Artificial light-harvesting system based on ESIPT-AIE-FRET triple fluorescence mechanism

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1. Supplementary characterization of L NPs

Scheme S1 The enol and keto forms of compound L.

Fig. S1. Solid-state fluorescence spectrum of L ($\lambda_{ex} = 327$ nm).

Fig. S2. UV-vis absorption spectrum of L nanoparticles (NPs) in mixed THF/H$_2$O ($f_w = 90\%$). $[L] = 2 \times 10^{-5}$ M.
Fig. S3. Zeta-potentials of (a) L NPs, (b) L-NDI NPs. [L] = 2.00 × 10^{-5} M and [NDI] = 1 × 10^{-7} M, respectively.

2. Supplementary characterization of L-NDI LHS

Fig. S4. (a) DLS data of L-NDI in THF/water (f_w = 90%). (b) TEM image of L-NDI NPs.
**Fig. S5.** Fluorescence decay profiles of L NPs (orange line) and L-NDI NPs (red line), inset: fluorescent photographs of L NPs (left) and L-NDI NPs (right).

**Table S1** Fluorescence lifetimes of L and L-NDI (D:A = 200:1) upon excitation at 327 nm, [L] = 2.00 × 10⁻⁵ M, [NDI] = 1.00 × 10⁻⁷ M, respectively.

<table>
<thead>
<tr>
<th>Sample</th>
<th>τ₁/ns</th>
<th>RW1[%]</th>
<th>τ₂/ns</th>
<th>RW2[%]</th>
<th>τ/ns</th>
<th>χ²</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>0.50</td>
<td>25.54</td>
<td>2.69</td>
<td>74.46</td>
<td>2.13</td>
<td>1.092</td>
</tr>
<tr>
<td>L-NDI (L : NDI = 200 : 1)</td>
<td>0.64</td>
<td>66.86</td>
<td>2.04</td>
<td>33.14</td>
<td>1.10</td>
<td>1.109</td>
</tr>
</tbody>
</table>
**Fig. S6.** Absolute fluorescence quantum yields ($\Phi_{\text{abs}}$) (a) of L, (b) of L-NDI (L/NDI = 400/1), (c) of L + Cu$^{2+}$ (L/Cu$^{2+}$ = 1/1), upon excitation at 327 nm in aqueous solution. [L] = 2.00 × 10$^{-5}$ M.

**Table S2** Fluorescence quantum yields of L and L-NDI. [L] = 2.00 × 10$^{-5}$ M, [NDI] = 1.00 × 10$^{-7}$ M, respectively.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fluorescence quantum yields ($\Phi_{\text{abs}}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>19.14%</td>
</tr>
<tr>
<td>L-NDI (L : NDI = 200 : 1)</td>
<td>59.76%</td>
</tr>
<tr>
<td>L + Cu$^{2+}$ (1:1)</td>
<td>0.18%</td>
</tr>
</tbody>
</table>
Fig. S7. Fluorescence spectra of \textbf{L} and \textbf{L-NDI} (D:A = 200:1) assembly upon excitation at 327 nm.

Energy-transfer efficiency ($\Phi_{ET}$) was calculated from fluorescence spectra by the equation S1\textsuperscript{[S1]};

$$\Phi_{ET} = 1 - \frac{I_{DA}}{I_D} \quad (\text{eq. S1})$$

Where $I_{DA}$ and $I_D$ are the fluorescence intensities of \textbf{L-NDI} (donor and acceptor) and \textbf{L} (donor) at 585 nm when excited at 327 nm, respectively.

\textbf{Table S3} Energy-transfer efficiency with different \textbf{L}/\textbf{NDI} ratio.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Concentration, respectively</th>
<th>Energy-transfer efficiency ($\Phi_{ET}$)</th>
</tr>
</thead>
</table>
| L-NDI (L : NDI = 200 : 1) | [L] = 2.00 \times 10^{-5} M  
[NDI] = 1.00 \times 10^{-7} M | 50.2% |
| L-NDI (L : NDI = 300 : 1) | [L] = 2.00 \times 10^{-5} M  
[NDI] = 6.67 \times 10^{-8} M | 41.1% |
| L-NDI (L : NDI = 400 : 1) | [L] = 2.00 \times 10^{-5} M  
[NDI] = 5.00 \times 10^{-8} M | 36.9% |
| L-NDI (L : NDI = 500 : 1) | [L] = 2.00 \times 10^{-5} M  
[NDI] = 4.00 \times 10^{-8} M | 32.8% |
| L-NDI (L : NDI = 750 : 1) | [L] = 2.00 \times 10^{-5} M  
[NDI] = 2.67 \times 10^{-8} M | 25.2% |
| L-NDI (L : NDI = 1000 : 1) | [L] = 2.00 \times 10^{-5} M  
[NDI] = 2.00 \times 10^{-8} M | 18.3% |
| L-NDI (L : NDI = 2000 : 1) | [L] = 2.00 \times 10^{-5} M  
[NDI] = 1.00 \times 10^{-8} M | 9.6% |
**Fig. S8.** Fluorescence spectra of L-NDI (red line: $\lambda_{\text{ex}} = 327$ nm; blue line: $\lambda_{\text{ex}} = 585$ nm). The black line represents the fluorescence spectrum of L, which was normalized according to the fluorescence intensity at 585 nm of the red line. [L] = $2.00 \times 10^{-5}$ M, [NDI] = $5.00 \times 10^{-8}$ M, respectively.

The antenna effect (AE) was calculated based on the emission spectra using equation S2:\[S1]:

$$\text{AE} = \frac{I_{\text{DA,327}}}{I_{\text{DA,585}}} = \frac{(I_{\text{DA,327}} - I_{\text{D,327}})}{I_{\text{DA,585}}}(\text{eq. S2})$$

Where $I_{\text{DA,327}}$ and $I_{\text{DA,585}}$ are the fluorescence intensities at 640 nm with the excitation of the light-harvesting system at 327 nm and 585 nm, respectively. $I_{\text{D,327}}$ is the fluorescence intensities at 640 nm of L, which was normalized with the L-NDI assembly at 585 nm.

**Table S4 Antenna effect with different L/NDI ratio.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Concentration, respectively</th>
<th>AE</th>
</tr>
</thead>
<tbody>
<tr>
<td>L-NDI (L : NDI = 200 : 1)</td>
<td>[L] = $2.00 \times 10^{-5}$ M [NDI] = $1.00 \times 10^{-7}$ M</td>
<td>20.9</td>
</tr>
<tr>
<td>L-NDI (L : NDI = 300 : 1)</td>
<td>[L] = $2.00 \times 10^{-5}$ M [NDI] = $6.67 \times 10^{-8}$ M</td>
<td>21.1</td>
</tr>
<tr>
<td>L-NDI (L : NDI = 400 : 1)</td>
<td>[L] = $2.00 \times 10^{-5}$ M [NDI] = $5.00 \times 10^{-8}$ M</td>
<td>23.0</td>
</tr>
<tr>
<td>L-NDI (L : NDI = 500 : 1)</td>
<td>[L] = $2.00 \times 10^{-5}$ M [NDI] = $4.00 \times 10^{-8}$ M</td>
<td>16.7</td>
</tr>
<tr>
<td>L-NDI (L : NDI = 750 : 1)</td>
<td>[L] = $2.00 \times 10^{-5}$ M [NDI] = $2.67 \times 10^{-8}$ M</td>
<td>15.4</td>
</tr>
<tr>
<td>L-NDI (L : NDI = 1000 : 1)</td>
<td>[L] = $2.00 \times 10^{-5}$ M [NDI] = $2.00 \times 10^{-8}$ M</td>
<td>13.4</td>
</tr>
<tr>
<td>L-NDI (L : NDI = 2000 : 1)</td>
<td>[L] = $2.00 \times 10^{-5}$ M [NDI] = $1.00 \times 10^{-8}$ M</td>
<td>6.6</td>
</tr>
</tbody>
</table>
3. Control experiment based on compound C

![Chemical structure of C](image)

**Scheme S2** Chemical structure of C.

**Fig. S9.** (a) Fluorescence spectra of L and C NPs. [L] = 2.00 × 10^{-5} M, [C] = 4.00 × 10^{-5} M, λ<sub>ex</sub> = 327 nm. (b) Fluorescence spectra of C-NDI (red line: λ<sub>ex</sub> = 327 nm; blue line: λ<sub>ex</sub> = 585 nm). The black line represents the fluorescence spectrum of C, which was normalized according to the fluorescence intensity at 585 nm of the red line. [C] = 2.00 × 10^{-5} M, [NDI] = 1.00 × 10^{-7} M, respectively.

**Table S5** The antenna effect value of C-NDI

<table>
<thead>
<tr>
<th>Sample</th>
<th>Concentration</th>
<th>AE</th>
</tr>
</thead>
</table>
| C-NDI (C : NDI = 200 : 1) | [C] = 2.00 × 10^{-5} M  
[NDI] = 1.00 × 10^{-7} M | 8.4 |

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4. Cu$^{2+}$ sensing by L and L-NDI

![Fig. S10. Photograph (a) of compound L (b) of compound L-NDI interacting with metal ions under a 365 nm UV lamp.](image)

![Fig. S11. FT-IR spectra of L and L + Cu$^{2+}$.](image)

![Fig. S12. XPS spectra of (a) L NPs and (b) L-Cu NPs, inset: enlarged picture of the Cu 2p$^{3/2}$ binding energy.](image)
Fig. S13. $^1$H NMR titration spectra of L on increasing concentrations of Cu$^{2+}$ in DMSO-$d_6$ solution.

Fig. S14. Bar diagram of the competitive experiments of various metal cations (a) and anions (b) on the fluorescence intensity of the L-Cu$^{2+}$ complex ($\lambda_{ex.}/\lambda_{em.} = 327/585$ nm).

Fig. S15. (a) The fluorescent titration experiment of L (20 μM) to detect Cu$^{2+}$ ($\lambda_{ex.} = 327$ nm, $\lambda_{em.} = 585$ nm). (b) The relationship between fluorescence intensity of the system at 585 nm and Cu$^{2+}$ concentration (0 μM–20 μM).
5. Synthesis of compound L and C

![Chemical structure of compound L]

**Fig. S16.** $^1$H NMR spectrum (300 MHz, DMSO-$d_6$, 298 K) of compound L.

**Fig. S17.** $^{13}$C NMR spectrum (75 MHz, CDCl$_3$, 298 K) of compound L.
Fig. S18. HR-MS (ESI, positive mode, CH₃CN) of L.

Scheme S2 Synthesis of C

Synthesis of C: a mixture of M (150.0 mg, 0.4 mmol) and aniline (40.0 μL, 0.4 mmol) in 10 mL anhydrous ethanol solution was stirred for 8 h at room temperature. The mixture was filtered and the precipitate was washed with ethanol for three times. The solid was dried under vacuum at 50 °C to obtain the product as a fluffy powder (165.5 mg, yield 92%). ¹H NMR (300 MHz, DMSO-d₆): δ (ppm) = 13.10 (s, 1H, Ar-OH), 8.76 (s, 1H, N=CH), 7.45-7.26 (m, 6H, Ar-H), 7.20-7.10 (m, 9H, Ar-H), 7.04-6.95 (m, 7H, Ar-H), 6.72 (d, J = 8.4 Hz, 1H, Ar-H). ¹³C NMR (75 MHz, DMSO-d₆): δ (ppm) = 163.5, 159.5, 148.3, 143.7, 143.5, 140.8, 140.1, 136.3, 134.9, 134.6, 131.2, 131.2, 131.1, 129.9, 128.4, 128.4, 128.3, 127.4, 127.1, 127.0, 127.0, 121.8, 119.3, 116.6. HR-ESI-MS: m/z calcd for C₃₃H₂₅NO [M + H]⁺ = 452.2009, found = 452.2007.
Fig. S19. $^1$H NMR spectrum (300 MHz, DMSO-$d_6$, 298 K) of the control compound C.

Fig. S20. $^{13}$C NMR spectrum (75 MHz, DMSO-$d_6$, 298 K) of contrast compound C.
Fig. S21. HR-MS (ESI, positive mode, CH₃CN) of C.

6. References

