Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting Information:

A modified cyclen azaxanthone ligand as a new fluorescent probe for zinc

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Table of Contents

Figure S1. Excitation and emission of the ligand L in the solid state

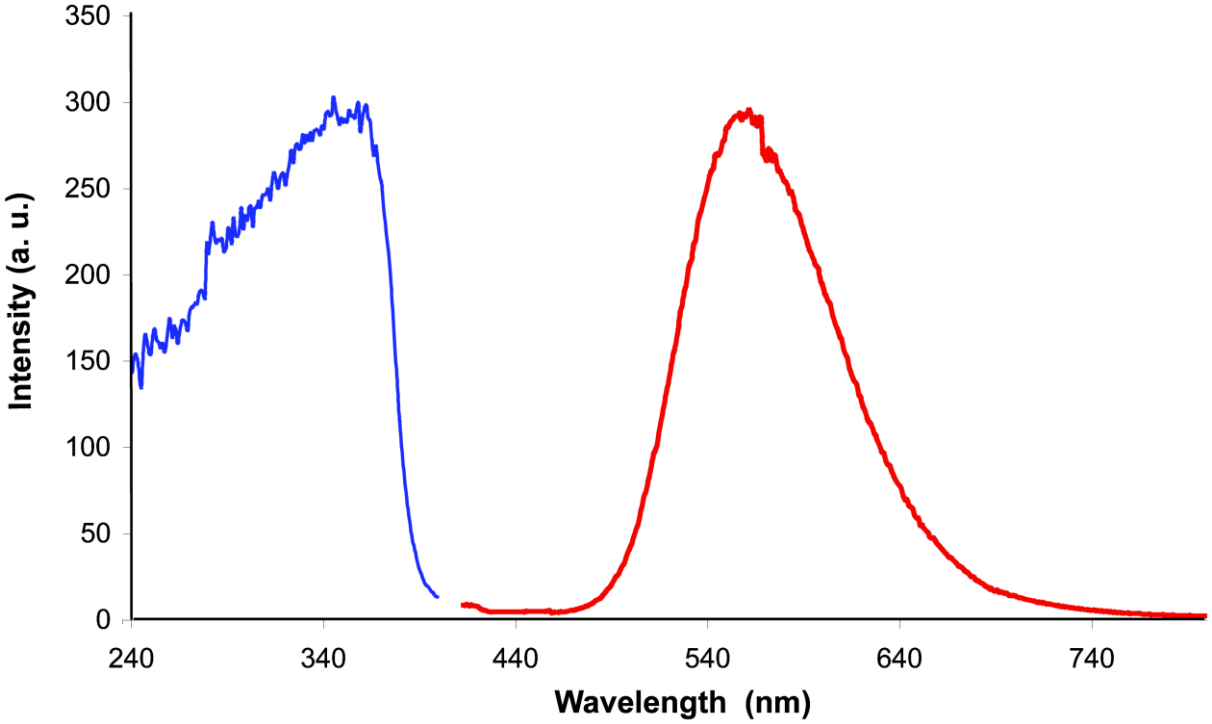
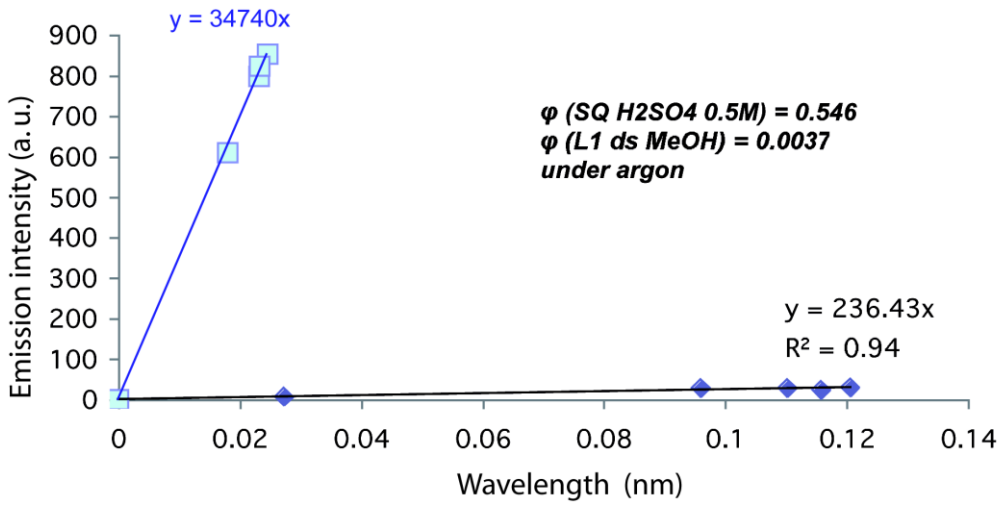
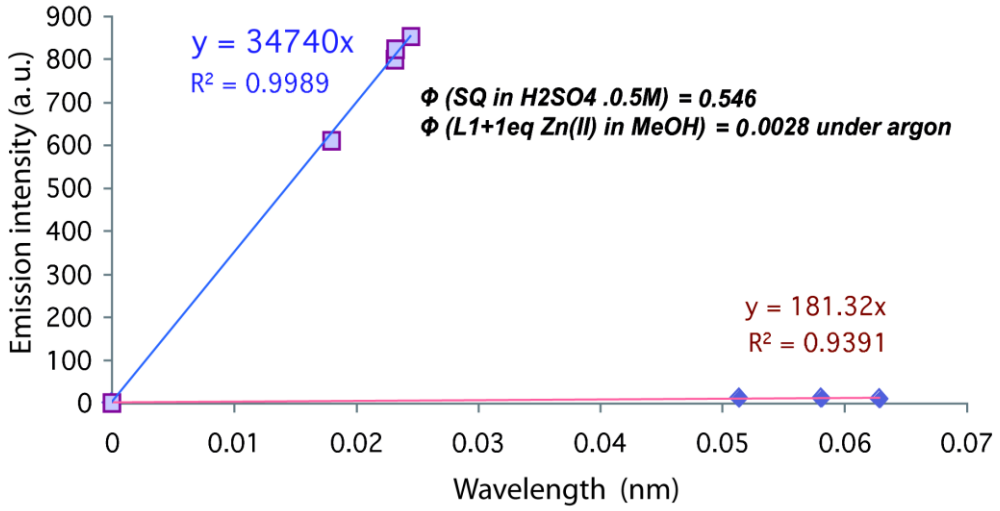


Figure S2. Quantum yields measurements for **L**, Zn**L**, and Zn_2:**L**





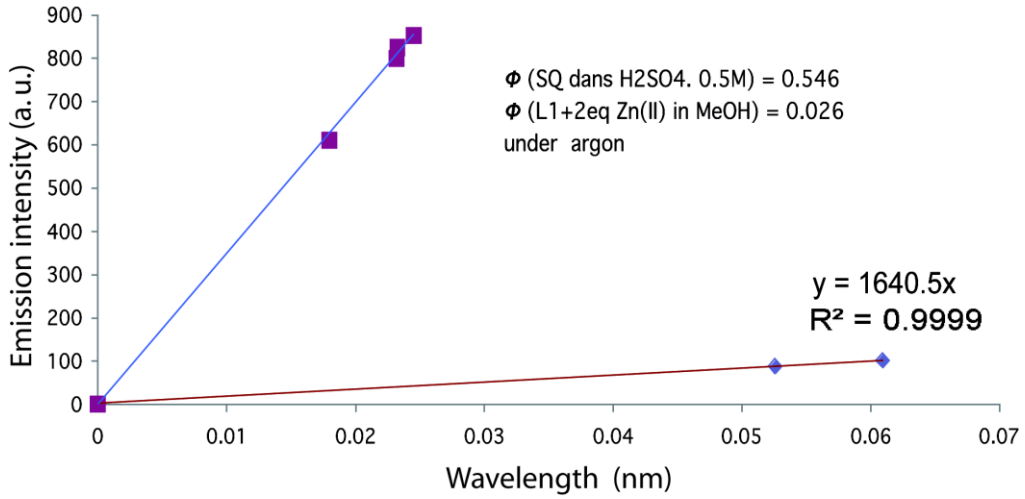


Figure S3: Superimposed optimized geometries of **L** and $[Zn\mathbf{L}]^{2+}$ in the gas phase (blue) and in MeOH (red) [PBE-D3/TZP results

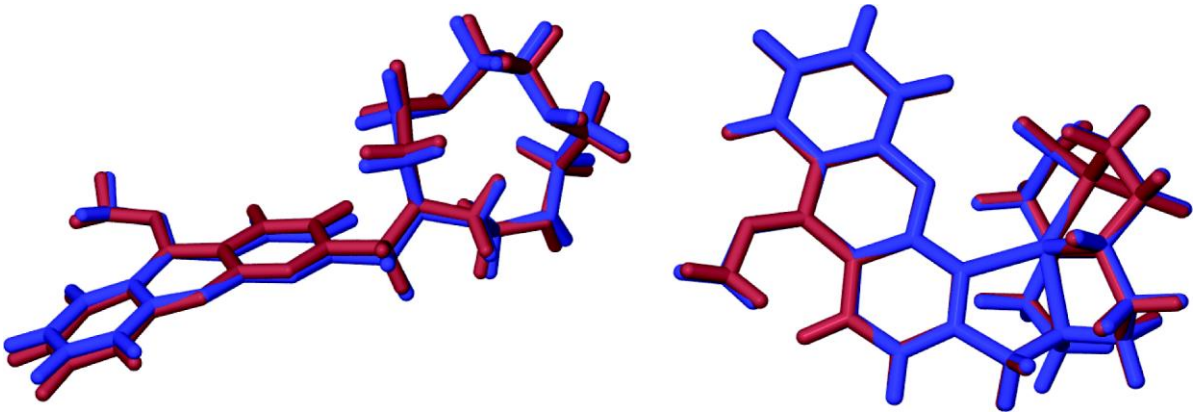


Table S1: Characterization of the 30 lowest-lying singlet excited state of **L** in MeOH (SAOP/TZP results).[a] The involved molecular orbitals are shown in Table S3.

State	Character	Energy (cm^{-1})	Oscillator strength (x 10^4)	Major MO → MO contributions (%)
S_1	n-π* CT	17612	96	HOMO → LUMO (99%)
S_2	n-π* CT	19839	30	HOMO-1 → LUMO (97%)
S_3	n-π* CT	20018	2	HOMO-2 → LUMO (100%)
S_4	n-π* CT	23840	37	HOMO-4 → LUMO (98%)
S_5	n-π* CT	25213	44	HOMO → LUMO+1 (98%)
S_6	n-π* CT	25655	46	HOMO → LUMO+2 (92%)
S_7	π-π*	26090	1121	HOMO-3 → LUMO (75%)
S_8	n-π* CT	27497	3	HOMO-1 → LUMO+1 (99%)
S_9	n-π* CT	27714	0	HOMO-2 → LUMO+1 (100%)
S_{10}	n-π* CT	27972	20	HOMO-1 → LUMO+2 (98%)
S_{11}	n-π* CT	28186	1	HOMO-2 → LUMO+2 (100%)
S_{12}		28732	22	HOMO → LUMO+3 (98%)
S_{13}	π-π*	29937	73	HOMO-3 → LUMO+1 (74%)
				HOMO-6 → LUMO (11%)
				HOMO-3 → LUMO+2 (10%)
S_{14}	π-π*	30472	74	HOMO-3 → LUMO+2 (60%)
				HOMO-5 → LUMO (26%)
S_{15}	n-π* CT	31047	16	HOMO-1 → LUMO+3 (93%)
S_{16}	n-π* CT	31265	1	HOMO-2 → LUMO+3 (100%)
S_{17}	π-π*+ n-π* CT	31481	83	HOMO-5 → LUMO (44%)
				HOMO-4 → LUMO+1 (28%)
				HOMO-3 → LUMO+2 (13%)
S_{18}	n-π* CT	31597	47	HOMO-4 → LUMO+1 (72%)
				HOMO-5 → LUMO (14%)
S_{19}	n-π* CT	32048	7	HOMO-4 → LUMO+2 (97%)
S_{20}	π-π*	34726	1308	HOMO-3 → LUMO+3 (47%)
				HOMO-6 → LUMO (24%)
S_{21}	n-π*	35038	495	HOMO-8 → LUMO (75%)
				HOMO-6 → LUMO (16%)
S_{22}	n-π* CT	35062	404	HOMO-4 → LUMO+3 (60%)
				HOMO-6 → LUMO (16%)
				HOMO-8 → LUMO (15%)

S_{23}	π-π*	35325	486	HOMO-4 → LUMO+3 (29%)
				HOMO-3 → LUMO+3 (24%)
				HOMO-6 → LUMO (16%)
				HOMO-7 → LUMO (10%)
S_{24}	n-π*	36157	288	HOMO-7 → LUMO (78%)
S_{25}	π-π*	37699	15	HOMO-9 → LUMO (56%)
				HOMO-5 → LUMO+1 (32%)
S_{26}	n-π* CT	38786	16	HOMO → LUMO+4 (86%)
				HOMO-10 → LUMO (14%)
S_{27}	n-π* CT	38832	22	HOMO-10 → LUMO (85%)
				HOMO → LUMO+4 (13%)
S_{28}	π-π*	39772	323	HOMO-5 → LUMO+1 (28%)
				HOMO-11 → LUMO (22%)
				HOMO-9 → LUMO (14%)
				HOMO-5 → LUMO+3 (14%)
S_{29}	n-π* CT	40038	19	HOMO-11 → LUMO (77%)
S_{30}	π-π*	40222	3470	HOMO-5 → LUMO+2 (53%)
				HOMO-6 → LUMO+1 (11%)

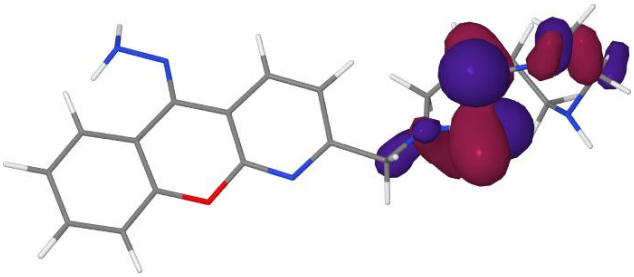
[a] n-*π** CT: the $S_0 \rightarrow S_n$ transition is a n-π* charge-transfer transition from the cyclen to the azaxanthone-hydrazone moiety. *π*-*π**: the $S_0 \rightarrow S_n$ transition is a *π*-*π** transition centered on the azaxanthone-hydrazone moiety. n-*π**: the $S_0 \rightarrow S_n$ (n=21) transition is a n-π* transition localized on the azaxanthone-hydrazone fragment.

Table S2: Characterization of the 10 lowest-lying triplet excited state of **L** in MeOH (SAOP/TZP results).[a] The involved molecular orbitals are shown in Table S3.

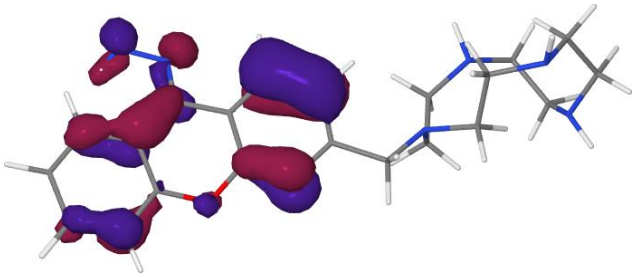
State	Character	Energy (cm^{-1})	Major MO → MO contributions (%)
T_1	n-π* CT	17317	HOMO → LUMO (98%)
T_2	π-π* CT	19259	HOMO-3 → LUMO (60%)
			HOMO-1 → LUMO (37%)
T_3	n-π* CT	19930	HOMO-1 → LUMO (62%)
			HOMO-3 → LUMO (36%)
T_4	n-π* CT	20014	HOMO-2 → LUMO (98%)
T_5	n-π* CT	23833	HOMO-4 → LUMO (100%)
T_6	n-π* CT	25067	HOMO → LUMO+1 (99%)
T_7	n-π*	25519	HOMO → LUMO+2 (99%)
T_8	n-π* CT	27370	HOMO-1 → LUMO+1 (93%)
T_9	n-π* CT	27708	HOMO-2 → LUMO+1 (100%)
T_{10}	n-π* CT	27788	HOMO-1 → LUMO+2 (83%)
			HOMO-3 → LUMO+2 (12%)

[a] n-*π** CT: the $S_0 \rightarrow T_n$ transition is a n-π* charge-transfer transition from the cyclen to the azaxanthone-hydrazone moiety. *π*-*π**: the $S_0 \rightarrow T_n$ transition is a *π*-*π** transition centred on the azaxanthone-hydrazone moiety.

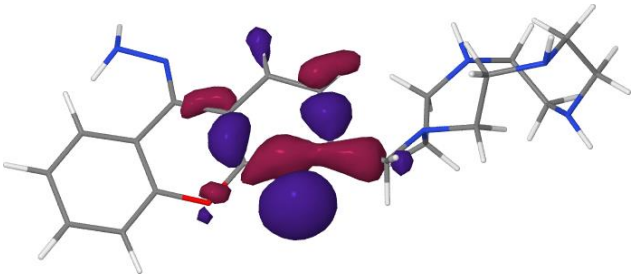
Figure S4: Ground-state frontier molecular orbitals of **L** in MeOH (SAOP/TZP results).



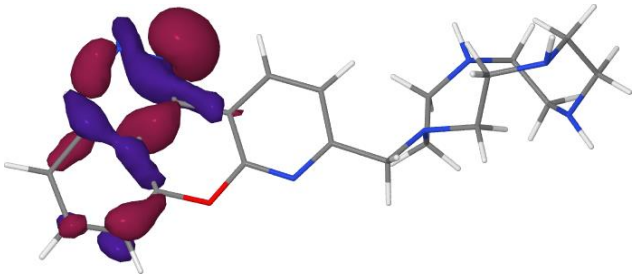
HOMO-10 (-11.285 eV)



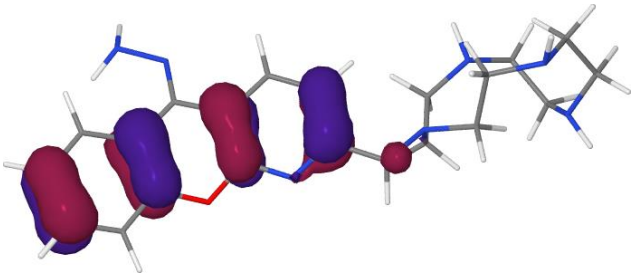
HOMO-9 (-10.995 eV)



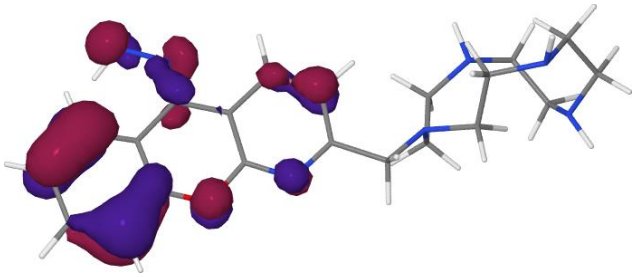
HOMO-8 (-10.751 eV)



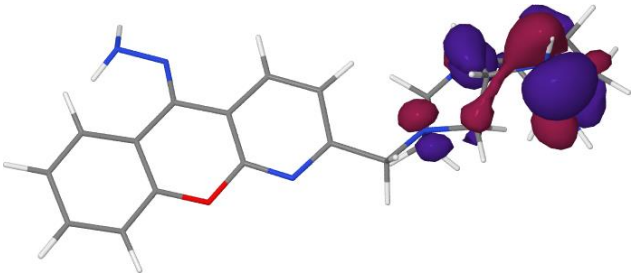
HOMO-7 (-10.722 eV)



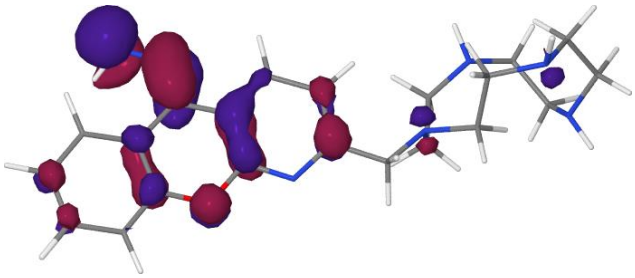
HOMO-6 (-10.446 eV)



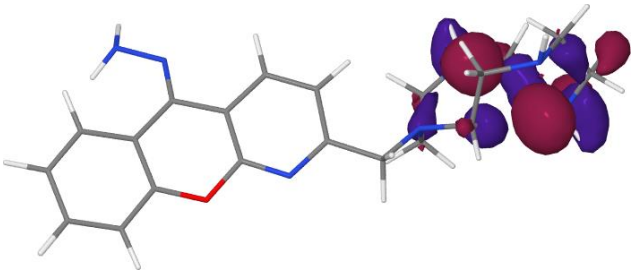
HOMO-5 (-10.114 eV)



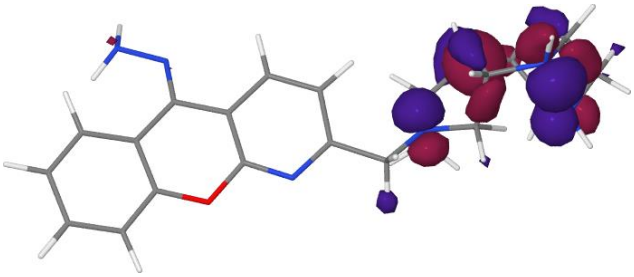
HOMO-4 (-9.431 eV)



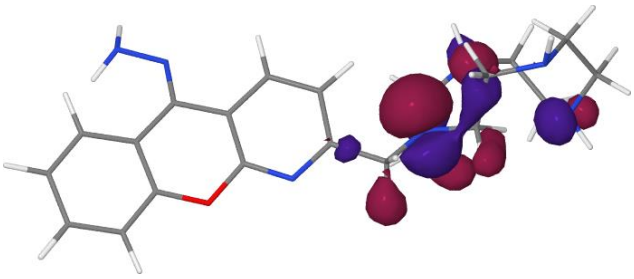
HOMO-3 (-9.110 eV)



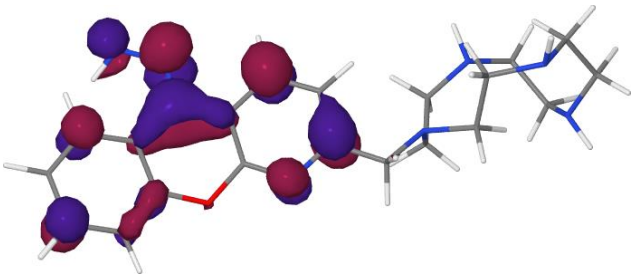
HOMO-2 (-8.956 eV)



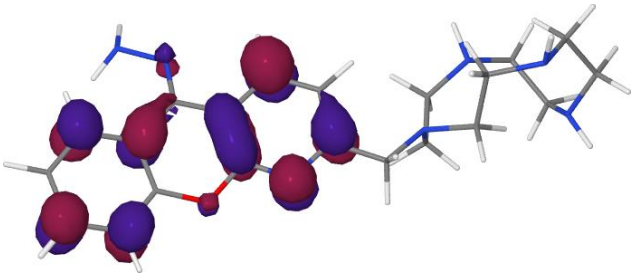
HOMO-1 (-8.923 eV)



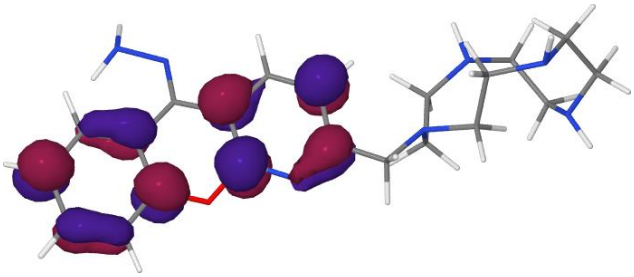
HOMO (-8.636 eV)



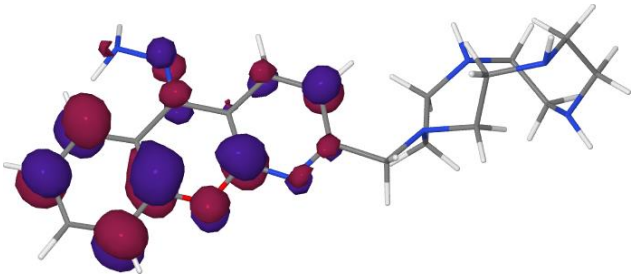
LUMO (-6.474 eV)



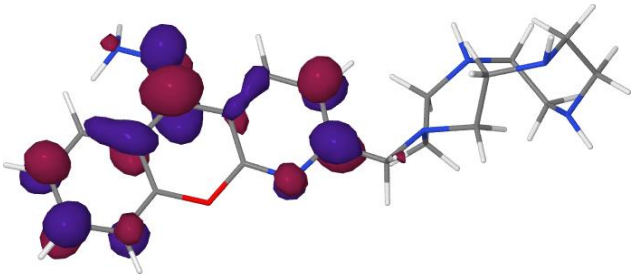
LUMO+1 (-5.520 eV)



LUMO+2 (-5.465 eV)



LUMO+3 (-5.080 eV)



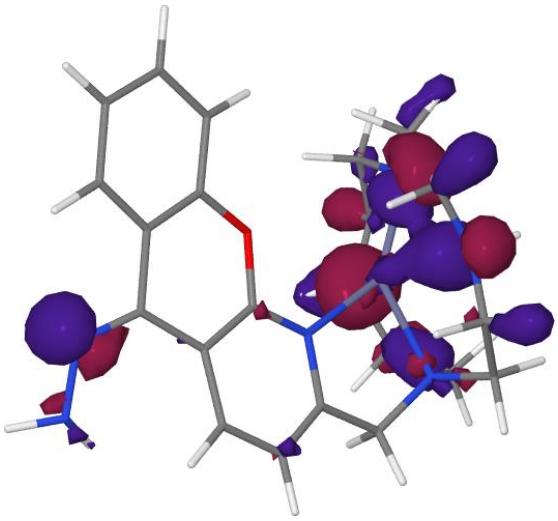
LUMO+4 (-3.840 eV)

Table S3: Characterization of the 10 lowest-lying singlet excited state of $[Zn\mathbf{L}]^{2+}$ in MeOH (SAOP/TZP results).a The involved molecular orbitals are shown in Table S5.

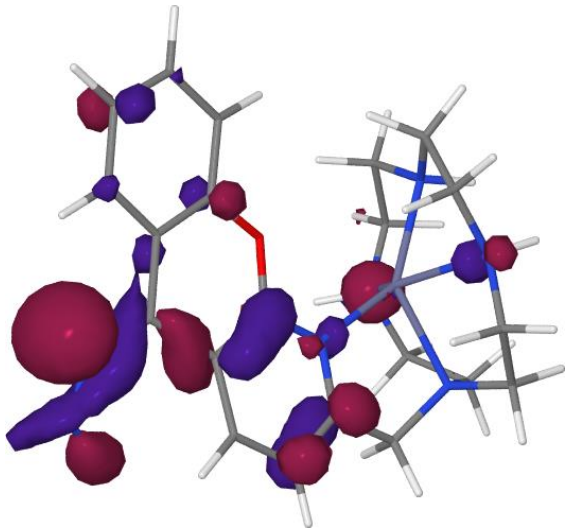
State	Character	Energy (cm^{-1})	Oscillator strength (x 10^4)	Major MO → MO contributions (%)
S_1	π-π*	22904	604	HOMO → LUMO (83%)
				HOMO → LUMO+1 (10%)
S_2	n-π* CT	25629	16	HOMO-1 → LUMO (100%)
S_3	π-π*	27441	309	HOMO → LUMO+1 (62%)
				HOMO-2 → LUMO (17%)
				HOMO → LUMO+2 (13%)
S_4	π-π*	27846	41	HOMO-2 → LUMO (78%)
				HOMO → LUMO+1 (11%)
S_5	"admix."	30999	168	HOMO-3 → LUMO (65%)
				HOMO → LUMO+2 (18%)
S_6	"admix."	31385	535	HOMO → LUMO+2 (36%)
				HOMO-4 → LUMO (31%)
				HOMO-3 → LUMO (11%)
S_7	n-π* CT	31813	14	HOMO-1 → LUMO+1 (99%)
S_8	"admix."	32366	103	HOMO-6 → LUMO (49%)
				HOMO-5 → LUMO (25%)
				HOMO-4 → LUMO (16%)
S_9	"admix."	32894	201	HOMO-6 → LUMO (41%)
				HOMO-4 → LUMO (29%)
				HOMO-3 → LUMO (11%)
S_{10}	"admix."	33981	84	HOMO-2 → LUMO+1 (44%)
				HOMO-5 → LUMO (33%)

[a] *π-π**: the $S_0 \rightarrow S_n$ transition is a *π-π** transition centered on the azaxanthone-hydrazone moiety. n-π* CT: the $S_0 \rightarrow S_n$ transition is a n-*π** charge-transfer transition from the cyclen to the azaxanthone-hydrazone moiety. "admix.": while the virtual orbitals involved in the MO → MO contributions are *π** centered on the azaxanthone-hydrazone moiety, the occupied orbitals extend over the whole molecule with varying contributions from the lone pairs of the nitrogen atoms of the hydrazone and cyclen fragments (see Table S5).

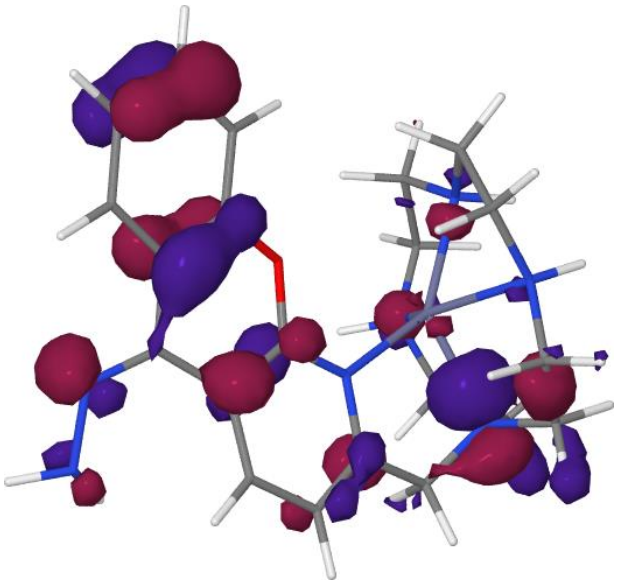
Figure S5: Ground-state frontier molecular orbitals of $[Zn\mathbf{L}]^{2+}$ in MeOH (SAOP/TZP results).



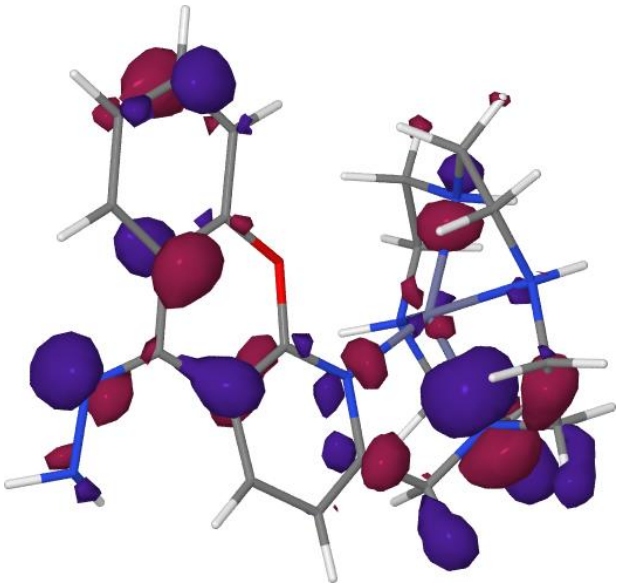
HOMO-6 (-11.152 eV)



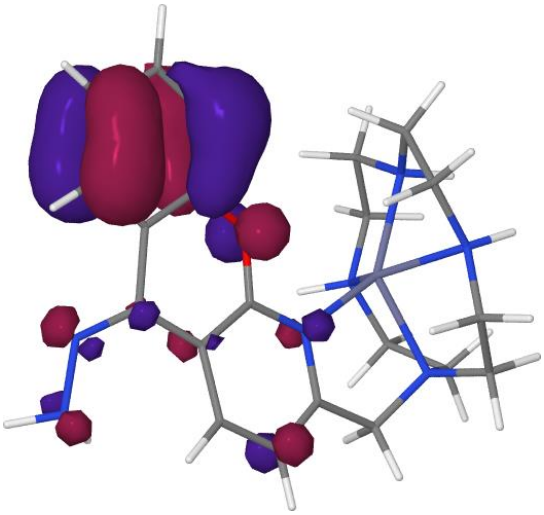
HOMO-5 (-11.113 eV)



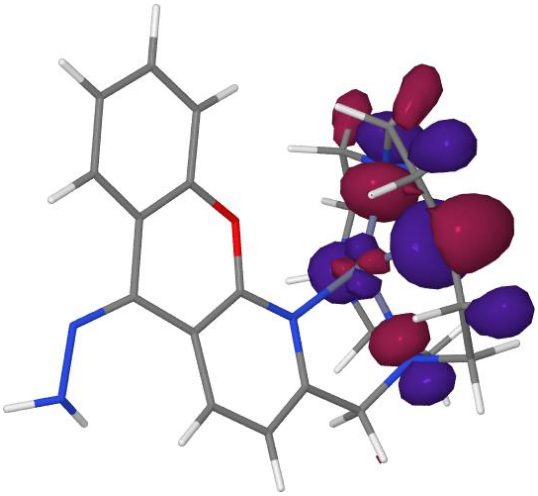
HOMO-4 (-11.048 eV)



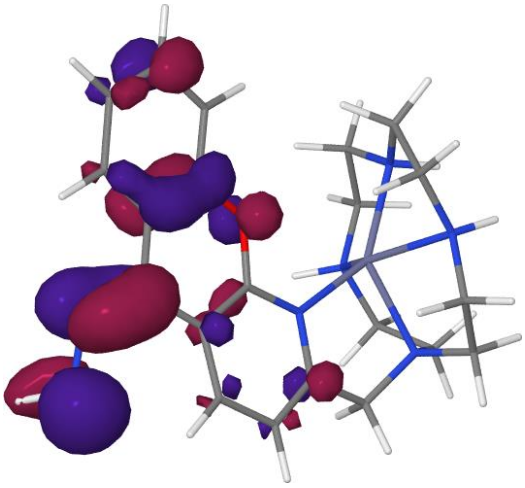
HOMO-3 (-10.946 eV)



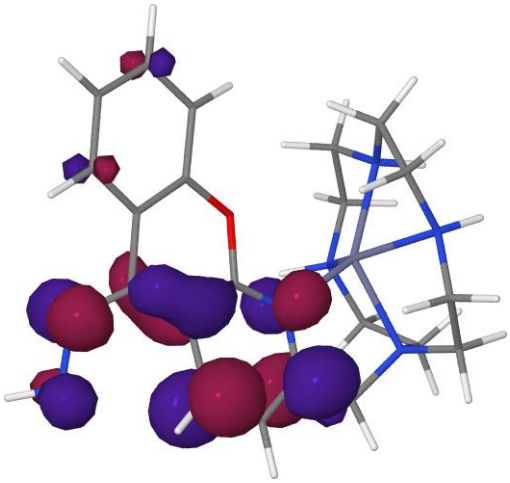
HOMO-2 (-10.489 eV)



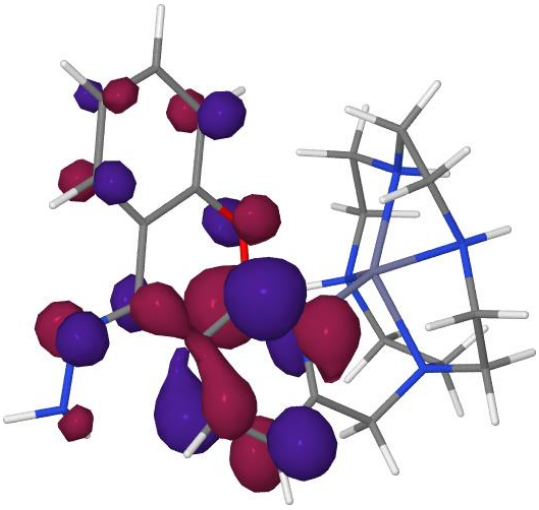
HOMO-1 (-10.306 eV)



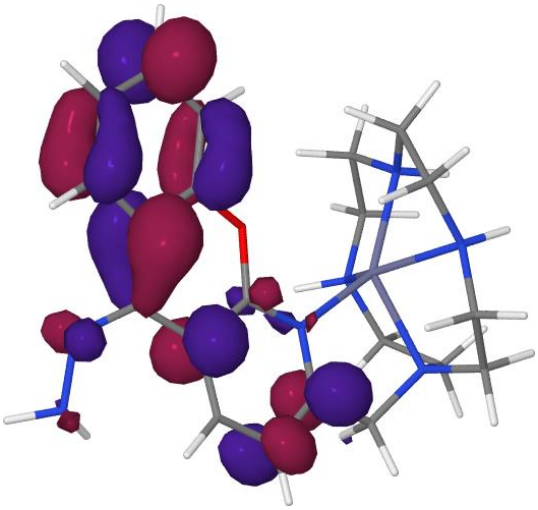
HOMO (-9.535 eV)



LUMO (-7.137 eV)



LUMO+1 (-6.368 eV)



LUMO+2 (-5.987 eV)