

Large Photoactive Supramolecular Ensembles Prepared from C₆₀- Pyridine Substrates and Multi-Zn(II)-Porphyrin Receptors

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Mourad Elhabiri,^a Nathalie Solladié,^{*b} Jean-François Nierengarten,^{*c} and
Anne-Marie Albrecht-Gary^{*a}**

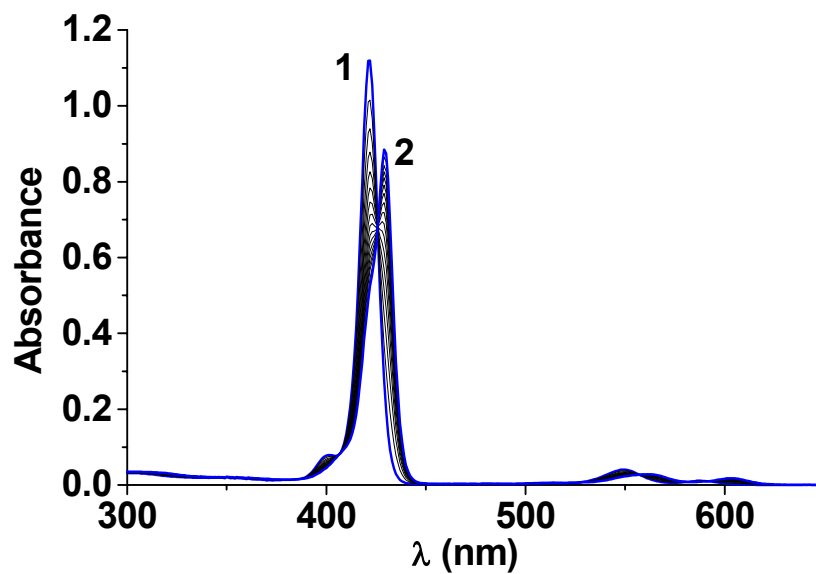
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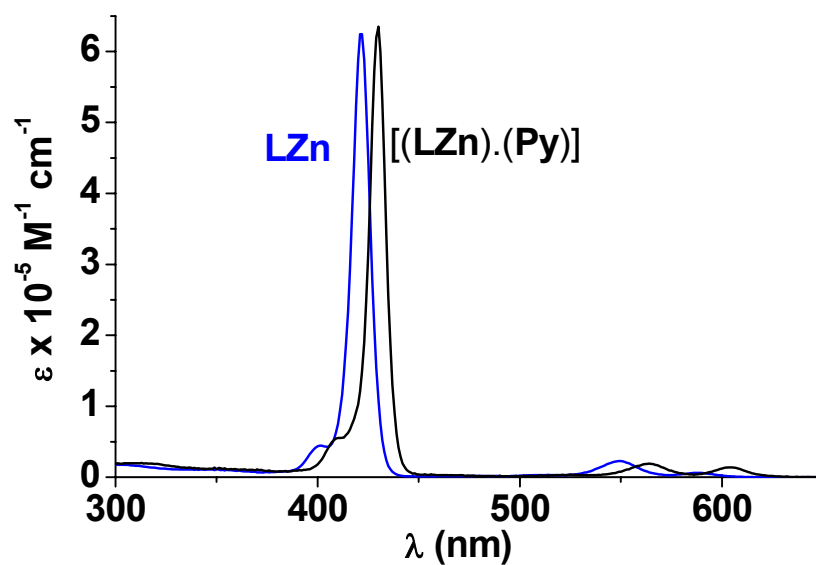
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Supporting Information

LZn + Py

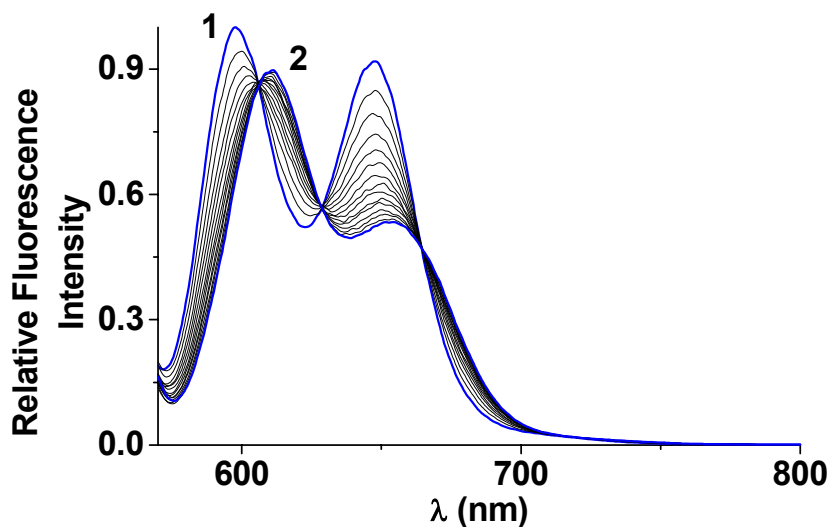


(a)

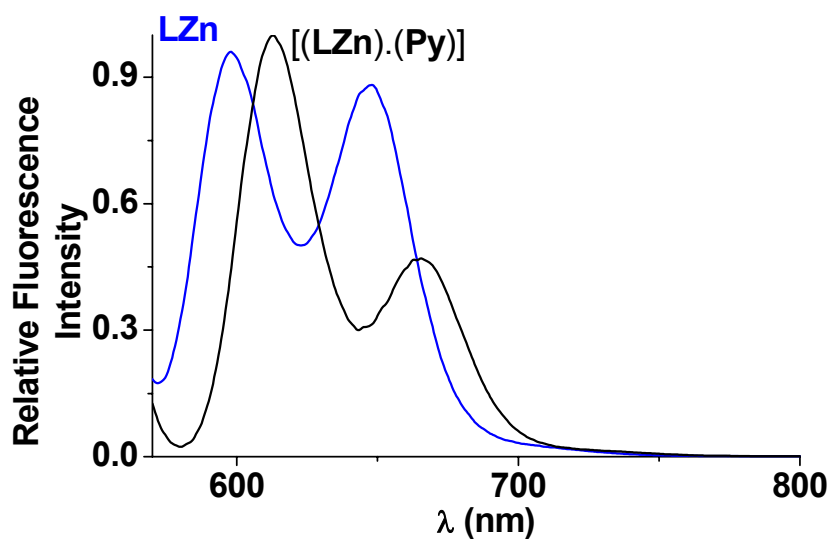


(b)

- a) UV-visible absorption spectrophotometric titration of LZn with Py. $l = 1$ cm; 1) $[\text{LZn}]_{\text{tot}} = 1.79 \times 10^{-6}$ M; 2) $[(\text{Py})]_{\text{tot}}/[\text{LZn}]_{\text{tot}} = 363$. Solvent: CH_2Cl_2 ; $T = 25.0(2)$ °C.
b) Absorption electronic spectra of LZn and $[(\text{LZn}).(\text{Py})]$. Solvent: CH_2Cl_2 ; $T = 25.0(2)$ °C.



(a)

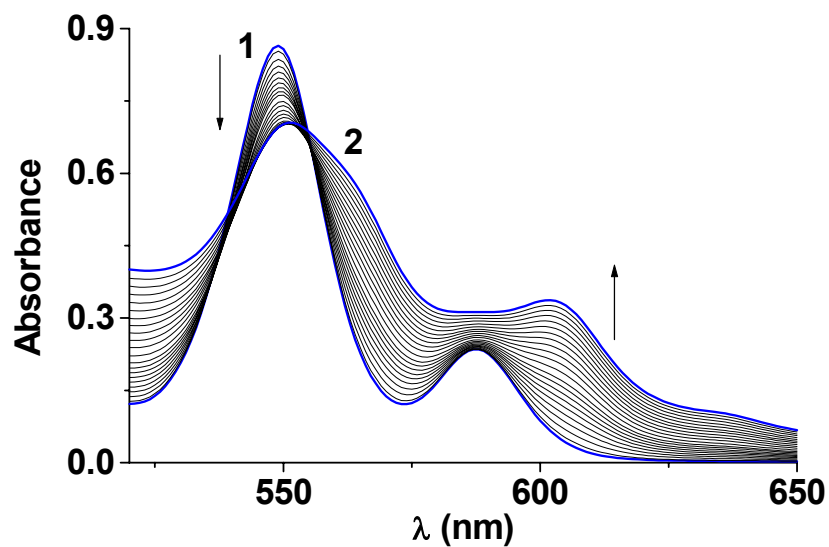


(b)

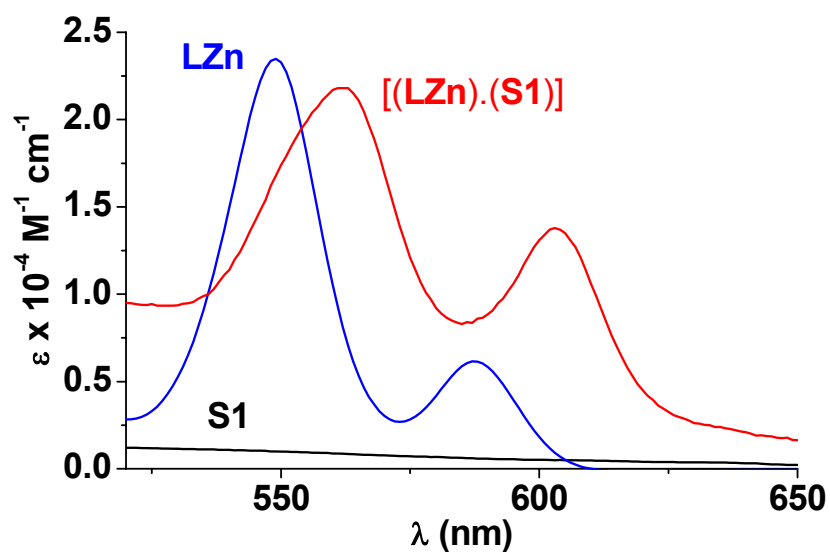
a) Luminescence spectrophotometric titration of **LZn** with **Py**. $\lambda_{\text{exc}} = 557 \text{ nm}$; emission and excitation slit widths 15 nm and 20 nm respectively; 1) $[\text{LZn}]_{\text{tot}} = 1.79 \times 10^{-6} \text{ M}$; 2) $[\text{Py}]_{\text{tot}}/[\text{LZn}]_{\text{tot}} = 314$. Solvent: CH_2Cl_2 ; $T = 25.0(2) \text{ }^\circ\text{C}$.

b) Relative recalculated fluorescence spectra of **LZn** and **[(LZn).(Py)]**. Solvent: CH_2Cl_2 ; $T = 25.0(2) \text{ }^\circ\text{C}$.

LZn + S1

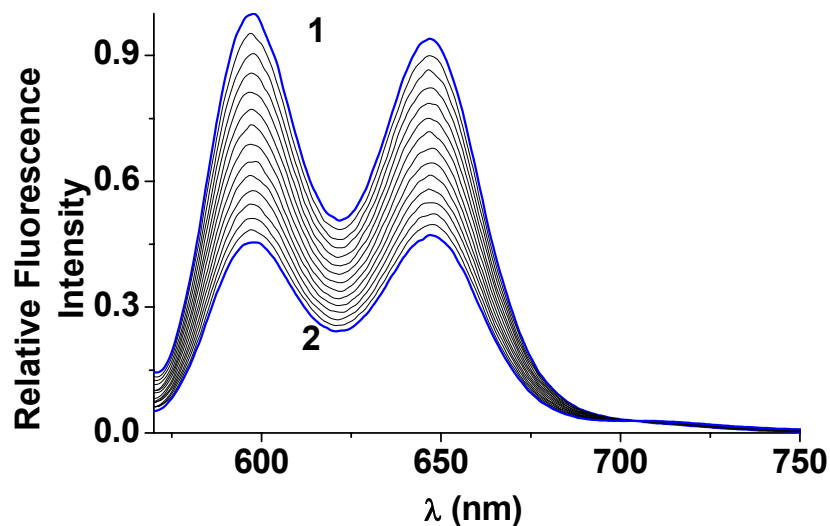


(a)

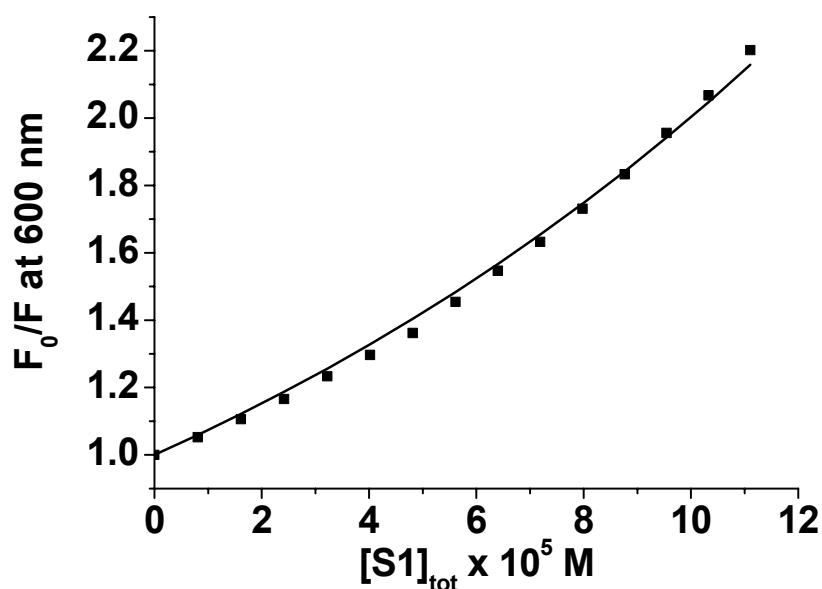


(b)

- a) UV-visible absorption spectrophotometric titration of LZn with S1. $l = 0.2$ cm; 1) $[\text{LZn}]_{\text{tot}} = 1.85 \times 10^{-4}$ M; 2) $[\text{S1}]_{\text{tot}}/[\text{LZn}]_{\text{tot}} = 6.8$. Solvent: CH_2Cl_2 ; $T = 25.0(2)$ °C.
b) Absorption electronic spectra of S1, LZn and $[(\text{LZn}).(\text{S1})]$ complex. Solvent: CH_2Cl_2 ; $T = 25.0(2)$ °C.



(a)

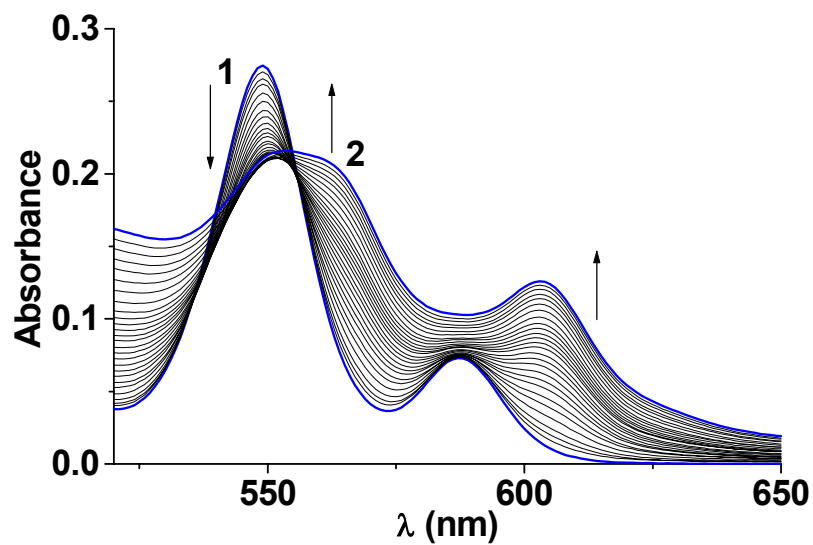


(b)

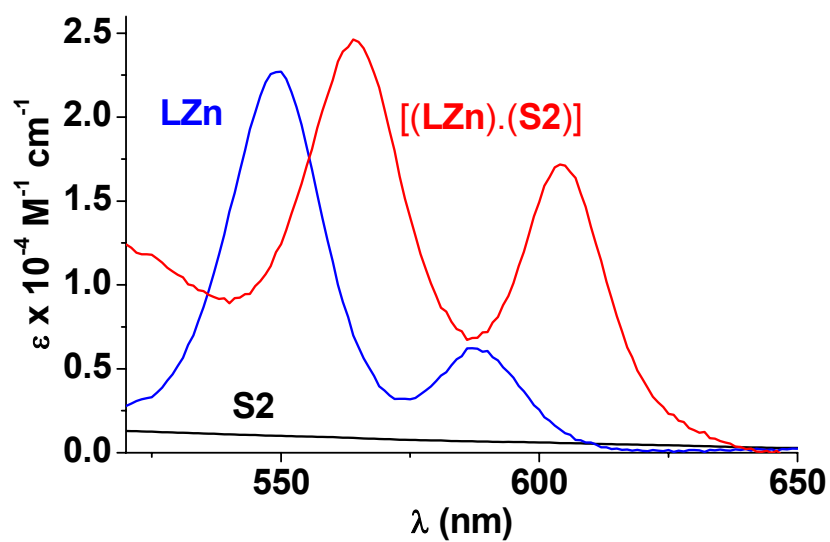
a) Luminescence spectrophotometric titration of **LZn** with **S1**. $\lambda_{\text{exc}} = 559$ nm; emission and excitation slit widths 15 nm and 20 nm respectively; 1) $[\text{LZn}]_{\text{tot}} = 1.79 \times 10^{-6}$ M; 2) $[\text{S1}]_{\text{tot}}/[\text{LZn}]_{\text{tot}} = 63$. Solvent: CH_2Cl_2 ; $T = 25.0(2)$ °C.

b) Variation of F_0/F at 600 nm versus the concentration of **S1**. The trend line is the result of the non linear least-square fit of the experimental data according to $F_0/F = (1 + K_{\text{SV}}[\text{S1}])\exp(K_1[\text{S1}])$.

LZn + S2



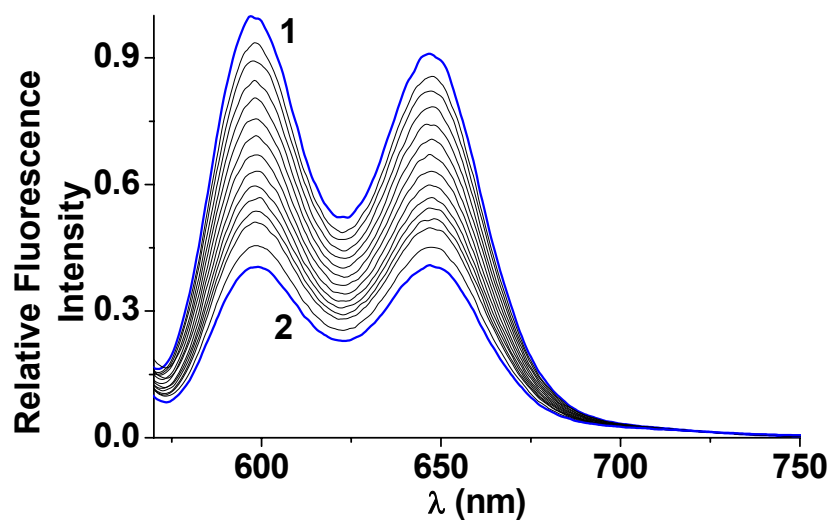
(a)



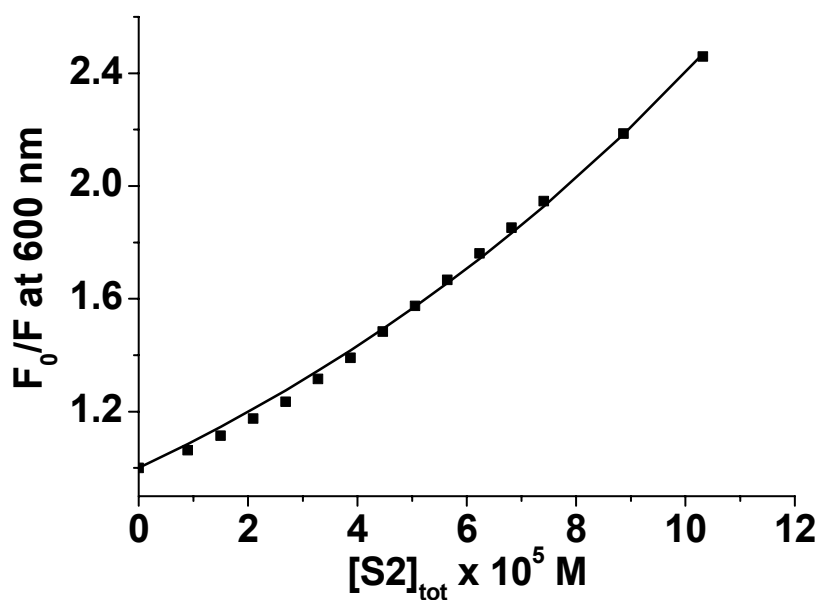
(b)

a) UV-visible absorption spectrophotometric titration of LZn with S2. $l = 0.2 \text{ cm}$; 1) $[\text{LZn}]_{\text{tot}} = 5.82 \times 10^{-5} \text{ M}$; 2) $[\text{S2}]_{\text{tot}}/[\text{LZn}]_{\text{tot}} = 7.4$. Solvent: CH_2Cl_2 ; $T = 25.0(2) \text{ }^\circ\text{C}$.

b) Absorption electronic spectra of S2, LZn and $[(\text{LZn}).(\text{S2})]$. Solvent: CH_2Cl_2 ; $T = 25.0(2) \text{ }^\circ\text{C}$.



(a)

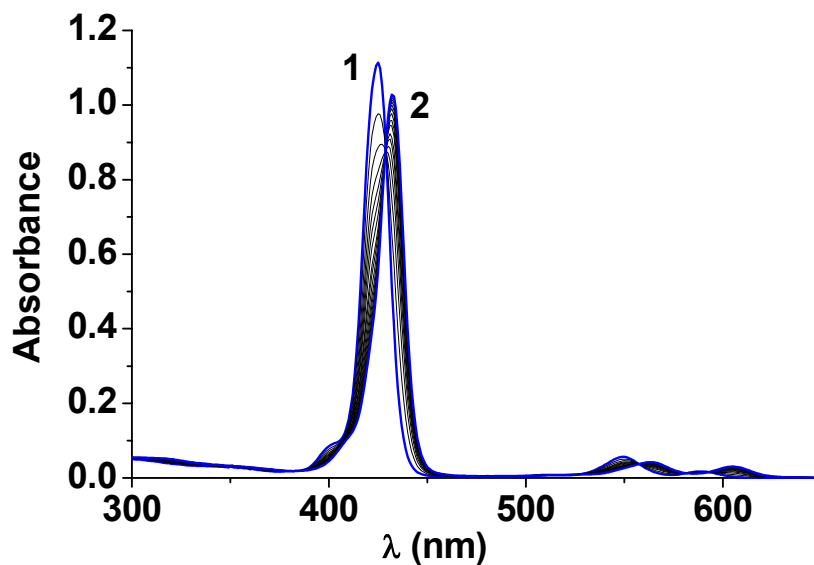


(b)

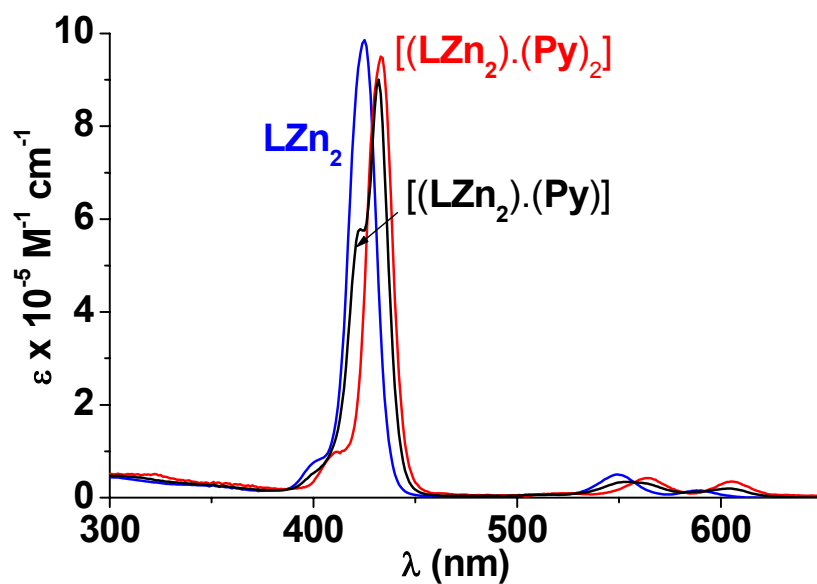
a) Luminescence spectrophotometric titration of **LZn** with **S2**. $\lambda_{\text{exc}} = 557 \text{ nm}$; emission and excitation slit widths 15 nm and 20 nm respectively; 1) $[\text{LZn}]_{\text{tot}} = 1.90 \times 10^{-6} \text{ M}$; 2) $[\text{S2}]_{\text{tot}}/[\text{LZn}]_{\text{tot}} = 48$. Solvent: CH_2Cl_2 ; $T = 25.0(2) \text{ }^\circ\text{C}$.

b) Variation of F_0/F at 600 nm versus the concentration of **S2**. The trend line is the result of the non linear least-square fit of the experimental data according to $F_0/F = (1 + K_{\text{SV}}[\text{S2}])\exp(K_1[\text{S2}])$. Solvent: CH_2Cl_2 ; $T = 25.0(2) \text{ }^\circ\text{C}$.

LZn₂ + Py

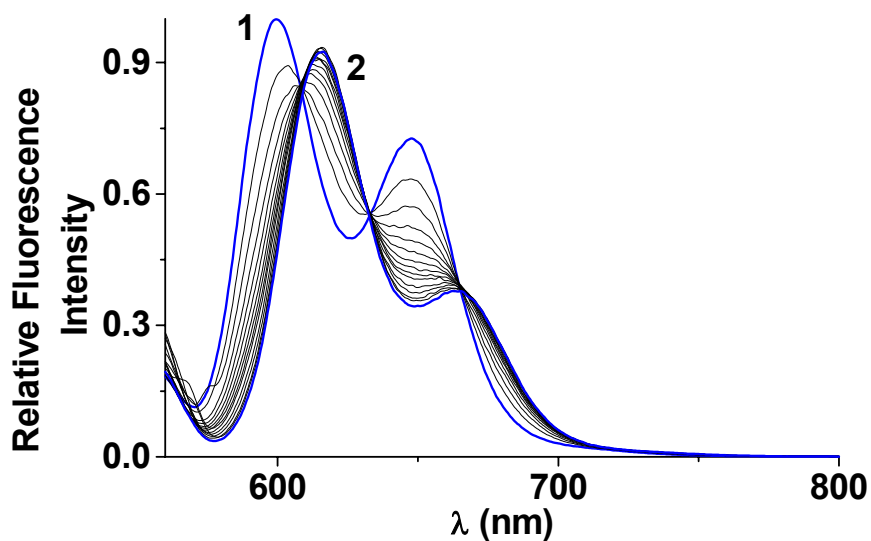


(a)

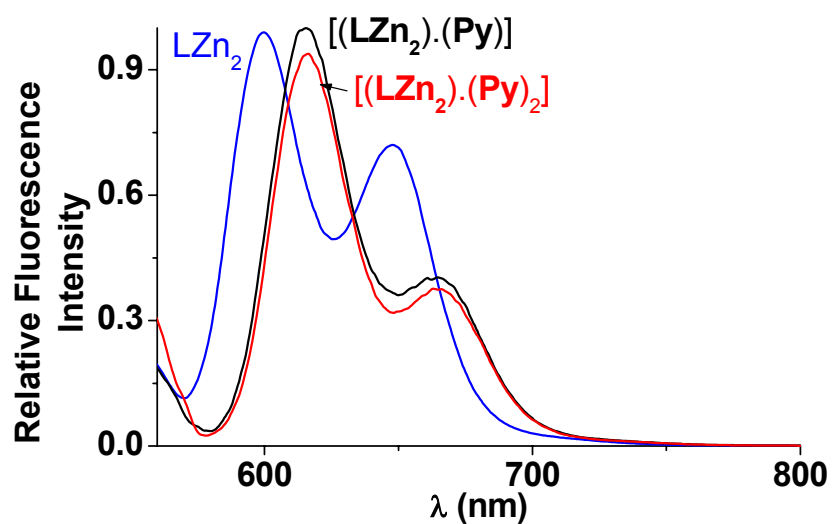


(b)

- a) UV-visible absorption spectrophotometric titration of LZn₂ with Py. $l = 1$ cm; 1) [LZn₂]_{tot} = 1.13×10^{-6} M; 2) [(Py)]_{tot}/[LZn₂]_{tot} = 863. Solvent: CH₂Cl₂; $T = 25.0(2)$ °C.
b) Absorption electronic spectra of LZn₂, [(LZn₂).Py] and [(LZn₂).Py]₂. Solvent: CH₂Cl₂; $T = 25.0(2)$ °C.



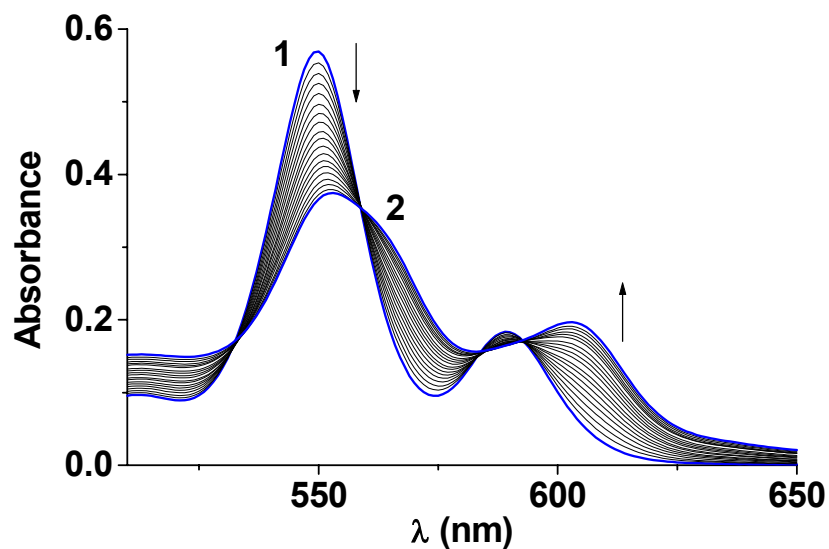
(a)



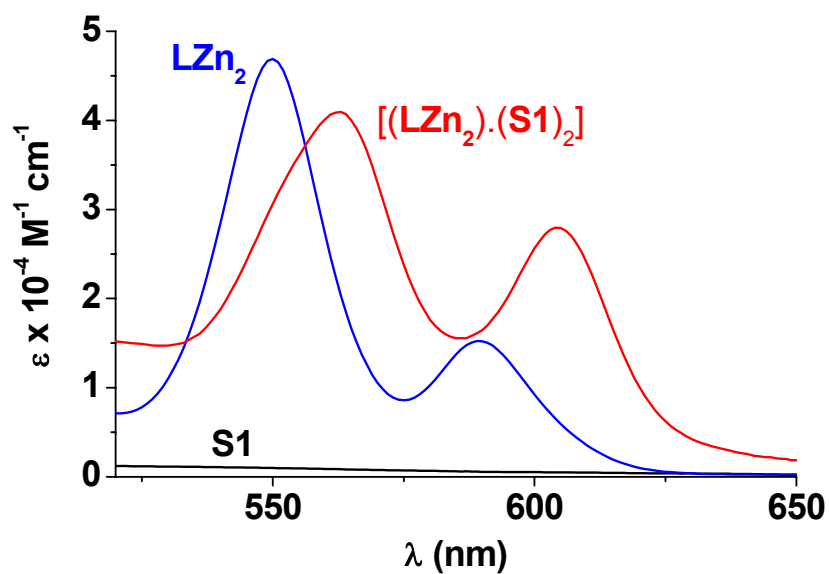
(b)

- a) Luminescence spectrophotometric titration of LZn_2 with Py. $\lambda_{\text{exc}} = 557$ nm; emission and excitation slit widths 15 nm and 20 nm respectively; 1) $[\text{LZn}_2]_{\text{tot}} = 1.13 \times 10^{-6}$ M; 2) $[(\text{Py})]_{\text{tot}}/[\text{LZn}_2]_{\text{tot}} = 531$. Solvent: CH_2Cl_2 ; $T = 25.0(2)$ °C.
- b) Relative recalculated fluorescence spectra of LZn_2 , $[(\text{LZn}_2)\cdot(\text{Py})]$ and $[(\text{LZn}_2)\cdot(\text{Py})_2]$. Solvent: CH_2Cl_2 ; $T = 25.0(2)$ °C.

LZn₂ + S1

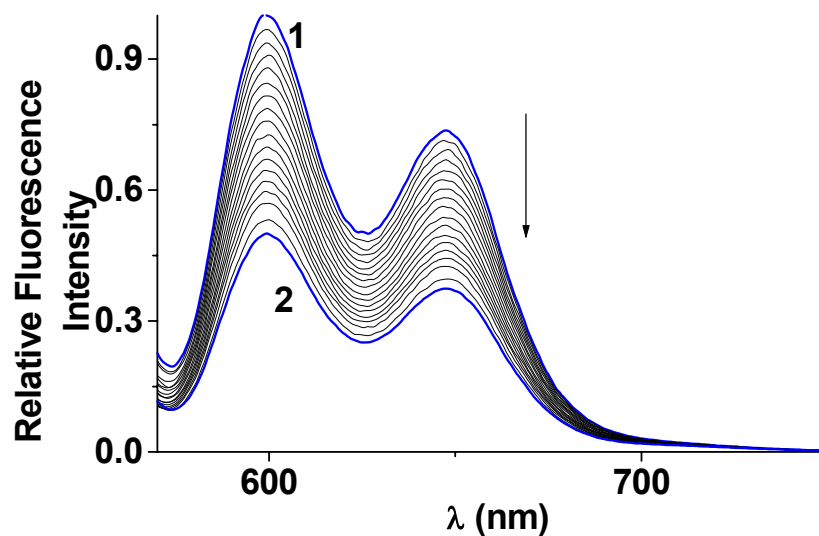


(a)

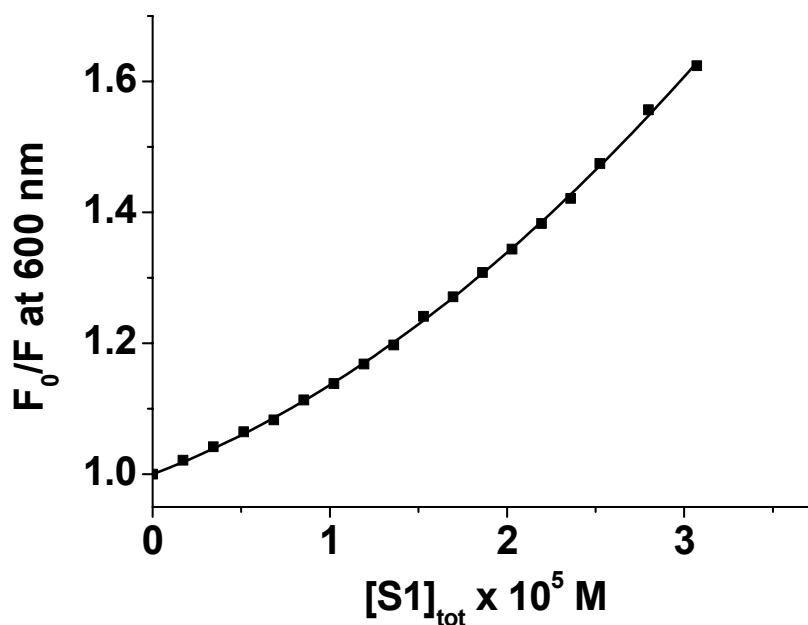


(b)

- a) UV-visible absorption spectrophotometric titration of LZn₂ with S1. $l = 0.2$ cm; 1) $[\text{LZn}_2]_{\text{tot}} = 5.65 \times 10^{-5}$ M; 2) $[\text{S1}]_{\text{tot}}/[\text{LZn}_2]_{\text{tot}} = 5$. Solvent: CH₂Cl₂; $T = 25.0(2)$ °C.
b) Absorption electronic spectra of S1, LZn₂ and [(LZn₂). (S1)₂]. Solvent: CH₂Cl₂; $T = 25.0(2)$ °C.



(a)

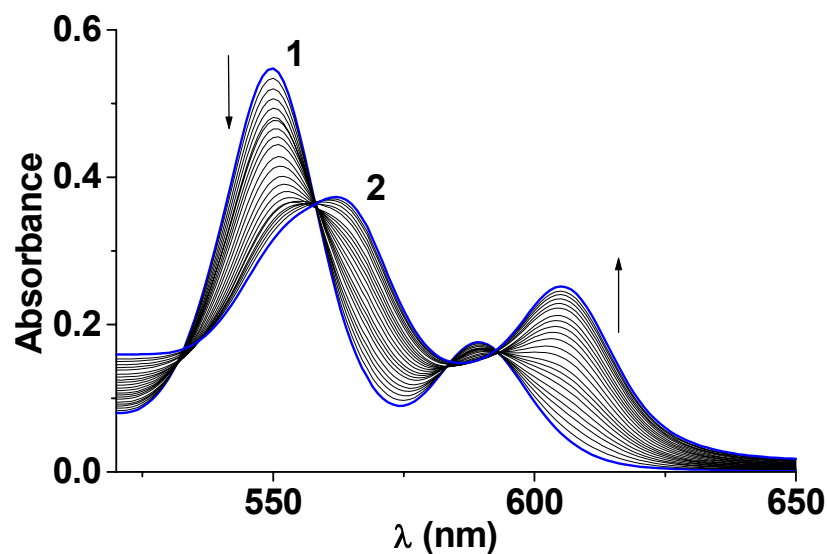


(b)

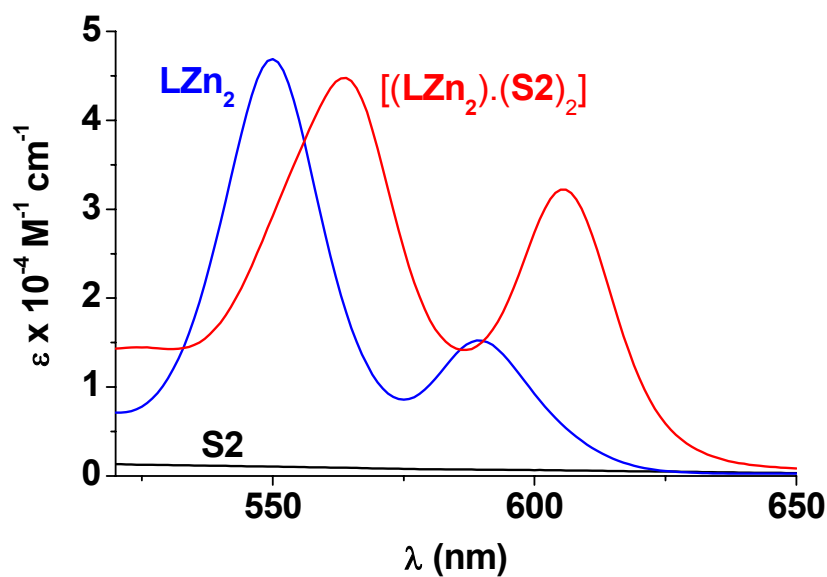
a) Luminescence spectrophotometric titration of **LZn₂** with **S1**. $\lambda_{\text{exc}} = 559 \text{ nm}$; emission and excitation slit widths 15 nm and 20 nm respectively; 1) $[\text{LZn}_2]_{\text{tot}} = 1.13 \times 10^{-6} \text{ M}$; 2) $[\text{S1}]_{\text{tot}}/[\text{LZn}_2]_{\text{tot}} = 27.2$. Solvent: CH_2Cl_2 ; $T = 25.0(2) \text{ }^\circ\text{C}$.

b) Variation of F^0/F at 600 nm versus the concentration of **S1**. The trend line is the result of the non linear least-square fit of the experimental data according to $(F_0/F) / (1 + K_{\text{SV}}[\text{S1}]) = (1 + K_1[\text{S1}] + K_1K_2[\text{S1}]^2)$. The absorption spectra of fullerene have been subtracted. Solvent: CH_2Cl_2 ; $T = 25.0(2) \text{ }^\circ\text{C}$.

LZn₂ + S2

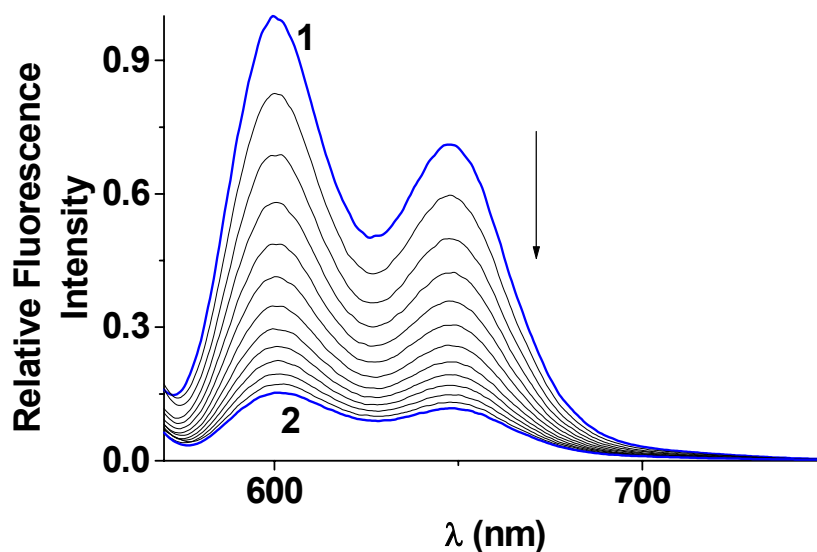


(a)

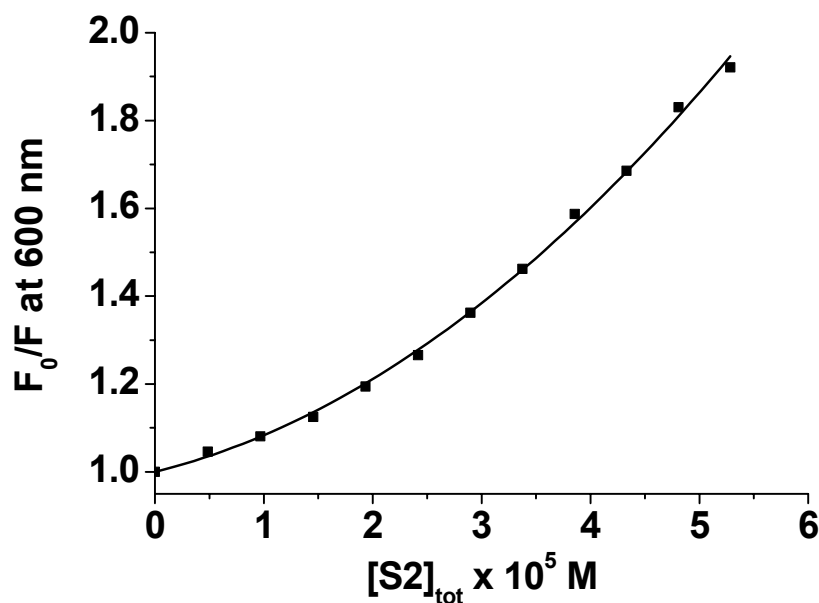


(b)

- a) UV-visible absorption spectrophotometric titration of LZn₂ with S2. $l = 0.2$ cm; 1) $[\text{LZn}_2]_{\text{tot}} = 5.65 \times 10^{-5}$ M; 2) $[\text{S2}]_{\text{tot}}/[\text{LZn}_2]_{\text{tot}} = 5.5$. Solvent: CH₂Cl₂; $T = 25.0(2)$ °C.
b) Absorption electronic spectra of LZn₂ and [(LZn₂).S2]₂. Solvent: CH₂Cl₂; $T = 25.0(2)$ °C.



(a)

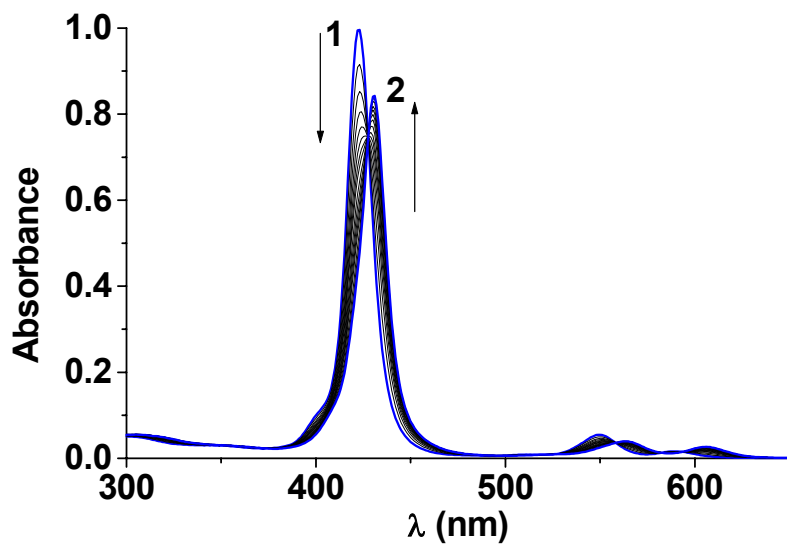


(b)

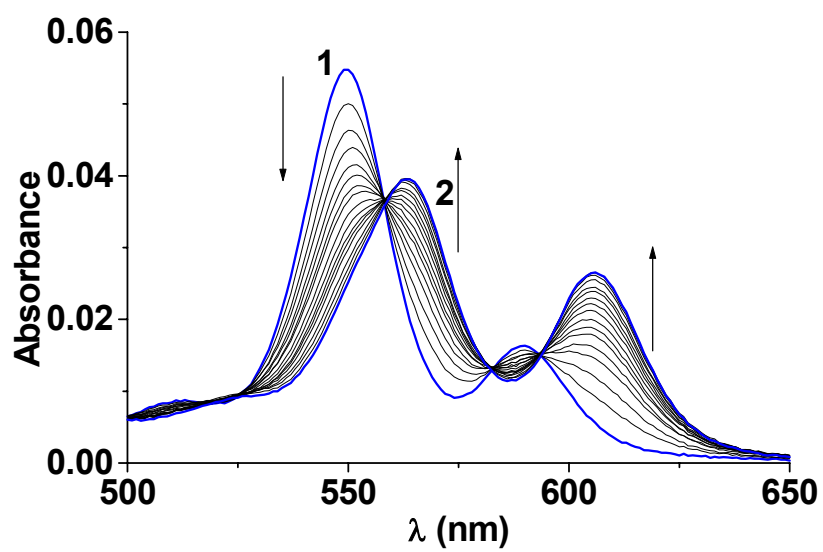
a) Luminescence spectrophotometric titration of **LZn₂** with **S2**. $\lambda_{\text{exc}} = 557 \text{ nm}$; emission and excitation slit widths 15 nm and 20 nm respectively; 1) $[\text{LZn}_2]_{\text{tot}} = 1.16 \times 10^{-6} \text{ M}$; 2) $[\text{S2}]_{\text{tot}}/[\text{LZn}_2]_{\text{tot}} = 46.8$. Solvent: CH_2Cl_2 ; $T = 25.0(2) \text{ }^\circ\text{C}$.

b) Variation of F_0/F at 600 nm versus the concentration of **S2**. The trend line is the result of the non linear least-square fit of the experimental data according to $(F_0/F) / (1 + K_{\text{SV}}[\text{S2}]) = (1 + K_1[\text{S2}] + K_1K_2[\text{S2}]^2)$. The absorption spectra of fullerene have been subtracted. Solvent: CH_2Cl_2 ; $T = 25.0(2) \text{ }^\circ\text{C}$.

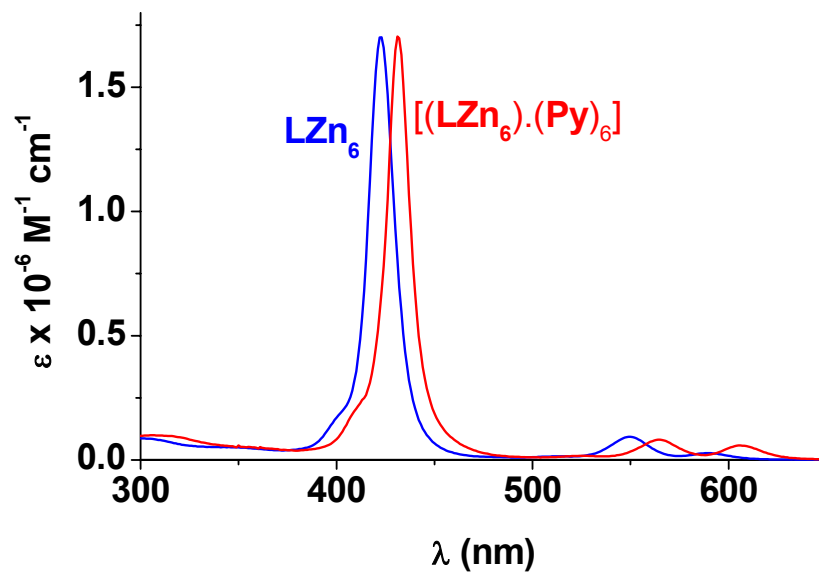
LZn₆ + Py



(a)

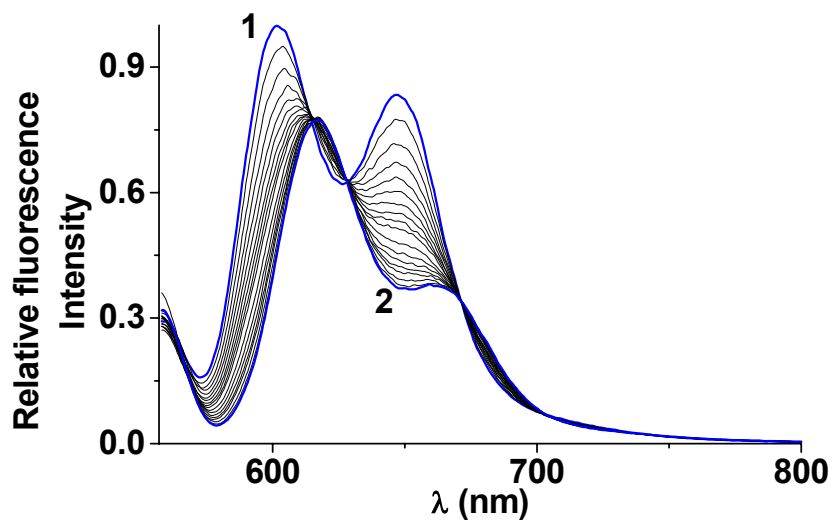


(b)



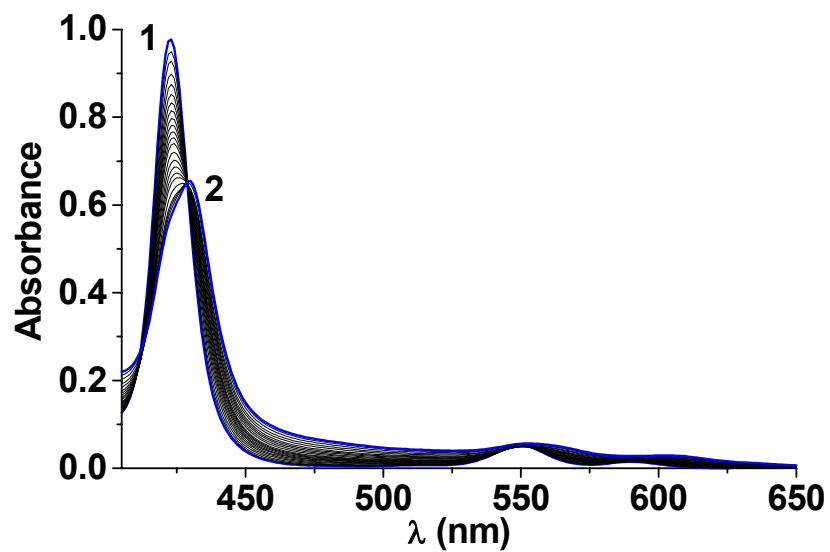
(c)

a,b) UV-visible absorption spectrophotometric titration of LZn_6 with Py . $l = 0.5$ cm; 1) $[\text{LZn}_6]_{\text{tot}} = 1.17 \times 10^{-6}$ M; 2) $[\text{Py}]_{\text{tot}}/[\text{LZn}_6]_{\text{tot}} = 735$. Solvent: CH_2Cl_2 ; $T = 25.0(2)$ °C.
c) Absorption electronic spectra of LZn_6 and $[(\text{LZn}_6) \cdot (\text{Py})_6]$. Solvent: CH_2Cl_2 ; $T = 25.0(2)$ °C.

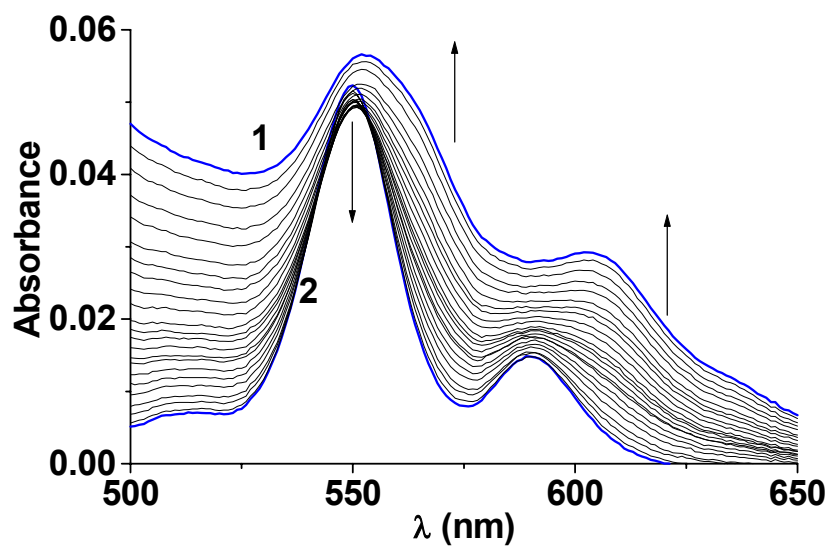


Luminescence titration of **LZn₆** with **Py**. $\lambda_{\text{ex}} = 558 \text{ nm}$; emission and excitation slit widths 15 and 20 nm respectively; 1) $[\text{LZn}_6]_{\text{tot}} = 1.17 \times 10^{-6} \text{ M}$; 2) $[\text{Py}]/[\text{LZn}_6]_{\text{tot}} = 312$. Solvent: CH_2Cl_2 ; $T = 25.0(2) \text{ }^\circ\text{C}$.

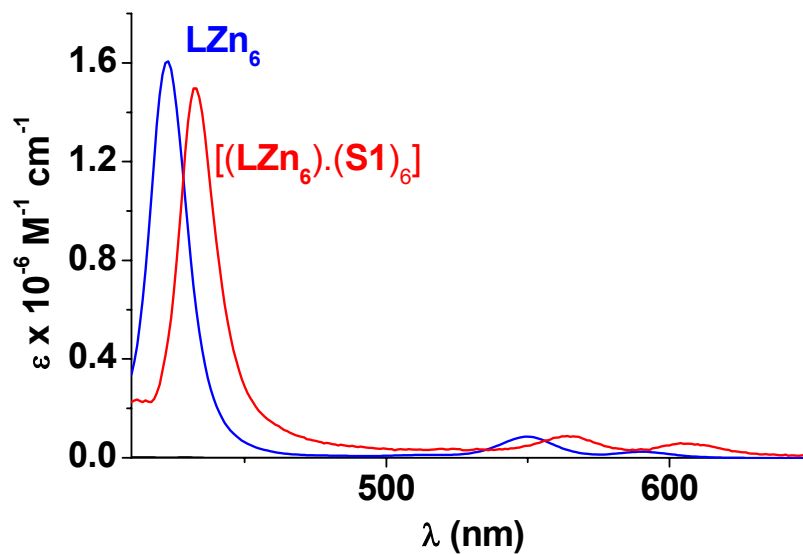
LZn₆ + S1



(a)

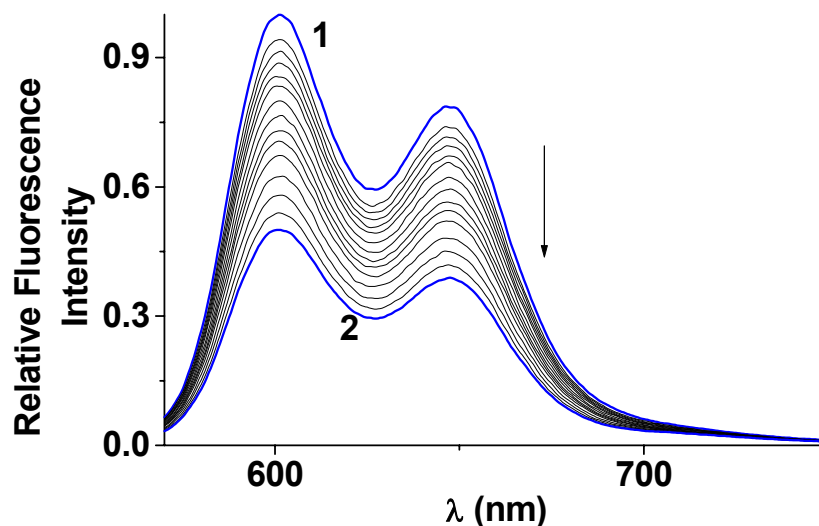


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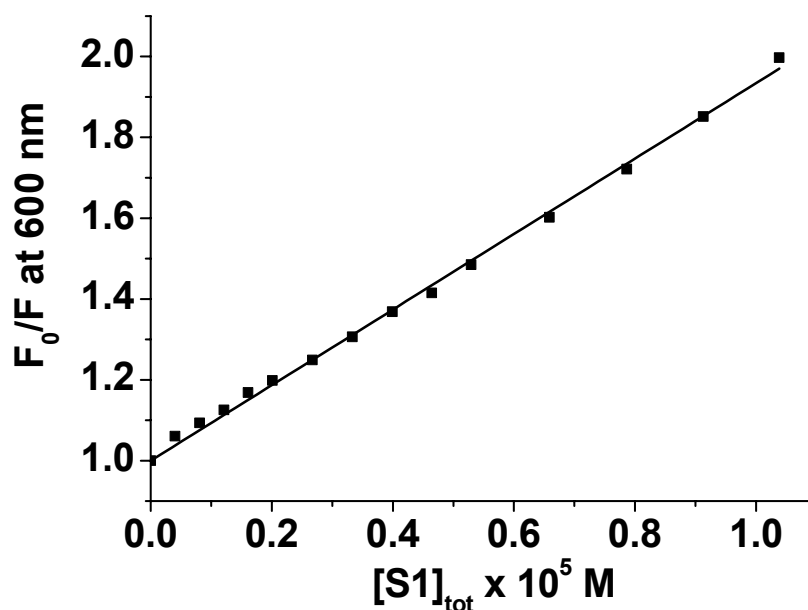


(c)

- a,b) UV-visible absorption spectrophotometric titration of LZn_6 with S1 . $l = 0.2 \text{ cm}$; 1) $[\text{LZn}_6]_{\text{tot}} = 2.93 \times 10^{-6} \text{ M}$; 2) $[\text{S1}]_{\text{tot}}/[\text{LZn}_6]_{\text{tot}} = 108$. Solvent: CH_2Cl_2 ; $T = 25.0(2) \text{ }^\circ\text{C}$.
c) Absorption electronic spectra of LZn_6 and $[(\text{LZn}_6) \cdot (\text{S1})_6]$. Solvent: CH_2Cl_2 ; $T = 25.0(2) \text{ }^\circ\text{C}$.



(a)

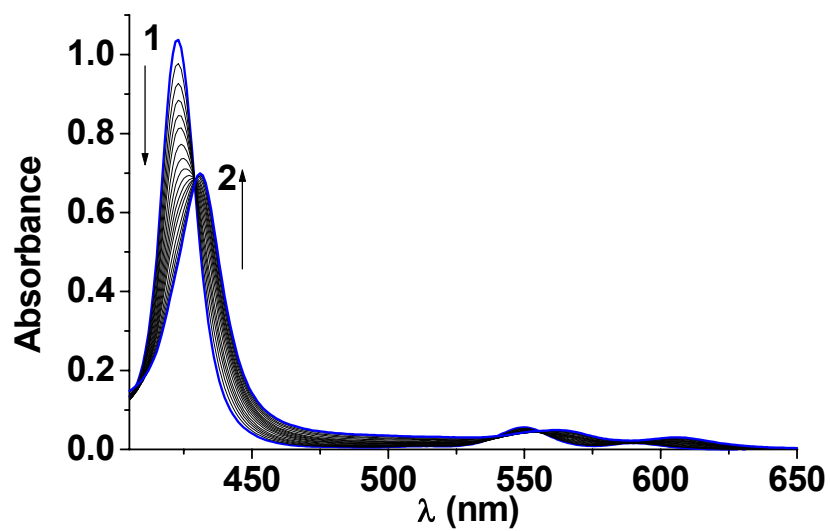


(b)

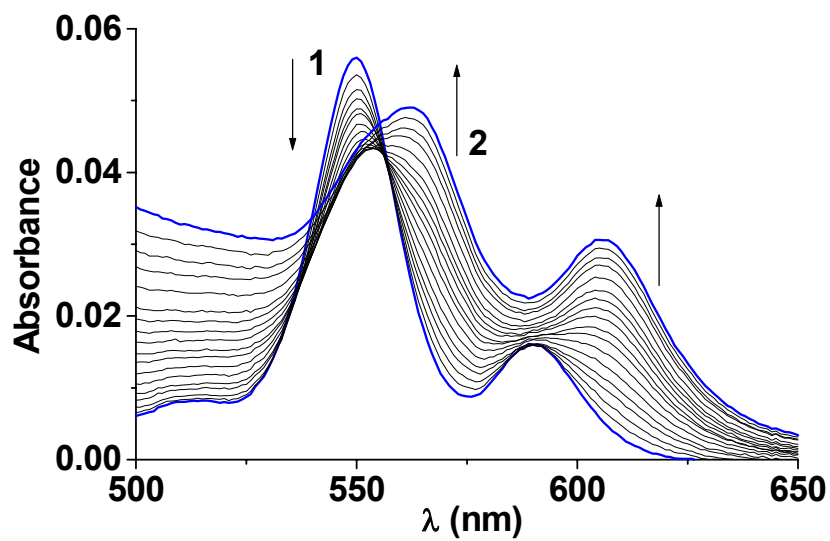
a) Luminescence titration of **LZn₆** with **S1**. $\lambda_{\text{ex}} = 428 \text{ nm}$; emission and excitation slit widths 15 and 20 nm respectively; 1) $[\text{LZn}_6]_{\text{tot}} = 4.91 \times 10^{-8} \text{ M}$; 2) $[\text{S1}]/[\text{LZn}_6]_{\text{tot}} = 220$. Solvent: CH_2Cl_2 ; $T = 25.0(2) \text{ }^\circ\text{C}$.

b) Variation of F_0/F at 600 nm versus the concentration of **S1**. The trend line is the result of the linear least-square fit of the experimental data according to $F_0/F = 1 + K^*[\text{S1}]$. Solvent: CH_2Cl_2 ; $T = 25.0(2) \text{ }^\circ\text{C}$.

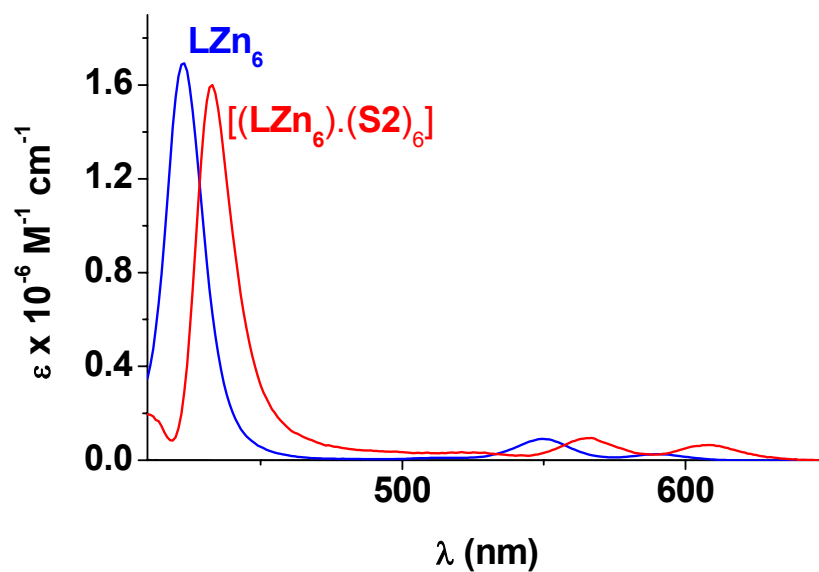
$LZn_6 + S_2$



(a)

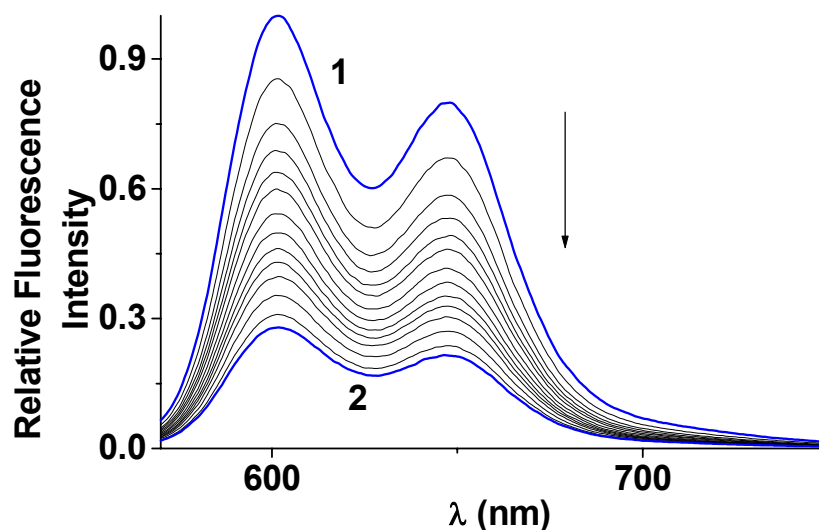


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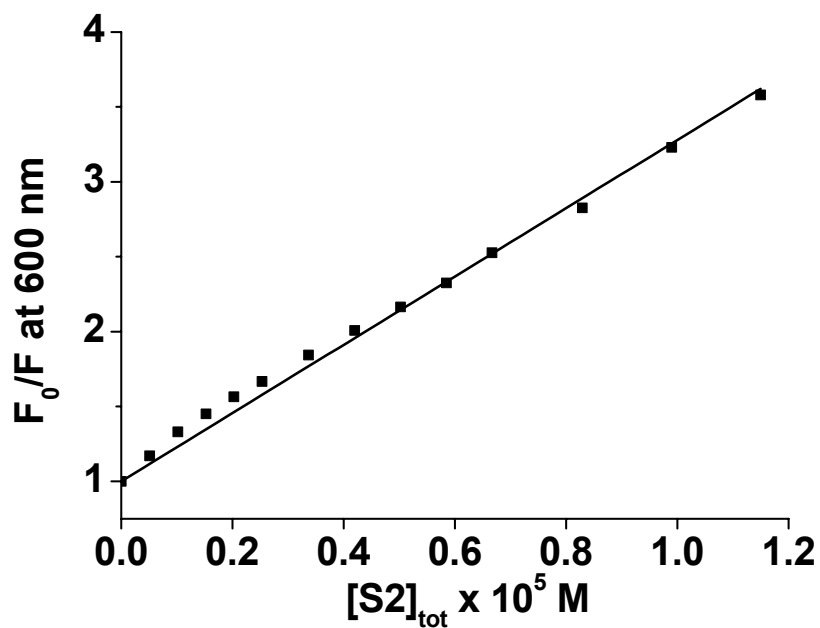


(c)

a,b) UV-visible absorption spectrophotometric titration of LZn_6 with S2 . $l = 0.2$ cm; 1) $[\text{LZn}_6]_{\text{tot}} = 3.04 \times 10^{-6}$ M; 2) $[\text{S2}]_{\text{tot}}/[\text{LZn}_6]_{\text{tot}} = 24.5$. Solvent: CH_2Cl_2 ; $T = 25.0(2)$ °C.
c) Absorption electronic spectra of LZn_6 and $[(\text{LZn}_6) \cdot (\text{S2})_6]$. Solvent: CH_2Cl_2 ; $T = 25.0(2)$ °C.



(a)



(b)

a) Luminescence titration of **LZn₆** with **S2**. $\lambda_{\text{ex}} = 428$ nm; emission and excitation slit widths 15 and 20 nm respectively; 1) $[\text{LZn}_6]_{\text{tot}} = 4.91 \times 10^{-8}$ M ; 2) $[\text{S2}]/[\text{LZn}_6]_{\text{tot}} = 277$. Solvent: CH_2Cl_2 ; $T = 25.0(2)$ °C.

b) Variation of F^0/F at 600 nm versus the concentration of **S2**. The trend line is the result of the linear least-square fit of the experimental data according to $F_0/F = 1 + K^*[\text{S2}]$. Solvent: CH_2Cl_2 ; $T = 25.0(2)$ °C.