Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting Information

Photoresponsive dendron-like metallocomplexes of the crown-containing styryl derivatives of 2,2'-bipyridine

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Contents

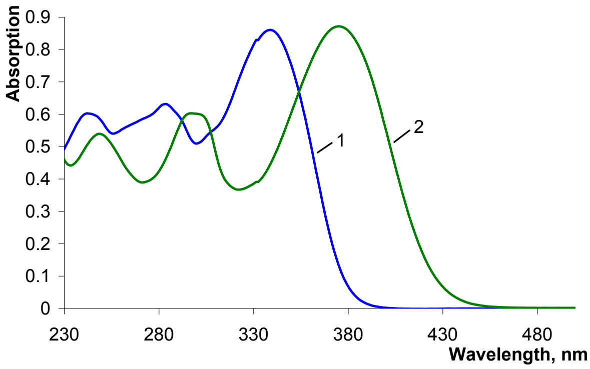


Figure S1. Absorption spectra of *E*-**1** *(1)* and its complex [$\mathbf{1}_3\cdot Zn^{2+}$] *(2)* in CH_3CN calculated from spectrophotometric titration data.

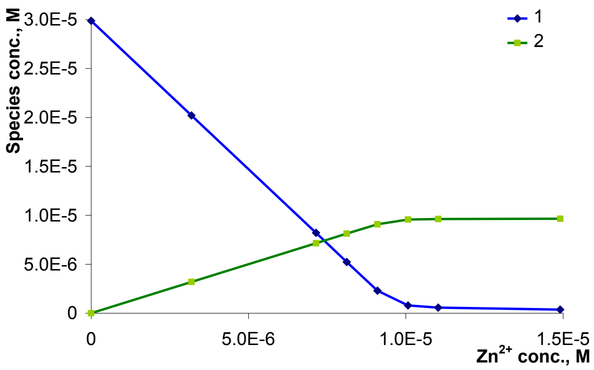


Figure S2. Concentrations of free **1** *(1)* and its complex [$\mathbf{1}_3\cdot(Zn^{2+})_1$] *(2)* as a function of total Zn^{2+} concentration, calculated from spectrophotometric titration data.

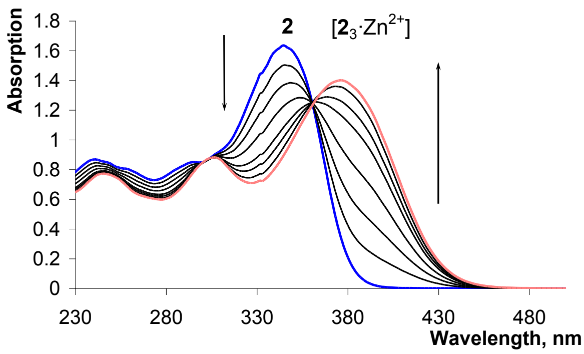


Figure S3. Variation of the *E,E*-**2** ([2]=2.1×10^{-5} M) absorption spectrum in CH_3CN *(2)* with increasing concentration of $Zn(ClO_4)_2$ ([Zn^{2+}] = from 0 *(2)* to 1.2×10^{-5} M *([$2_3\cdot Zn^{2+}$])*).

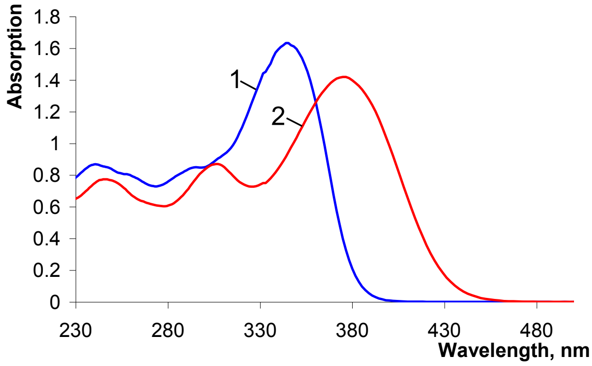


Figure S4. Absorption spectra of *E,E*-**2** *(1)* and its complex [$\mathbf{2}_3$·Zn^{2+}] *(2)* in CH_3CN calculated from spectrophotometric titration data.

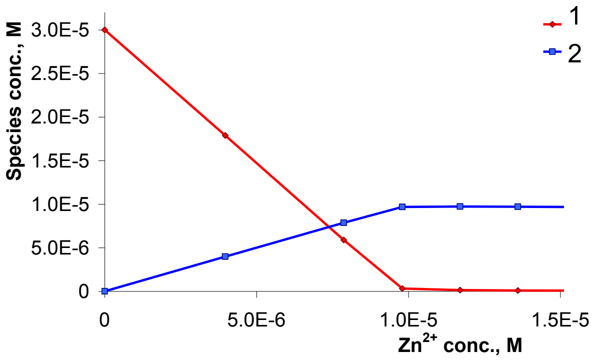


Figure S5. Concentrations of free *E,E*-**2** *(1)* and its complex [$\mathbf{2}_3$·$(Zn^{2+})_1$] *(2)* as a function of total Zn^{2+} concentration, calculated from spectrophotometric titration data.

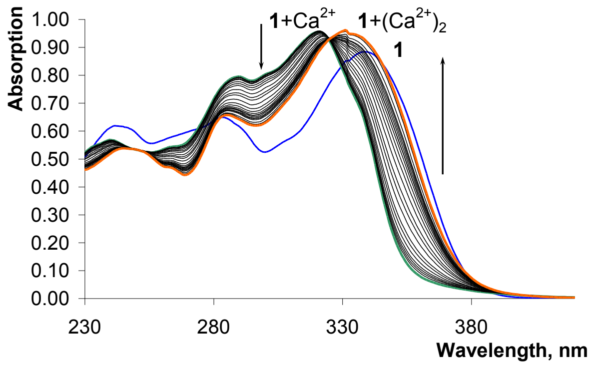


Fig. S6. Variation of the *E*-**1** *(1)* ([1]=3.1×10^{-5} M) absorption spectrum in CH_3CN with increasing concentrations of $Ca(ClO_4)_2$ ([Ca^{2+}] = from 9.9×10^{-5} M to 7.0×10^{-3} M).

Electronic Supplementary Material (ESI) for Dalton Transactions

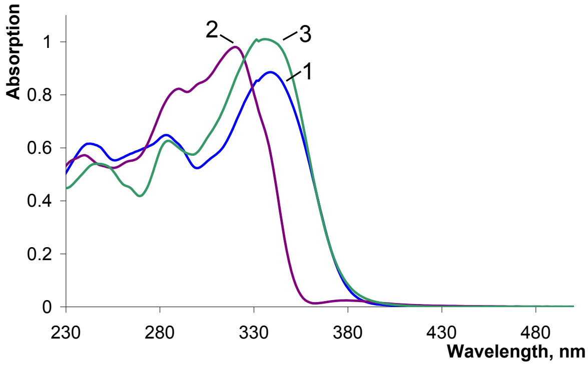


Figure S7. Absorption spectra of **1** *(1)* and its complexes [$\mathbf{1}_1\cdot(Ca^{2+})_1$] *(2)* and [$\mathbf{1}_1\cdot(Ca^{2+})_2$] *(3)* in CH_3CN calculated from spectrophotometric titration data.

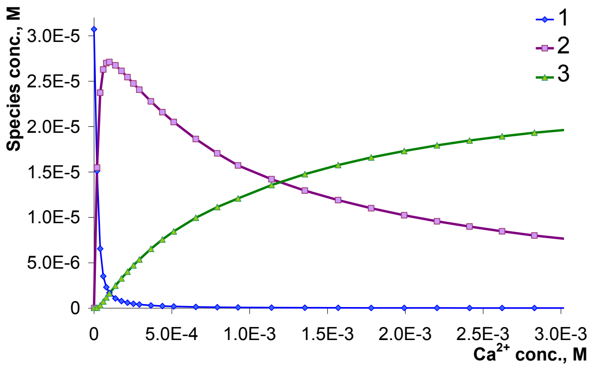


Figure S8. Concentrations of free **1** *(1)* and its complexes [$\mathbf{1}_1\cdot(Ca^{2+})_1$] *(2)* and [$\mathbf{1}_1\cdot(Ca^{2+})_2$] *(3)* as a function of total Ca^{2+} concentration, calculated from spectrophotometric titration data.

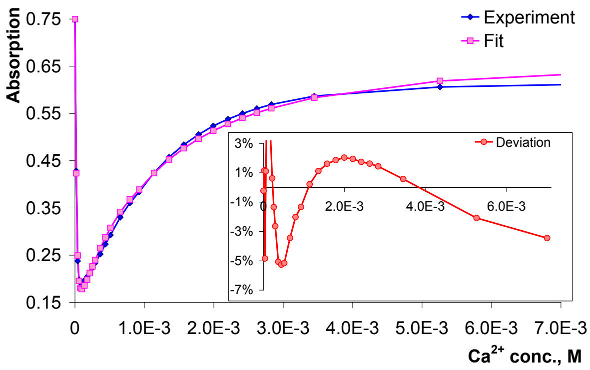


Figure S9. Spectrophotometric titration at 351 nm of a 3.1×10^{-5} M acetonitrile solution of **1** with $Ca(ClO_4)_2$. The magenta line indicates the best fit curve.

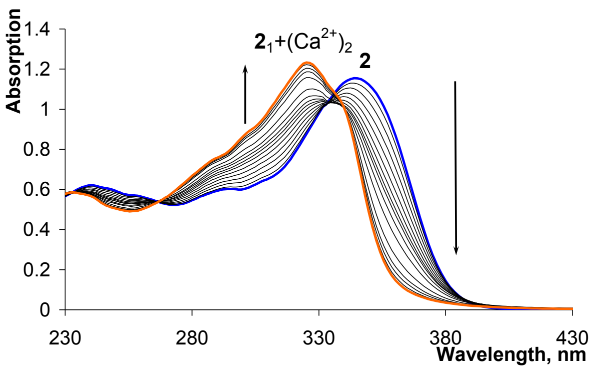


Figure S10. Variation of the *E*,*E*-**2** ([2]=2.1×10^{-5} M) absorption spectrum in CH_3CN *(2)* with increasing concentration of $Ca(ClO_4)_2$ ([Ca^{2+}] = from 0 *(2)* to 3.8×10^{-4} M *([2·(Ca^{2+})$_2$])*).

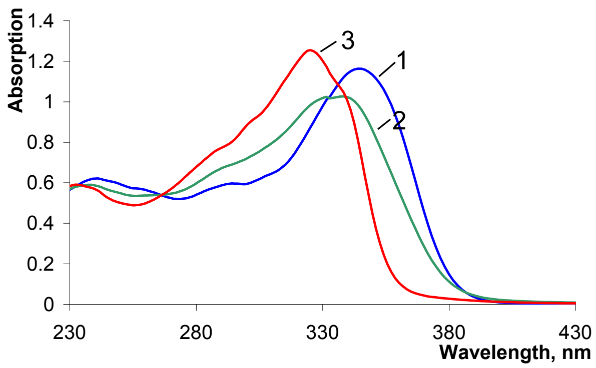


Figure S11. Absorption spectra of *E*,*E*-**2** *(1)* and its complexes [$\mathbf{2}_1$·(Ca^{2+})$_1$] *(2)* and [$\mathbf{2}_1$·(Ca^{2+})$_2$] *(3)* in CH_3CN calculated from spectrophotometric titration data.

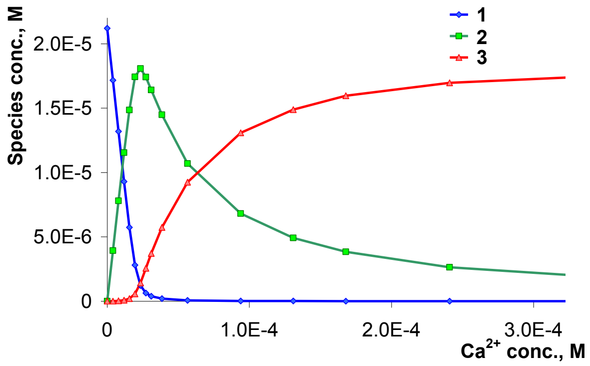


Figure S12. Concentrations of free *E*,*E*,-**2** *(1)* and its complexes [$\mathbf{2}_1$·(Ca^{2+})$_1$] *(2)* and [$\mathbf{2}_1$·(Ca^{2+})$_2$] *(3)* as a function of total Ca^{2+} concentration, calculated from spectrophotometric titration data.

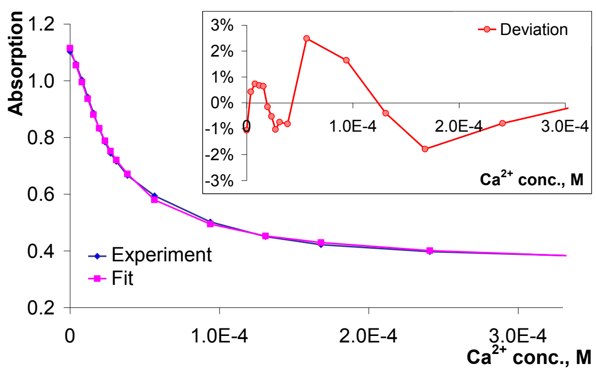


Figure S13. Spectrophotometric titration at 351 nm of a 2.1×10^{-5} M acetonitrile solution of *E*,*E*-**2** with $Ca(ClO_4)_2$. The magenta line indicates the best fit curve.

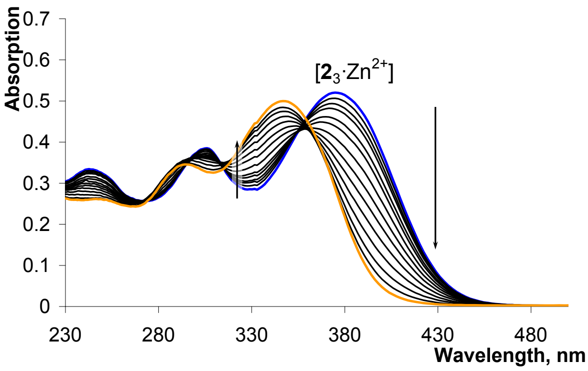


Figure S14. Variation of the **2**$_3$•(Zn^{2+})$_1$ ([C]=3.5×10^{-6} M) absorption spectra in CH$_3$CN *([***2***$_3$•Zn^{2+}])* with increasing concentration of Ca(ClO$_4$)$_2$ ([Ca^{2+}] = from 0 *([***2***$_3$•Zn^{2+}])* to 8.3×10^{-3} M).

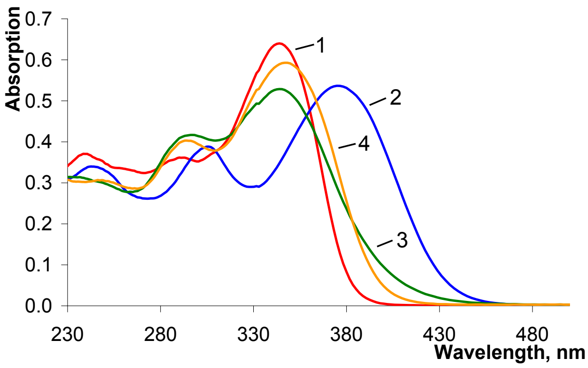


Figure S15. Absorption spectra of *E,E*-**2** (1) and its complexes [2$_3$•Zn^{2+}] *(2)*, [(Ca^{2+})$_1$•**2**$_3$•(Zn^{2+})$_1$] *(3)* and [(Ca^{2+})$_2$•**2**$_2$•(Zn^{2+})$_1$] *(4)* in CH$_3$CN calculated from spectrophotometric titration data.

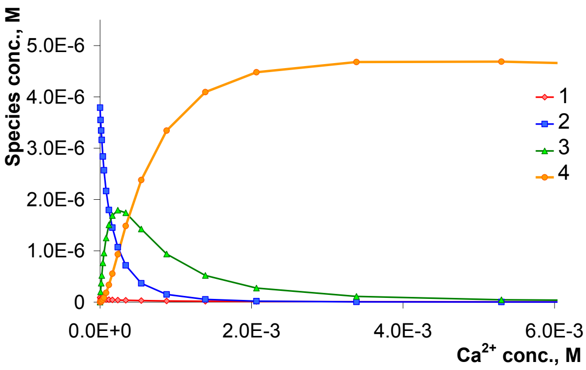


Figure S16. Concentrations of free *E,E*,-**2** *(1)* and its complexes [**2**$_3$·(Zn^{2+})$_1$] *(2)*, [(Ca^{2+})$_1$•**2**$_3$•(Zn^{2+})$_1$] *(3)* and [(Ca^{2+})$_2$•**2**$_2$•(Zn^{2+})$_1$] *(4)* as a function of total Ca^{2+} concentration, calculated from spectrophotometric titration data.

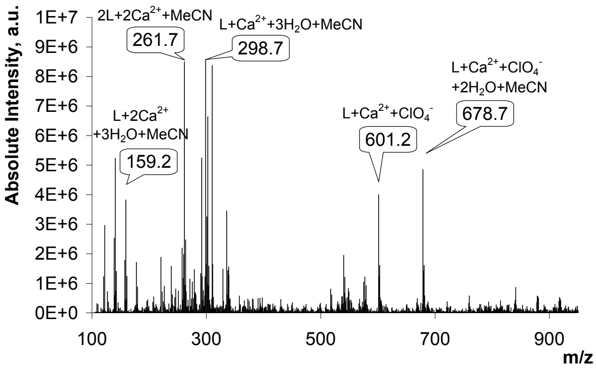
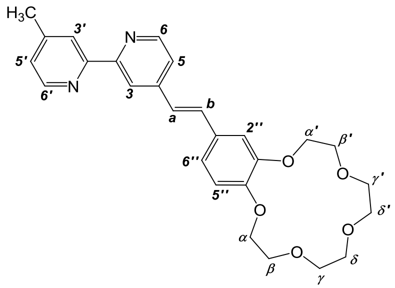


Figure S17. ESI-MS spectra of **1** in CH_3CN in the presence of $Ca(ClO_4)_2$ ([**1**] = 1×10^{-4} M, [Ca^{2+}] = 8×10^{-4} M)

Electronic Supplementary Material (ESI) for Dalton Transactions

Table S1. Chemical shifts (δ, ppm) of protons of *E*-**1** and their changes by complex formation in the presence of Zn^{2+} or/and Ca^{2+} ($\Delta\delta = \delta_1 - \delta_{complex}$), CD_3CN, 25°C.



	3	3'	5	5'	6	6'	a	b	2''	5''	6''	α	α'	β, β'	γ, γ'	δ, δ'	CH_3
1	8.50	8.27	7.49	7.23	8.59	8.52	7.45	7.18	7.27	6.94	7.17	4.11	4.15	3.80, 3.82	3.62	3.66	2.44
$\mathbf{1}_2\cdot(Ca^{2+})_2$	8.40	8.21	7.51	7.28	8.62	8.55	7.45	7.17	7.27	6.99	7.27	4.21	4.30	3.95	3.85	3.85	2.45
Δδ	*-0.10*	*-0.06*	*0.02*	*0.05*	*0.03*	*0.03*	*0*	*-0.01*	*0*	*0.05*	*0.10*	*0.10*	*0.15*	*0.15, 0.13*	*0.23*	*0.19*	*0.01*
$\mathbf{1}\cdot(Ca^{2+})_2$	8.44	8.27	7.66	7.44	8.72	8.64	7.68	7.33	7.58	7.24	7.45	4.44	4.52	4.05, 4.08	3.98	3.96	2.45
Δδ	*-0.06*	*0*	*0.17*	*0.21*	*0.13*	*0.12*	*0.13*	*0.15*	*0.31*	*0.30*	*0.28*	*0.33*	*0.37*	*0.25, 0.26*	*0.36*	*0.30*	*0.01*
$\mathbf{1}_3\cdot Zn^{2+}$	8.61	8.50	7.70	7.54	8.30	8.21	7.73	7.22	7.29	6.99	7.24	4.13	4.17	3.81, 3.85	3.67	3.63	2.60
Δδ	*0.11*	*0.23*	*0.21*	*0.31*	*-0.29*	*-0.31*	*0.28*	*0.04*	*0.02*	*0.05*	*0.07*	*0.02*	*0.02*	*0.01, 0.03*	*0.05*	*-0.03*	*0.16*
$\mathbf{1}_3\cdot Ca^{2+}\cdot Zn^{2+}$	8.60	8.48	7.55	7.39	7.87/ 7.79	7.84/ 7.77	7.69	7.22	7.35	7.04	7.27	4.22	4.22	3.88	3.72	3.72	2.60
Δδ	*0.10*	*0.21*	*0.06*	*0.16*	*-0.72/ -0.80*	*-0.68/ -0.75*	*0.24*	*0.04*	*0.08*	*0.10*	*0.10*	*0.11*	*0.07*	*0.08, 0.06*	*0.10*	*0.06*	*0.16*
$\mathbf{1}_3\cdot(Ca^{2+})_3\cdot Zn^{2+}$	8.72	8.58	7.77	7.55	8.37	8.24	7.81	7.41	7.64	7.27	7.48	4.46	4.54	4.06, 4.08	3.98	3.96	2.62
Δδ	*0.22*	*0.31*	*0.28*	*0.32*	*-0.22*	*-0.28*	*0.36*	*0.23*	*0.37*	*0.33*	*0.31*	*0.35*	*0.39*	*0.26, 0.26*	*0.36*	*0.30*	*0.18*

1_2·$(Ca^{2+})_2$·Zn^{2+} *Δδ*	8.66	8.53	7.85	7.65	8.68	8.62	7.81	7.41	7.64	7.27	7.48	4.46	4.54	4.06, 4.08	3.98	3.96	2.62
	0.16	*0.26*	*0.36*	*0.42*	*0.09*	*0.10*	*0.36*	*0.23*	*0.37*	*0.33*	*0.31*	*0.35*	*0.39*	*0.26, 0.26*	*0.36*	*0.30*	*0.18*

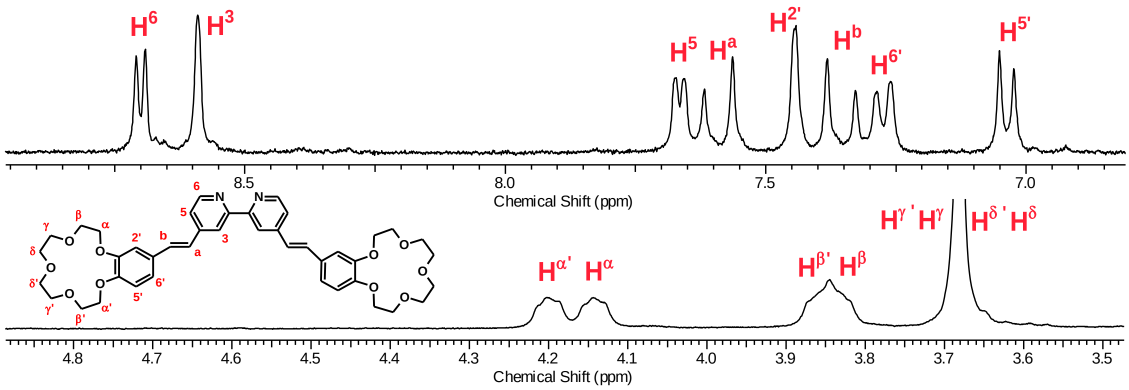


Fig. S17 . NMR specrum of *E*, *E*-**2** in $(CD_3)_2SO$, T = 25°C.

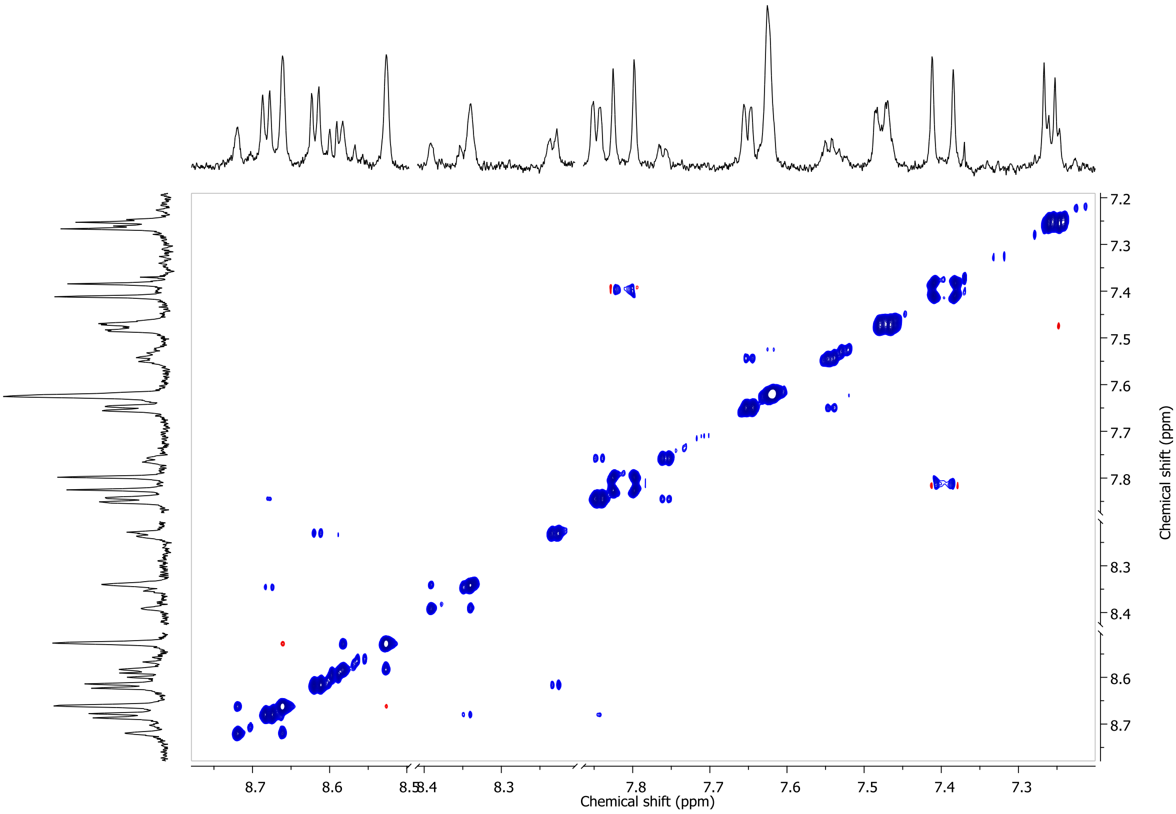


Fig. S18 . NMR EXSY spectrum of [$\mathbf{1}_3\cdot Zn^{2+}$] + 40 eq. Ca^{2+} + 3 eq. Zn^{2+} sample. CD_3CN, 25°C, EXSY mixing time 300 ms.

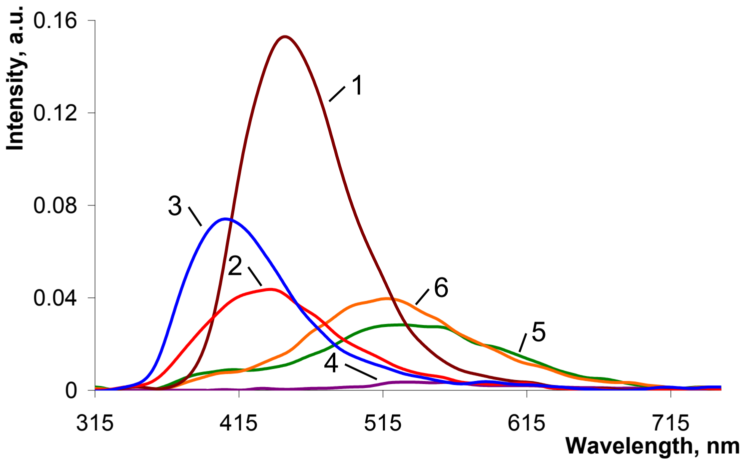


Fig. S19. Fluorescence emission spectra of **2** ([**2**] = 2.1×10^{-6} M) as free ligand *(1)*, in the presence of Zn^{2+} ([Zn^{2+}] = 0.7×10^{-6} M) *(4)*, in the presence of Ca^{2+} ([Ca^{2+}] = 2.0×10^{-5} M) *(2)*, ([Ca^{2+}] = 1.9×10^{-4} M) *(3)*, and in the presence of both Ca^{2+} and Zn^{2+} ([Ca^{2+}] = 2.0×10^{-4} M, [Zn^{2+}] = 2.0×10^{-6} M) *(5)*, ([Ca^{2+}] = 9.8×10^{-4} M, [Zn^{2+}] = 2.0×10^{-6} M) *(6)*. $\lambda_{excit.}$ = 300 nm, CH_3CN, 20°C.