Artificial light-harvesting nanoparticles based on a tripodal fluorescent sensor mediated by multiple luminescence mechanisms

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Table of Contents

1. ESIPT mechanism of G	2
2. Fluorescence lifetime and quantum yield of G and G-NDI	3
3. Energy transfer efficiency and antenna effect of G-NDI	5
4. Sensing abilities of G and G-NDI towards Fe^{3+} and Cu^{2+}	7
5. Real water sample detection	. 10
6. Job's plot and possible binding mechanism	11
7. Synthesis of compound G	. 12
8. References	. 14

1. ESIPT mechanism of G



Fig. S1. Normalized UV-Vis absorption and fluorescence spectra of compound G in mixed THF/H₂O (v/v = 1/9). [G] = 5.00×10^{-5} M, $\lambda_{ex} = 325$ nm.



Scheme S1. The enol and keto forms of compound G.

2. Fluorescence lifetime and quantum yield of G and G-NDI



Fig. S2. Fluorescence decay profiles of G NPs (yellow line) and G-NDI NPs (orange line).

Table S1. Fluorescence lifetimes of **G** and **G-NDI** (D:A = 200:1) upon excitation at 325 nm, $[\mathbf{G}] = 5.00 \times 10^{-5} \text{ M}$, $[\mathbf{NDI}] = 2.50 \times 10^{-7} \text{ M}$, respectively.

Sample	τ_1/ns	RW1 [%]	τ_2/ns	RW2 [%]	τ/ns	χ^2
G	0.76	83.76	3.55	16.24	1.21	1.1664
G-NDI (G:NDI = 200:1)	0.52	78.87	2.67	21.13	0.98	1.1882

Fig. S3. Absolute fluorescence quantum yields ($\Phi_{f(abs)}$) of G (a) and G-NDI (G:NDI = 200:1) (b). λ_{ex} = 325 nm, [G] = 5.00 × 10⁻⁵ M, [NDI] = 2.50 × 10⁻⁷ M, respectively.

Table S2. Fluorescence quantum yields data of G and G-NDI.

Sample	Flourescence quantum yields $(\Phi_{f(abs)})$		
G	2.76%		
G-NDI (G : NDI = 200:1)	5.64%		

3. Energy transfer efficiency and antenna effect of G-NDI

Fig. S4. Fluorescence spectra of **G** and **G-NDI** (D:A = 200:1) upon excitation at 325 nm. Energy-transfer efficiency (Φ_{ET}) was calculated from fluorescence spectra by the equation S1^[S1]:

$$\Phi_{\rm ET} = 1 - I_{\rm DA} / I_{\rm D} (\rm eq. \ S1)$$

Where I_{DA} and I_D are the fluorescence intensities of **G-NDI** (donor mixed with acceptor) and **G** (individual donor) at 550 nm when excited at 325 nm, respectively.

Sample	Concentration, respectively	Energy-transfer efficiency (Φ_{ET})
G-NDI (G : NDI = $200 : 1$)	$[G] = 5.00 \times 10^{-5} \text{ M}$ $[NDI] = 2.50 \times 10^{-7} \text{ M}$	22.0%
G-NDI (G : NDI = $300 : 1$)	$[G] = 5.00 \times 10^{-5} \text{ M}$ $[NDI] = 1.67 \times 10^{-7} \text{ M}$	16.0%
G-NDI (G : NDI = $400 : 1$)	$[\mathbf{G}] = 5.00 \times 10^{-5} \text{ M}$ $[\mathbf{NDI}] = 1.25 \times 10^{-7} \text{ M}$	14.1%
G-NDI (G : NDI = 500 : 1)	$[G] = 5.00 \times 10^{-5} \text{ M}$ $[NDI] = 1.00 \times 10^{-7} \text{ M}$	11.0%
G-NDI (G : NDI = $750 : 1$)	$[G] = 5.00 \times 10^{-5} \text{ M}$ $[NDI] = 6.70 \times 10^{-8} \text{ M}$	6.60%
G-NDI (G : NDI = 1000 : 1)	$[G] = 5.00 \times 10^{-5} \text{ M}$ $[NDI] = 5.00 \times 10^{-8} \text{ M}$	5.30%

Table S3. Energy-transfer efficiency of G-NDI at different D/A ratio.

Fig. S5. Fluorescence spectra of G-NDI (red line: $\lambda_{ex} = 325$ nm; blue line: $\lambda_{ex} = 550$ nm). The black line represents the fluorescence spectrum of G, which was normalized according to the fluorescence intensity at 550 nm of the red line. [G] = 5.00×10^{-5} M, [NDI] = 2.50×10^{-7} M, respectively.

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

$$AE = I'_{DA,325} / I_{DA,550} = (I_{DA,325} - I_{D,325}) / I_{DA,550} (eq. S2)$$

Where $I_{DA,325}$ and $I_{DA,550}$ are the fluorescence intensities at 640 nm with the excitation of the light-harvesting system at 325 nm and 550 nm, respectively. $I_{D,325}$ is the fluorescence intensity at 640 nm of **G**, which was normalized with the **G-NDI** assembly at 550 nm.

Sample	Concentration, respectively	AE
G-NDI (G : NDI = $200 : 1$)	$[G] = 5 \times 10^{-5} \text{ M}$ [NDI] = 2.5 × 10 ⁻⁷ M	11.4
G-NDI (G : NDI = $300 : 1$)	$[G] = 5 \times 10^{-5} \text{ M}$ $[NDI] = 1.67 \times 10^{-7} \text{ M}$	10.7
G-NDI (G : NDI = $400 : 1$)	$[G] = 5 \times 10^{-5} \text{ M}$ $[NDI] = 1.25 \times 10^{-7} \text{ M}$	9.50
G-NDI (G : NDI = $500 : 1$)	$[G] = 5 \times 10^{-5} \text{ M}$ $[NDI] = 1 \times 10^{-7} \text{ M}$	9.10
G-NDI (G : NDI = 750 : 1)	$[G] = 5 \times 10^{-5} \text{ M}$ $[NDI] = 6.7 \times 10^{-8} \text{ M}$	7.40
G-NDI (G : NDI = $1000 : 1$)	$[G] = 5 \times 10^{-5} M$ [NDI] = 5 × 10 ⁻⁸ M	5.90

Table S4. Antenna effect with different G/NDI ratio.

Fig. S6. ¹H NMR titration spectra of **G** on increasing concentrations of Cu^{2+} in DMSO- d_6 solution.

Fig. S7. ¹H NMR titration spectra of **G** on increasing concentrations of Fe^{3+} in DMSO- d_6 solution.

Fig. S8. Photos of G interacting with metal ions under natural light

Fig. S9. Bar diagram of the competitive experiments of various metal cations (a) and anions (b) on the fluorescence intensity of the G-Cu²⁺ complex ($\lambda_{ex} = 325$ nm and $\lambda_{em} = 550$ nm).

Fig. S10. Bar diagram of the competitive experiments of various metal cations (a) and anions (b) on the fluorescence intensity of the **G**-Fe³⁺ complex ($\lambda_{ex} = 325$ nm and $\lambda_{em} = 550$ nm).

Fig. S11. (a) The fluorescent titration experiment of G (50 μ M) towards the detection of Cu²⁺ (λ_{ex} = 325 nm, λ_{em} = 550 nm). (b) The relationship between fluorescence intensity of the system at 550 nm and Cu²⁺ concentration (0 μ M–75 μ M).

Fig. S12. (a) The fluorescent titration experiment of **G** (50 μ M) towards the detection of Fe³⁺ (λ_{ex} = 325 nm, λ_{em} = 550 nm). (b) The relationship between fluorescence intensity of the system at 550 nm and Fe³⁺ concentration (0 μ M–75 μ M).

5. Real water sample detection

Samples	Added/µM	$Detected/\mu M$	Recovery/%	RSD/%
Tap water	4	4.15	103.8	3.035
	6	6.21	103.5	1.966
	8	8.00	100.0	0.537
	10	9.39	93.9	4.322
	4	4.41	110.3	1.146
Divervetor	6	6.42	107.0	0.380
Kıver water	8	8.26	103.3	0.705
	10	10.03	100.3	2.552
Green tea	4	3.67	91.8	1.947
	6	5.76	96.0	1.800
	8	7.50	93.8	2.325
	10	9.93	99.3	1.786

Table S	5. Dete	ction of	Cu ²⁺ in	water	samples

Table S6. Detection of Fe^{3+} in water samples

Samples	Added/µM	Detected/µM	Recovery/%	RSD/%
T	4	4.27	106.8	1.040
	6	5.86	97.7	0.488
Tap water	8	8.08	101.0	0.698
	10	10.80	108.0	1.364
River water	4	3.70	92.5	0.665
	6	5.54	92.3	0.917
	8	7.93	99.1	0.711
	10	10.60	106.0	1.176
Green tea	4	3.98	99.5	1.032
	6	6.14	102.3	0.959
	8	8.58	107.3	1.704
	10	10.99	109.9	2.354

6. Job's plot and possible binding mechanism

Fig. S13. (a) Fluorescence spectra of **G** with continuous variation of Cu^{2+} concentration ([**G**] + [Cu^{2+}] = 50 µM) (λ_{ex} = 325 nm, λ_{em} = 550 nm). (b) Job's plot of **G** toward Cu^{2+} , indicating a 1:1 stoichiometry for **G**: Cu^{2+} . (c) Diagram of possible binding mechanism of Cu^{2+} to compound **G**.

Fig. S14. (a) Fluorescence spectra of **G** with continuous variation of Fe³⁺ concentration ([**G**] + [Fe³⁺] = 50 μ M) (λ_{ex} = 325 nm, λ_{em} = 550 nm). (b) Job's plot of **G** toward Fe³⁺, indicating a 2:1 stoichiometry for **G**: Fe³⁺. (c) Diagram of possible binding mechanism of Fe³⁺ to compound **G**.

7. Synthesis of compound G

Scheme S2. Synthetic route of G.

Compound **P** was synthesized according to our previous report.^[S2] To a 150 mL flask, **P** (1.00 g, 2.66 mmol), tris(2-aminoethyl)amine (TAEA) (0.13 g, 0.89 mmol) and anhydrous ethanol (70 mL) were added. The mixture was stirred at room temperature for 12 hours. After that, the obtained mixture was filtered and the solid was washed with ethanol thoroughly. The orange residue was further purified by recrystallization using dichloromethane and hexane to give the yellow solid product **G** (0.90 g, 83%). ¹H NMR (300 MHz, CDCl₃): δ (ppm) = 13.35 (s, 3H, Ar-OH), 7.87 (s, 3H, -CH=N-), 7.08 – 6.99 (m, 45H, Ar-H), 6.90 (d, *J* = 8.4 Hz, 3H, Ar-H), 6.83 (s, 3H, Ar-OH), 6.59 (d, *J* = 8.7 Hz, 3H, Ar-H), 3.47(br s, 6H, -CH₂-), 2.82 (br s, 6H, -CH₂-). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 165.94, 160.15, 143.95, 143.91, 143.74, 140.43, 140.03, 135.71, 134.36, 134.20, 131.55, 131.44, 131.42, 127.98, 127.84, 127.77, 126.66, 126.52, 126.45, 118.11, 116.54, 58.58, 56.03. HR-ESI-MS: *m/z* calcd for C₈₇H₇₂N₄O₃ [M + H]⁺ = 1221.5677, found = 1221.5620.

Fig. S16. ¹³C NMR spectrum (100 MHz, CDCl₃, 298 K) of contrast compound G.

Fig. S17. HR-MS (ESI, positive mode, CH₃CN) of G.

8. References

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[S2] T. Xiao, C. Bao, L. Zhang, K. Diao, D. Ren, C. Wei, Z.-Y. Li and X.-Q. Sun, *J. Mater. Chem. A*, 2022, **10**, 8528-8534.