2.8-3.7, tunable</td>
<td>9</td>
</tr>
<tr>
<td>Mn:CdZnSe</td>
<td>~25</td>
<td>580</td>
<td>~0.6</td>
<td>~3.1</td>
<td>10</td>
</tr>
<tr>
<td>Mn:CuInS/ZnS</td>
<td>66</td>
<td>610</td>
<td>3.78</td>
<td>~2.7</td>
<td>11</td>
</tr>
<tr>
<td>Mn:Zn-In-S</td>
<td><strong>56</strong></td>
<td><strong>600</strong></td>
<td><strong>4.2</strong></td>
<td><strong>2.88-3.68,</strong> tunable</td>
<td>The present work</td>
</tr>
</tbody>
</table>

The present work
**Table S2.** Fitting parameters of PL dynamics of Mn$^{2+}$ doped Zn-In-S QDs with different Zn precursor injection times

<table>
<thead>
<tr>
<th>Zn precursor injection times</th>
<th>$A_1$</th>
<th>$\tau_1$(ms)</th>
<th>$A_2$</th>
<th>$\tau_2$(ms)</th>
<th>$\tau_{ave}$(ms)</th>
<th>PL QY(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.57</td>
<td>0.08</td>
<td>0.41</td>
<td>0.31</td>
<td>0.25</td>
<td>5</td>
</tr>
<tr>
<td>1</td>
<td>0.82</td>
<td>0.52</td>
<td>0.17</td>
<td>2.44</td>
<td>1.45</td>
<td>21</td>
</tr>
<tr>
<td>2</td>
<td>0.77</td>
<td>0.65</td>
<td>0.23</td>
<td>3.82</td>
<td>2.66</td>
<td>45</td>
</tr>
<tr>
<td>3</td>
<td>0.52</td>
<td>0.72</td>
<td>0.44</td>
<td>4.89</td>
<td>4.27</td>
<td>56</td>
</tr>
</tbody>
</table>
Figure S1. Typical PL spectra of Mn$^{2+}$ doped Zn-In-S QDs before (black line, CHCl$_3$ dispersions) and after (red line, aqueous dispersions) ligand exchange. The inset shows the digital photographs of the Mn$^{2+}$ doped Zn-In-S QDs dissolved in CHCl$_3$ (left) and water (right) excited at 365 nm.
Figure S2. The linear extrapolation of $(ahv)^2$ vs photon energy of Mn$^{2+}$ doped Zn-In-S QDs under different nominal Zn/In precursor ratios.
Figure S3. Typical EDX spectra of Mn$^{2+}$ doped Zn-In-S QDs under different nominal Zn/In precursor ratios.
**Figure S4.** Typical TEM images of the Mn doped Zn-In-S QDs with nominal Zn/In precursor molar ratios of 7/3 (a.), 5/5 (b.), 4/6 (c.), and 3/7(d), indicating that the particle sizes are almost kept a constant regardless of various Zn/In precursor ratios introduced.
**Table S3. Chemical Compositions of Mn^{2+} doped Zn-In-S QDs under different nominal Zn/In precursor ratios**

<table>
<thead>
<tr>
<th>Nominal Zn/In Ratios for Mn:ZnInS cores</th>
<th>Nominal Zn/In Ratios for Mn^{2+}-doped QDs</th>
<th>Real Zn/In Ratios</th>
<th>S /atom.%</th>
<th>Zn /atom.%</th>
<th>In /atom.%</th>
<th>Mn /atom.%</th>
<th>Mn^{2+} doping Concentration/ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>10/0</td>
<td>10/0</td>
<td>60.84</td>
<td>37.55</td>
<td>0</td>
<td>1.61</td>
<td>4.1</td>
<td></td>
</tr>
<tr>
<td>7/3</td>
<td>88/12=7.3</td>
<td>3.5</td>
<td>60.81</td>
<td>28.86</td>
<td>8.21</td>
<td>2.12</td>
<td>5.4</td>
</tr>
<tr>
<td>5/5</td>
<td>80/20=4</td>
<td>1.25</td>
<td>57.26</td>
<td>22.55</td>
<td>17.95</td>
<td>2.24</td>
<td>5.2</td>
</tr>
<tr>
<td>4/6</td>
<td>76/24=3.2</td>
<td>0.89</td>
<td>54.03</td>
<td>20.4</td>
<td>22.83</td>
<td>2.74</td>
<td>5.9</td>
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<tr>
<td>3/7</td>
<td>72/28=2.6</td>
<td>0.68</td>
<td>58.91</td>
<td>14.20</td>
<td>22.97</td>
<td>2.92</td>
<td>7.1</td>
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</table>
Table S4. Chemical Compositions of Mn$^{2+}$ doped Zn-In-S QDs under different nominal Mn$^{2+}$ doping concentrations.

<table>
<thead>
<tr>
<th>Nominal Mn$^{2+}$ Doping Concentration / %</th>
<th>S /atom.%</th>
<th>Zn /atom.%</th>
<th>In /atom.%</th>
<th>Mn /atom.%</th>
<th>Real Mn$^{2+}$ doping Concentration / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>75.23</td>
<td>19.31</td>
<td>4.72</td>
<td>0.74</td>
<td>3.1</td>
</tr>
<tr>
<td>3</td>
<td>83.97</td>
<td>11.24</td>
<td>4</td>
<td>0.79</td>
<td>5.2</td>
</tr>
<tr>
<td>4.5</td>
<td>77.05</td>
<td>15.25</td>
<td>6.48</td>
<td>1.22</td>
<td>5.6</td>
</tr>
<tr>
<td>6.5</td>
<td>74.03</td>
<td>18.32</td>
<td>6.12</td>
<td>1.53</td>
<td>6.3</td>
</tr>
<tr>
<td>7.5</td>
<td>80.92</td>
<td>12.34</td>
<td>5.32</td>
<td>1.42</td>
<td>8.1</td>
</tr>
<tr>
<td>9</td>
<td>70.55</td>
<td>19.62</td>
<td>7.32</td>
<td>2.51</td>
<td>9.3</td>
</tr>
</tbody>
</table>
Figure S5. Typical absorption and PL spectra of Mn$^{2+}$-doped Zn-In-S (red lines) and undoped Zn-In-S QDs (blue lines).
References


