

Role of spacer in single or two-step FRET: studies in presence of two connected cryptands with properly chosen fluorophores

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Supporting Information

Captions for the Figures and Tables:

- Fig. S1-S3:** 400 MHz ¹H-NMR, 100 MHz ¹³C-NMR and ESI-MS, spectra of **L_d**.
- Fig. S4-S6:** 400 MHz ¹H-NMR, 100 MHz ¹³C-NMR and ESI-MS, spectra of **L_{1a}**.
- Fig. S7-S9:** 400 MHz ¹H-NMR, 100 MHz ¹³C-NMR and ESI-MS, spectra of **L₁**.
- Fig. S10-S11:** 400 MHz ¹H-NMR and ESI-MS, spectra of **L_{2a}**.
- Fig. S12-S13:** 400 MHz ¹H-NMR and FAB-MS, spectra of **L₂**.
- Fig. S14-S16:** 400 MHz ¹H-NMR, 100 MHz ¹³C-NMR and FAB-MS, spectra of **L_{3a}**.
- Fig. S17-S19:** 400 MHz ¹H-NMR, 100 MHz ¹³C-NMR and ESI-MS, spectra of **L_{3b}**.
- Fig. S20-S22:** 400 MHz ¹H-NMR, 100 MHz ¹³C-NMR and FAB-MS, spectra of **L₃**.
- Fig. S23:** Absorption spectra of **L₂** in presence of selected metal ions in MeCN.
- Table ST1-ST2:** Absorption and molar extinction coefficient (ϵ) of **L₁** and **L₃** in presence of different metal ions in MeCN.
- Fig. S24:** Emission spectra of **L₂** in presence of selected metal ions in MeCN.
- Fig. S25:** Emission spectra of (a) anthracene and (b) diazole of **L₁** in presence of Cu(II) ionic input in MeCN.
- Fig. S26:** Time resolved emission spectra of **L₃** in presence of different ionic input in MeCN ($\lambda_{\text{ex}} = 295$ nm).
- Table ST3:** Time resolved fluorescence decay analysis of **L₃** in presence of different ionic input in MeCN.
- Table ST4:** Fluorescence anisotropy data of the systems **L₃** and its metal complexes.

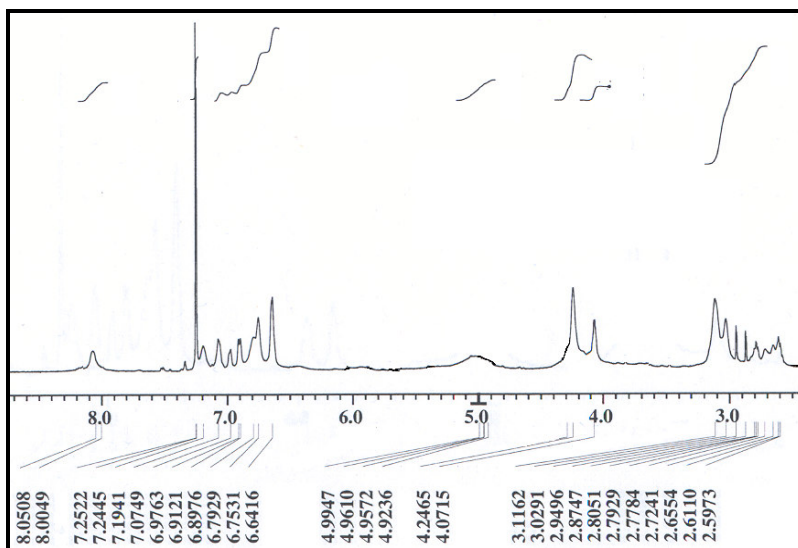


Figure S1: 400 MHz ^1H -NMR spectrum of L_d .

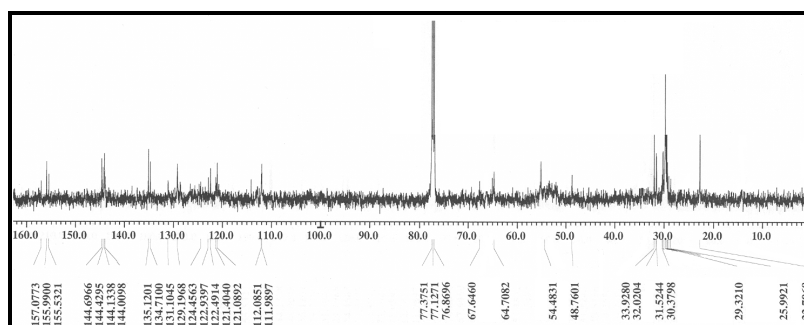


Figure S2: 100 MHz ^{13}C -NMR spectrum of L_d .

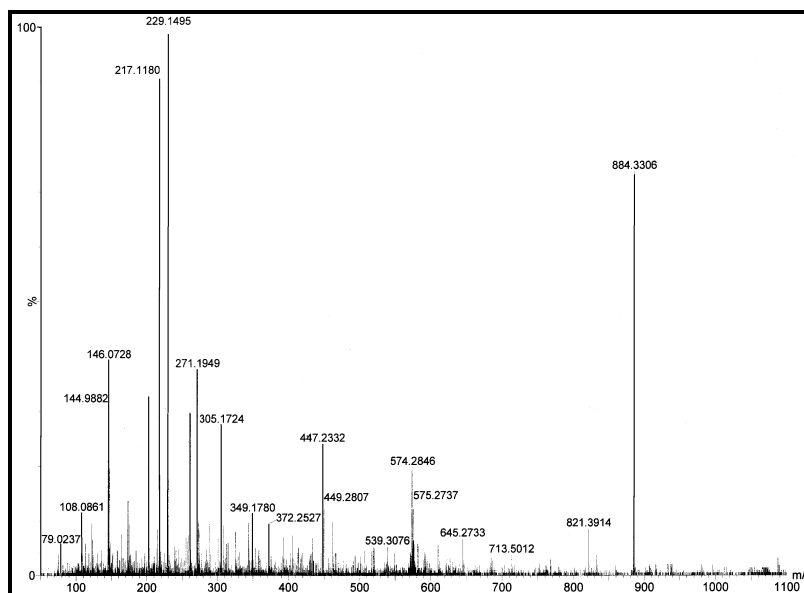


Figure S3: ESI-MS spectrum of L_d .

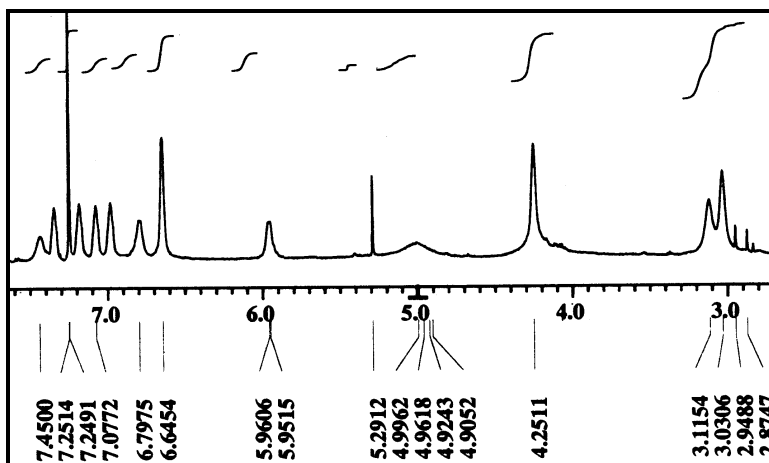


Figure S4: 400 MHz ^1H -NMR spectrum of L_{1a} .

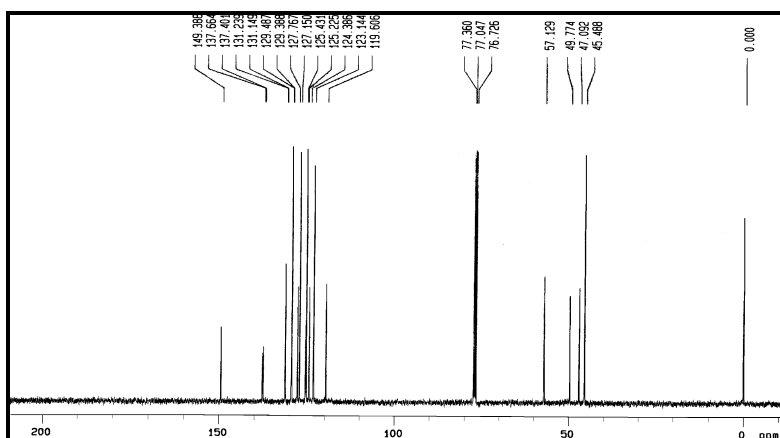


Figure S5: 100 MHz ^{13}C -NMR spectrum of L_{1a} .

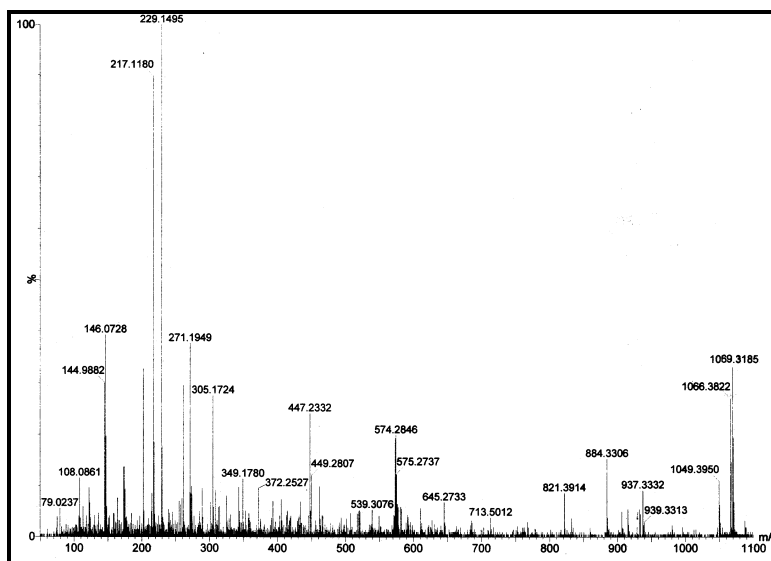


Figure S6: ESI-MS spectrum of L_{1a} .

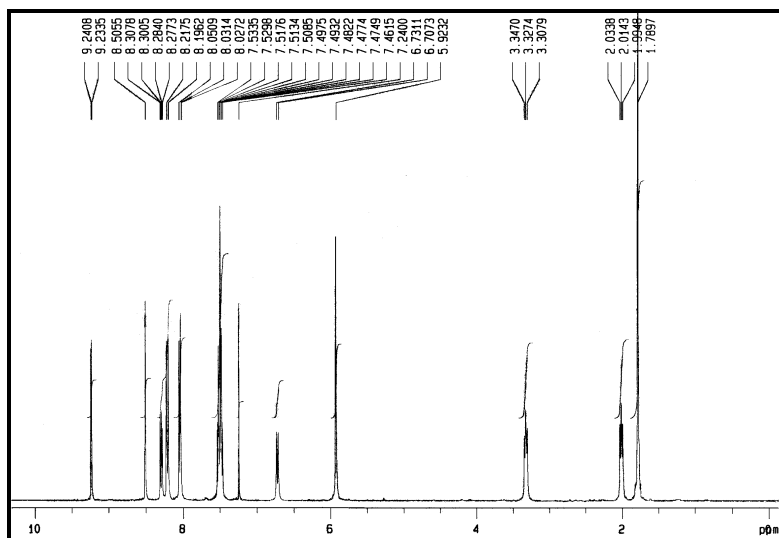


Figure S7: 400 MHz ¹H-NMR spectrum of L₁.

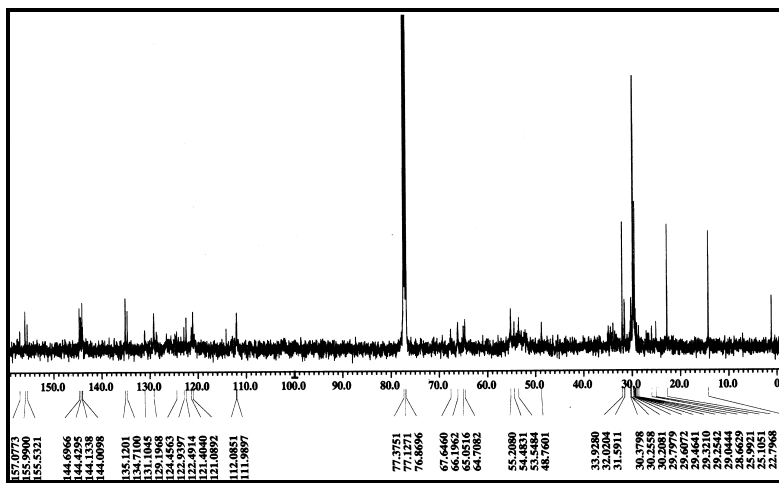


Figure S8: 100 MHz ¹³C-NMR spectrum of L₁.

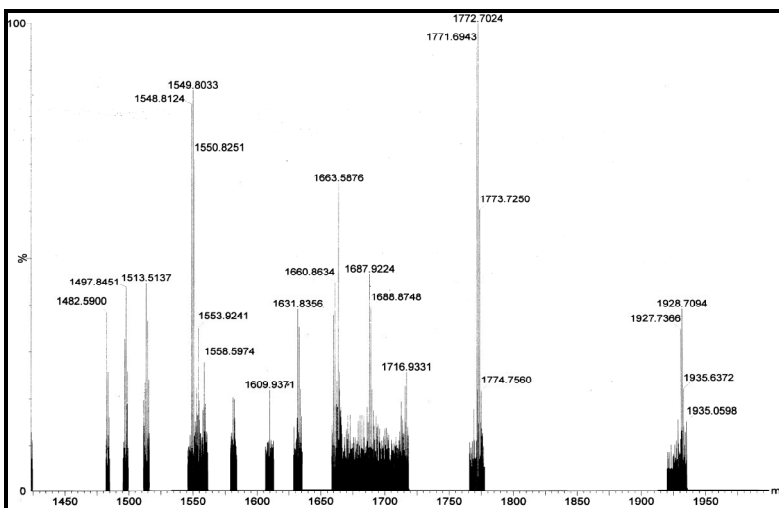


Figure S9: ESI-MS spectrum of L₁.

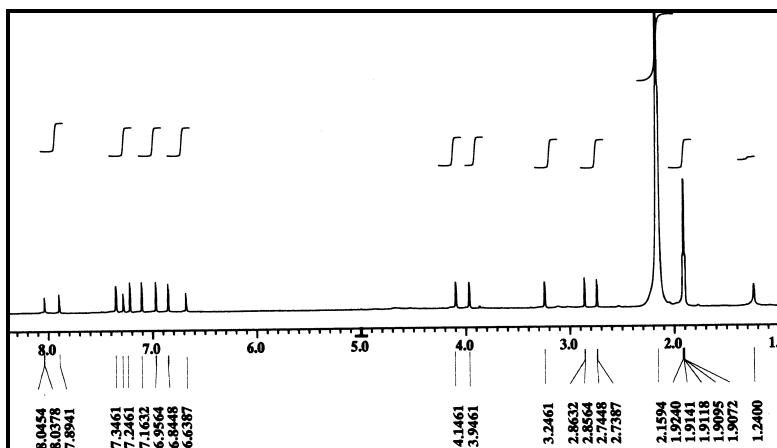


Figure S10: 400 MHz $^1\text{H-NMR}$ spectrum of L_{2a} .

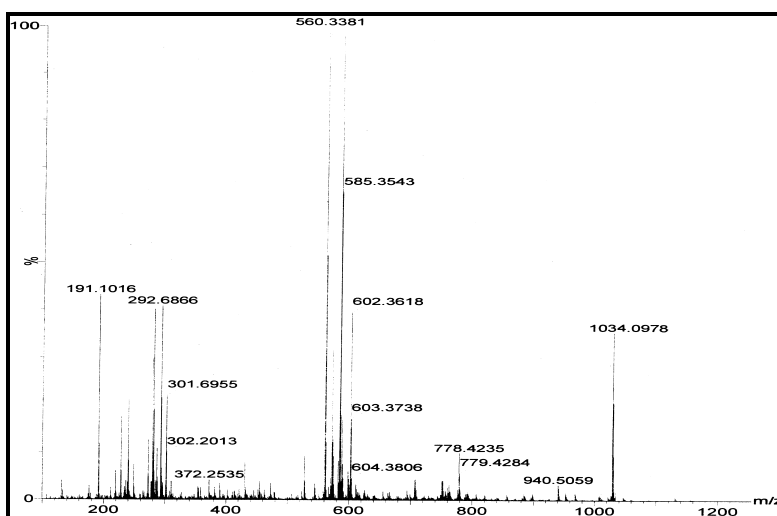


Figure S11: ESI-MS spectrum of L_{2a} .

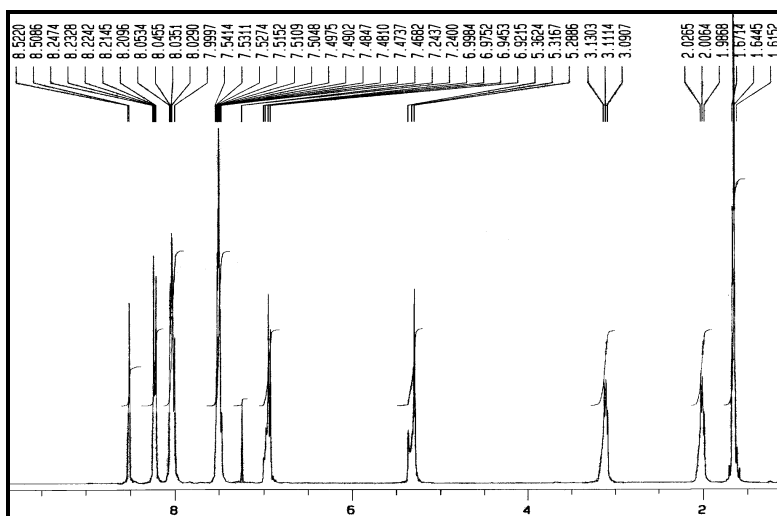


Figure S12: 400 MHz $^1\text{H-NMR}$ spectrum of L_2 .

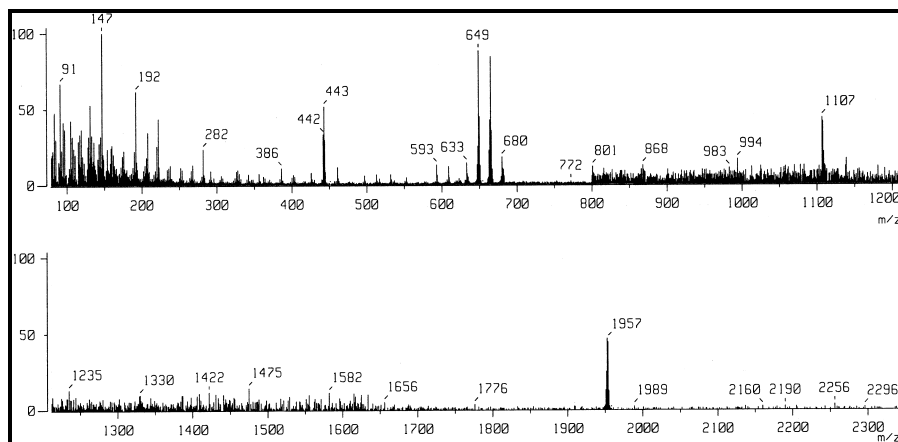


Figure S13: FAB-MS spectrum of L_2 .

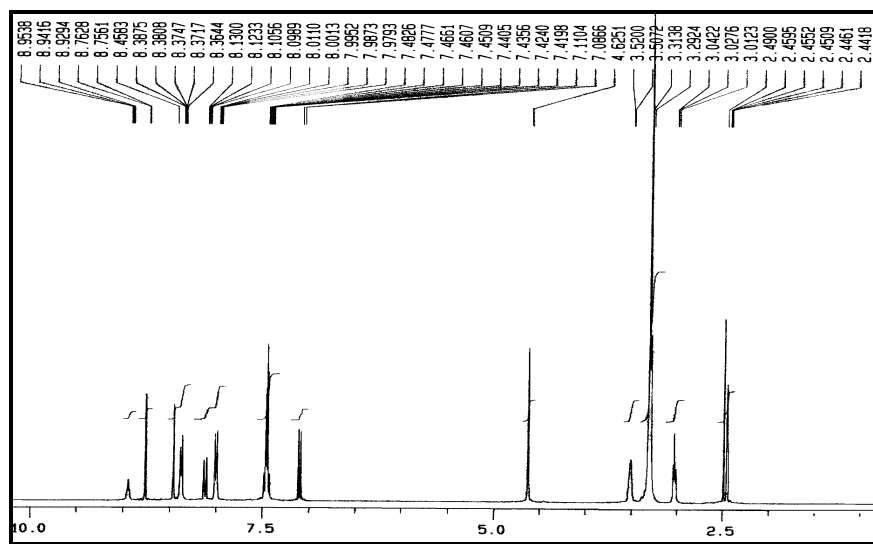


Figure S14: 400 MHz ^1H -NMR spectrum of L_{3a} .

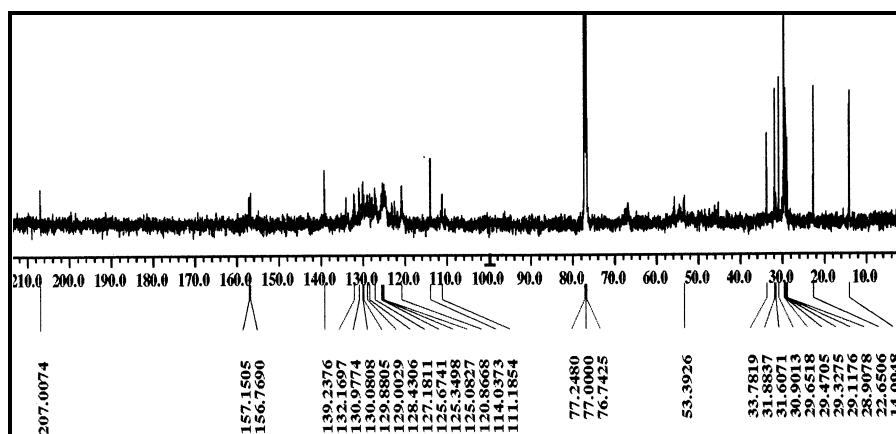


Figure S15: 100 MHz ^{13}C -NMR spectrum of L_{3a} .

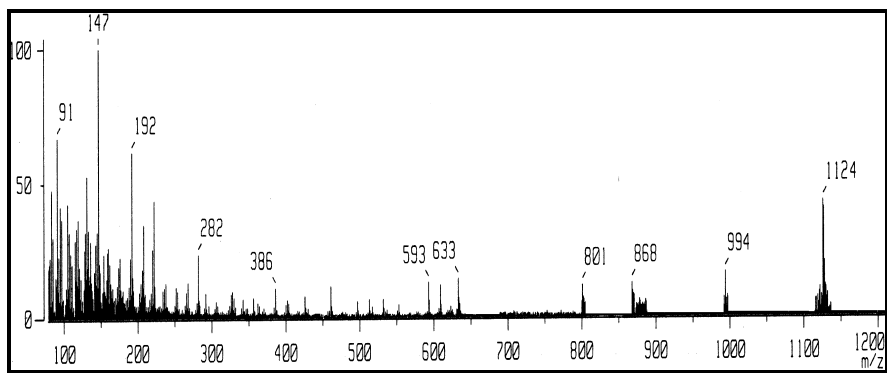


Figure S16: FAB-MS spectrum of L_{3a}.

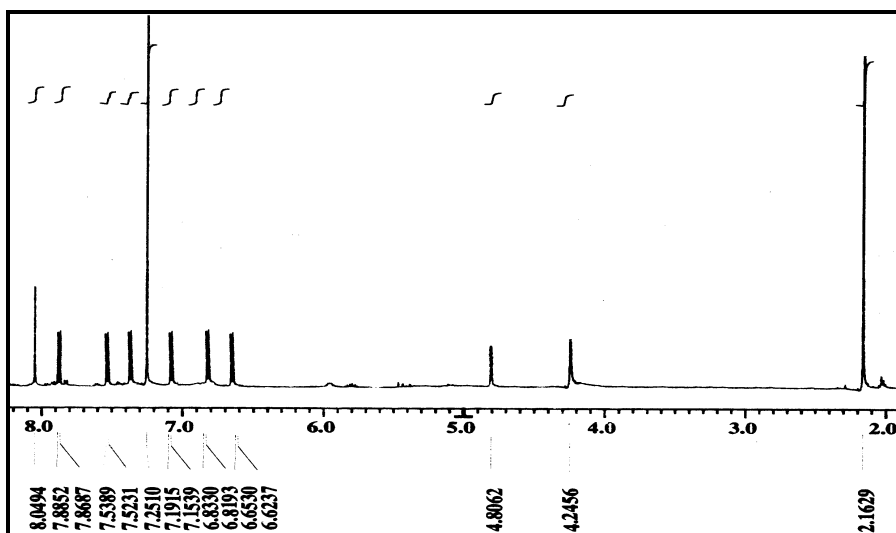


Figure S17: 400 MHz ¹H-NMR spectrum of L_{3b}.

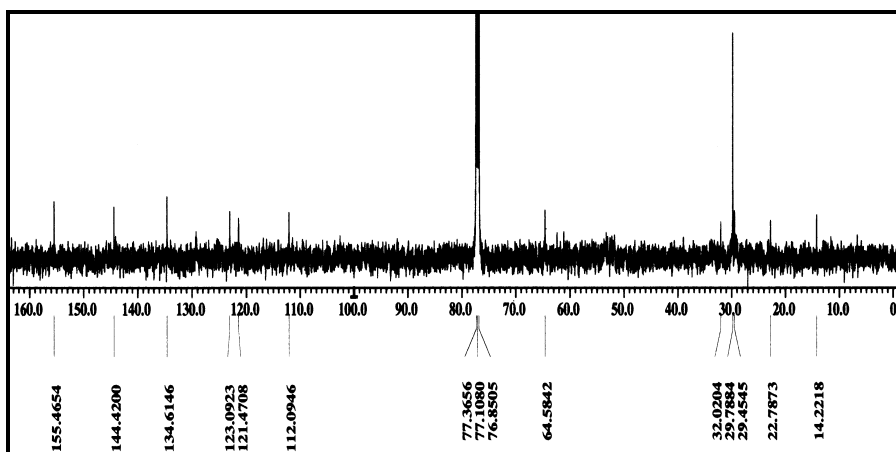


Figure S18: 100 MHz ¹³C-NMR spectrum of L_{3b}.

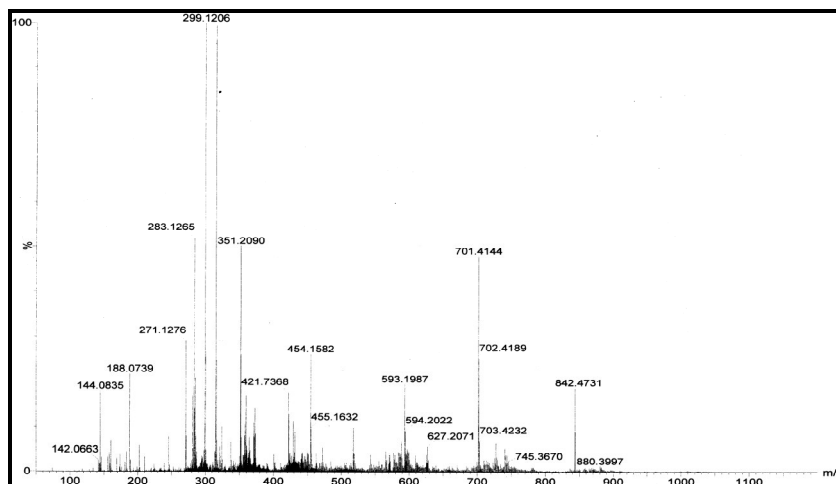


Figure S19: ESI-MS spectrum of L_{3b} .

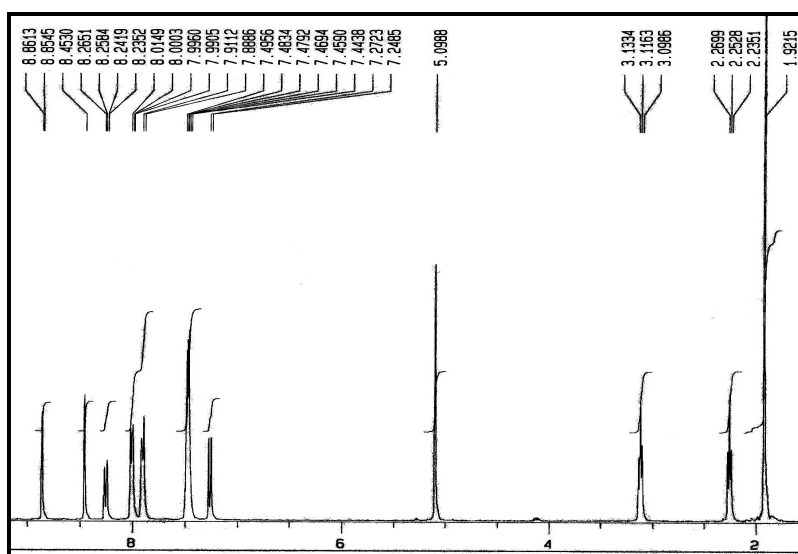


Figure S20: 400 MHz 1H -NMR spectrum of L_3 .

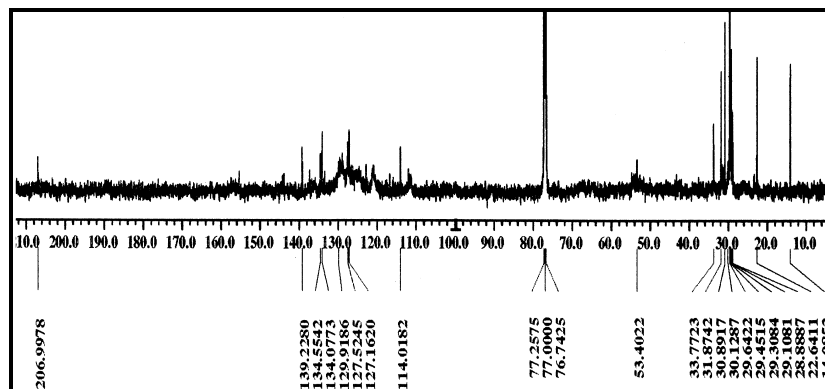


Figure S21: 100 MHz ^{13}C -NMR spectrum of L_3 .

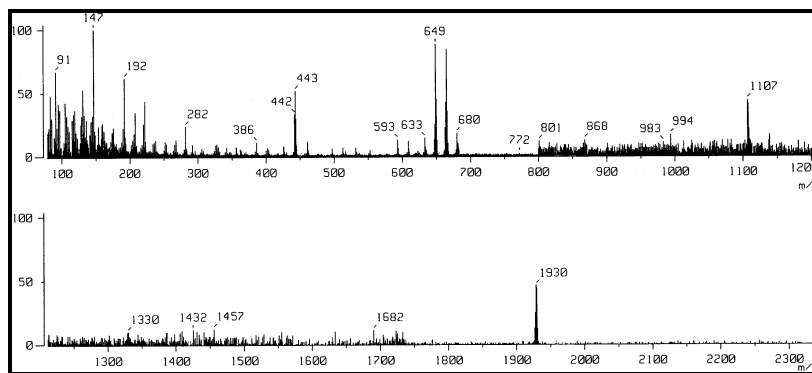


Figure S22: FAB-MS spectrum of L_3 .

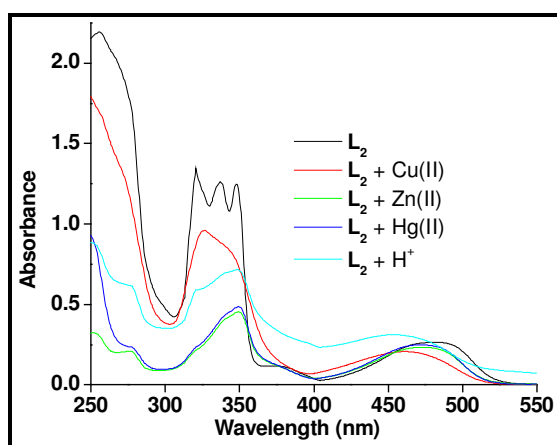


Figure S23: UV-vis spectra of L_2 , $L_2+Cu(II)$, $L_2+Zn(II)$, $L_2+Hg(II)$, L_2+H^+ (conc. of $L_2 = 3.1 \times 10^{-4}$ M) in MeCN.

Table S1: Absorption and molar extinction coefficient (ϵ) of L_1 with metal ions in MeCN (conc. of $L_1 = 1.7 \times 10^{-5}$ M).

	λ , nm (ϵ , $dm^3 mol^{-1} cm^{-1}$)
L_1	478 (4795) 386 (6385) 368 (6392) 349 (5888) 332 (5332) 254 (69724)
$L_1+Mn(II)$	474 (5131) 389 (6645) 369 (6611) 351 (6174) 333 (5729) 254 (74129)
$L_1+Fe(II)$	459 (4349) 389 (5234) 366 (6215) 353 (6259) 254 (77047)
$L_1+Co(II)$	474 (5840) 389 (6193) 370 (6294) 349 (5899) 333 (5713) 255 (76071)
$L_1+Ni(II)$	478 (4193) 389 (6166) 369 (6524) 349 (6142) 332 (5380) 254 (77038)
$L_1+Cu(II)$	451 (3492) 389 (4142) 371 (4999) 350 (5432) 253 (65775)
$L_1+Zn(II)$	471 (4382) 391 (6074) 370 (6220) 351 (5923) 334 (5721) 255 (75025)
$L_1+Cd(II)$	474 (4948) 386 (6934) 368 (6929) 349 (6586) 332 (6182) 255 (84222)
$L_1+Hg(II)$	465 (4791) 391 (7255) 371 (7161) 351 (6688) 332 (6825) 254 (90249)
$L_1+Ag(I)$	478 (4273) 387 (5983) 367 (6259) 351 (5862) 332 (5280) 254 (75418)
$L_1+Pb(II)$	476 (4261) 391 (6293) 372 (6496) 351 (6194) 255 (78078)
L_1+H^+	459 (4158) 389 (6079) 369 (6465) 353 (5935) 254 (73299)

Table S2: Absorption and molar extinction coefficient (ϵ) of L_3 with metal ions in MeCN
 (conc. of $L_3 = 1.5 \times 10^{-5}$ M).

	λ , nm (ϵ , $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$)
L_3	483 (14192) 392 (6933) 377 (7527) 344 (12335) 317 (14403) 302 (13919) 256 (64055)
$L_3+\text{Mn(II)}$	476 (14249) 396 (7218) 373 (7791) 343 (12757) 318 (15901) 303 (15308) 256 (65187)
$L_3+\text{Fe(II)}$	467 (13785) 393 (9284) 372 (10173) 319 (19660) 257 (64036)
$L_3+\text{Co(II)}$	474 (18133) 395 (8292) 372 (8499) 344 (12764) 318 (17164) 304 (16704) 257 (68407)
$L_3+\text{Ni(II)}$	476 (14079) 391 (7552) 373 (8606) 344 (12863) 317 (16063) 304 (15341) 257 (66574)
$L_3+\text{Cu(II)}$	453 (11199) 388 (8243) 372 (8602) 317 (22771) 250 (84620)
$L_3+\text{Zn(II)}$	472 (14402) 395 (8808) 372 (9080) 344 (12423) 317 (17699) 307 (16803) 257 (64301)
$L_3+\text{Cd(II)}$	475 (14655) 395 (7705) 373 (8007) 343 (12765) 318 (16837) 305 (15989) 257 (66375)
$L_3+\text{Hg(II)}$	468 (12391) 392 (8983) 372 (9596) 343 (12765) 321 (20491) 250 (86109)
$L_3+\text{Ag(I)}$	479 (13457) 395 (6766) 373 (7406) 346 (11631) 318 (14432) 304 (14059) 256 (62487)
$L_3+\text{Pb(II)}$	474 (14581) 395 (9168) 375 (9449) 341 (13559) 317 (18268) 308 (17547) 250 (74572)
$L_3+\text{H}^+$	453 (13346) 394 (11071) 372 (11450) 343 (12765) 322 (23896) 250 (77403)

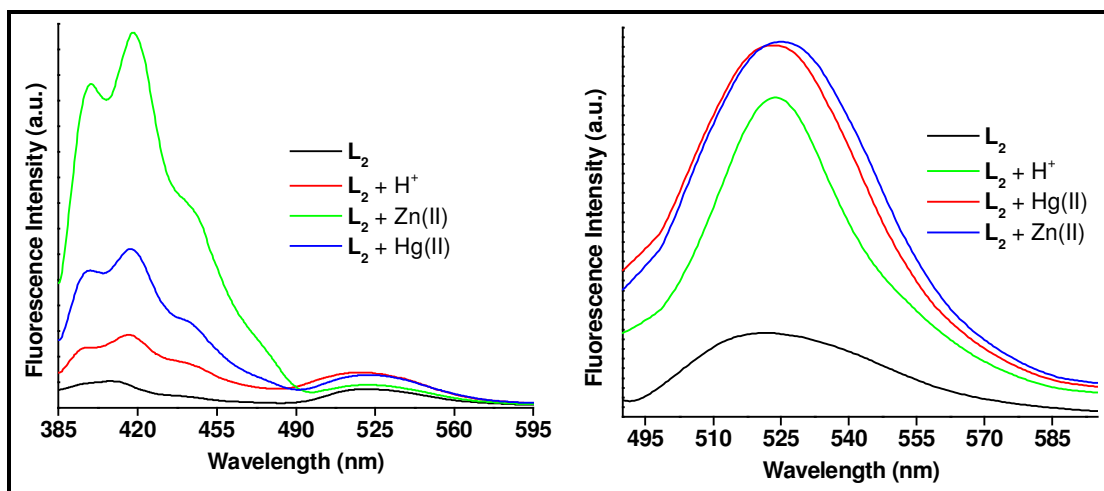


Figure S24: Emission spectrum of L_2 , $L_2+\text{H}^+$, $L_2+\text{Zn(II)}$ and $L_2+\text{Hg(II)}$
 (conc. of $L_2 = 1.7 \times 10^{-6}$ M) excitation at (a) 350 nm and (b) 476 nm in MeCN.

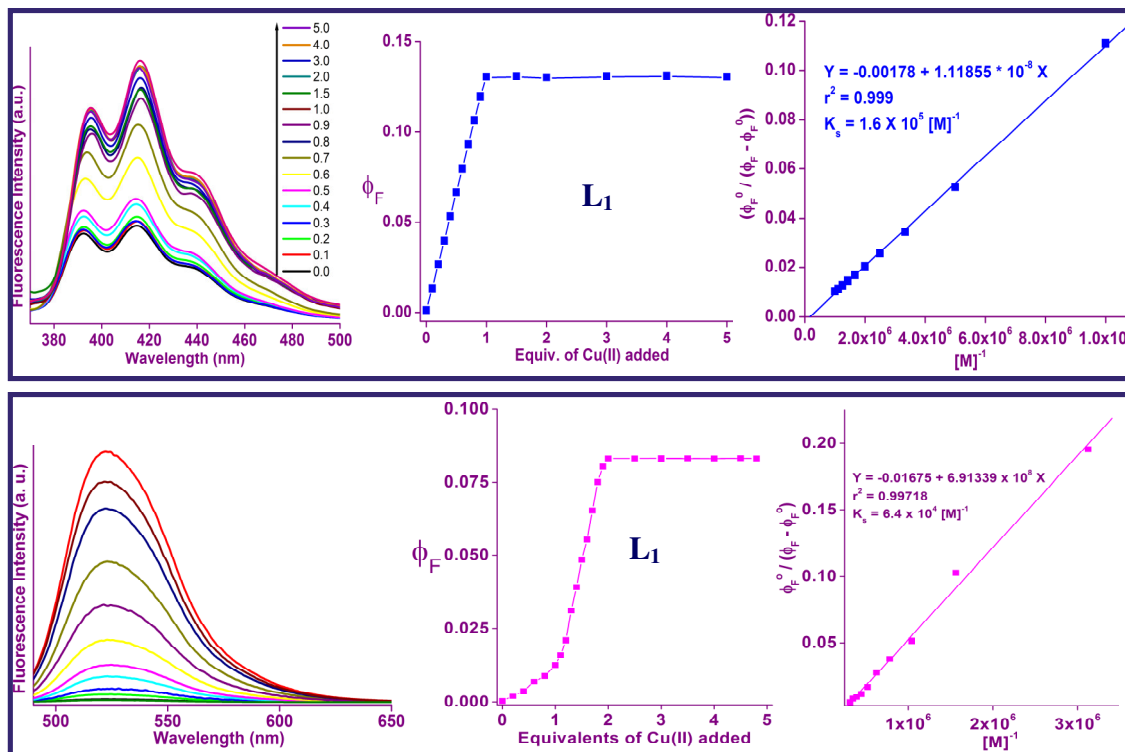


Figure S25: Emission spectra of (a) anthracene and (b) diazole of L_1 in presence of Cu(II) ionic input in MeCN.

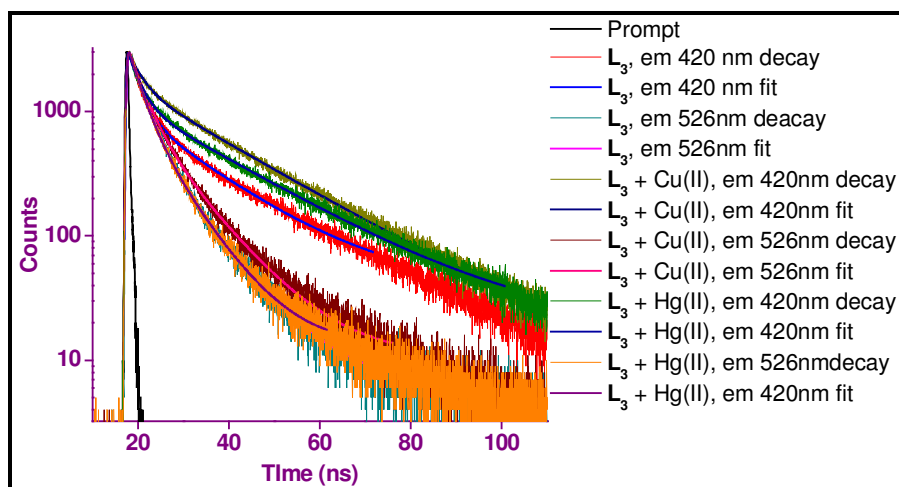


Figure S26: Time resolved emission spectra of L_3 in presence of different ionic input in MeCN ($\lambda_{ex} = 295$ nm).

Table S3: Time resolved fluorescence decay analysis of **L₃** in presence of different ionic input in MeCN.

Sample	A ₁	T ₁ (ns)	A ₂	T ₂ (ns)
L₃ (420 nm)	0.72	2.49	0.29	16.27
L₃ (526 nm)	0.78	3.20	0.22	9.56
L₃ + Cu(II) (420 nm)	0.50	2.94	0.50	20.62
L₃ + Cu(II) (526 nm)	0.71	3.35	0.29	10.09
L₃ + Hg(II) (420 nm)	0.64	2.63	0.36	20.76
L₃ + Hg(II) (526 nm)	0.70	2.80	0.30	8.00

Table S4: Fluorescence anisotropy data of the systems **L₃** and its metal complexes.

(a) Excitation at 317 nm

Sample	Anisotropy(Donor)	Anisotropy(Acceptor)
L₃	0.11	0.03
L₃ + Cu(II)	0.07	0.06
L₃ + Hg(II)	0.11	0.07

(b) Excitation at 350 nm

Sample	Anisotropy(Donor)	Anisotropy(Acceptor)
L₃	0.01	0.39
L₃ + Cu(II)	0.12	0.26
L₃ + Hg(II)	0.05	0.02