Electronic Supporting Information (ESI) for:

Cooperative Self-Assembly of a Macrocyclic Schiff Base Complex

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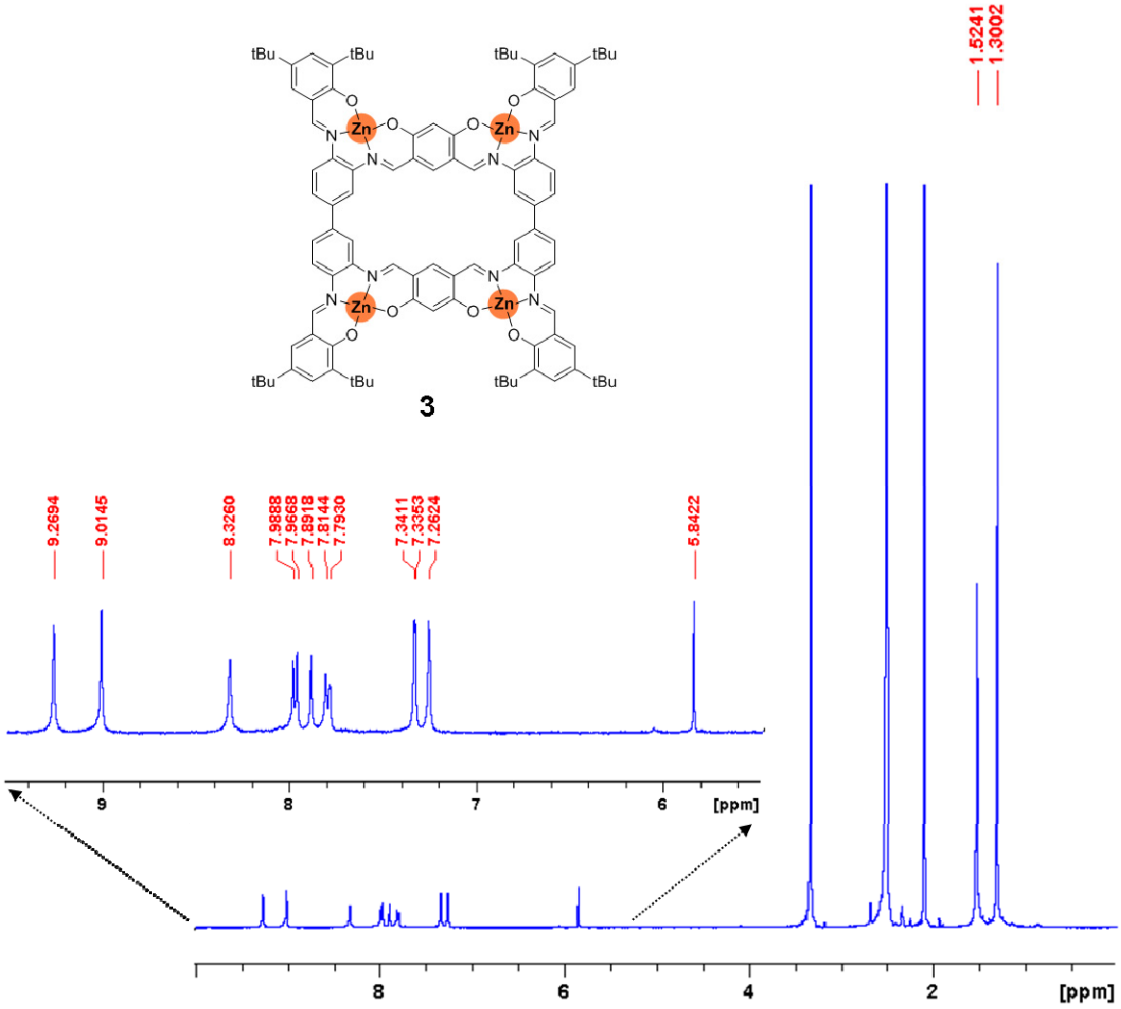
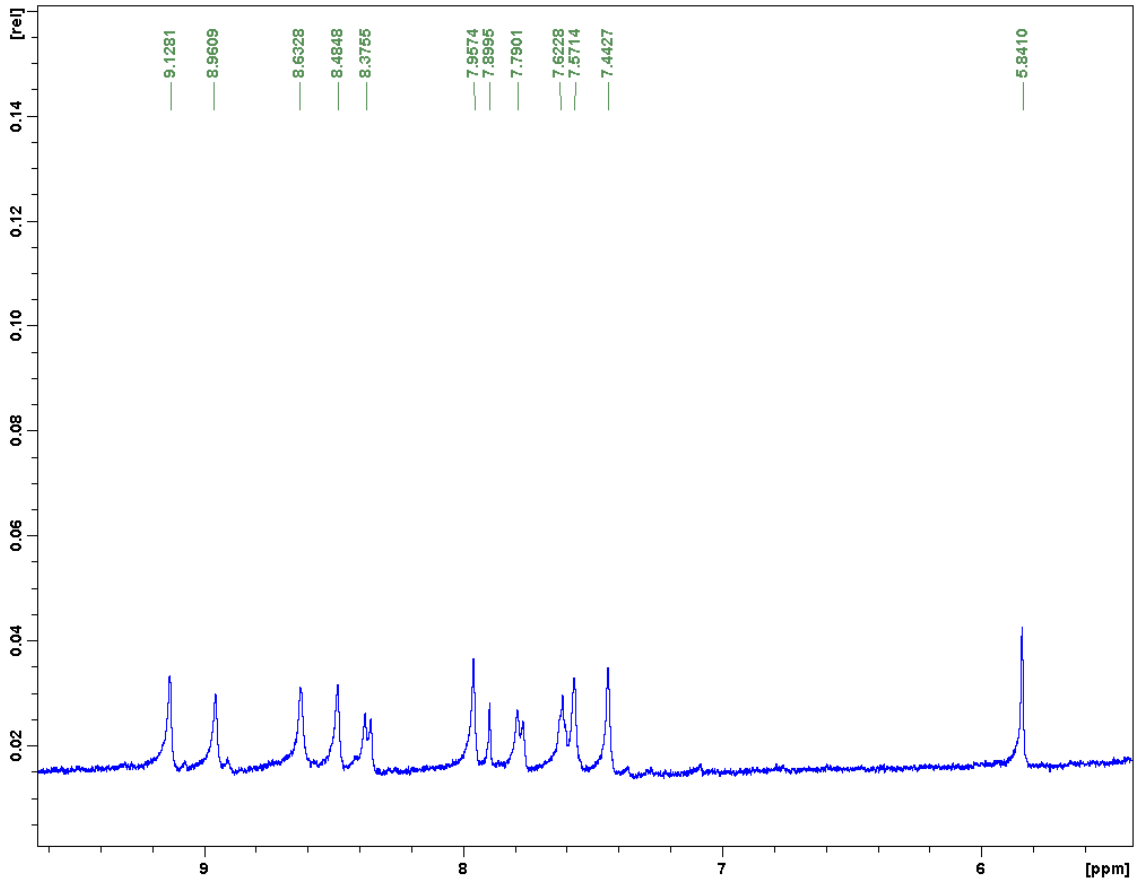
Contents:

^{1}H NMR (DMSO-d_6) spectrum for Zn_4 complex **3**:

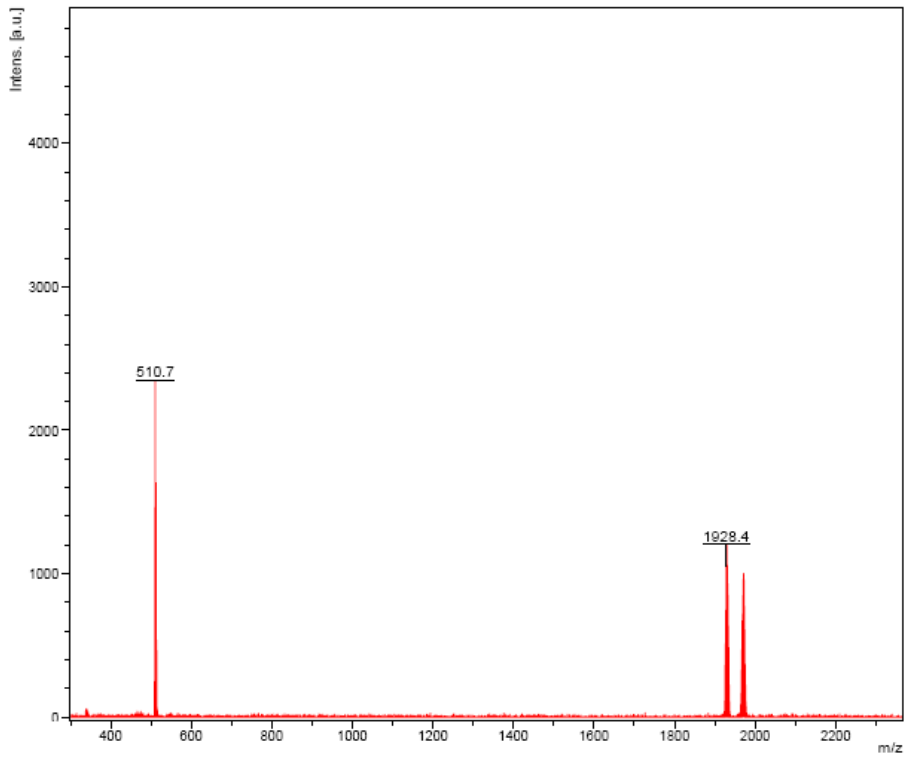


^{1}H NMR (DMSO-d_6 + added pyr/Bu-NH_2) spectrum for **4**:



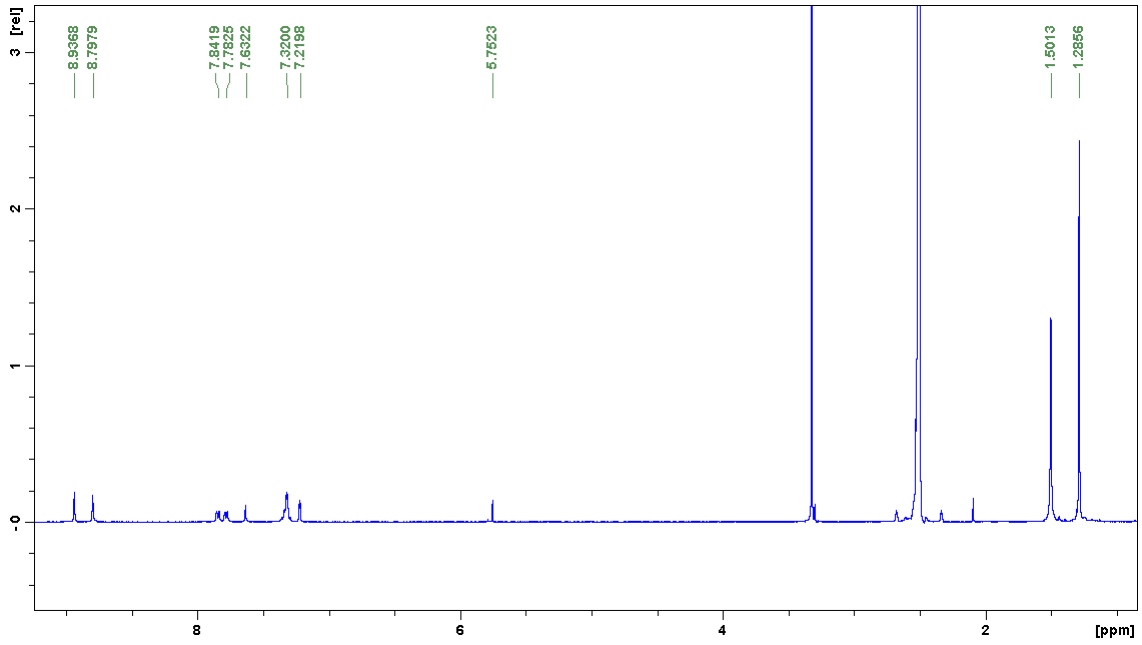
Only the aromatic region is shown here. The complex proved to be rather insoluble and additives needed to be added (pyridine, *n*-butyl amine) to record a ^{1}H NMR spectrum. Nonetheless, from the pattern above and comparison with the ^{1}H aromatic region for **3** we can confirm the proposed connectivity pattern for **4**.

MALDI-TOF mass spectrum for **4** (pyrene matrix):

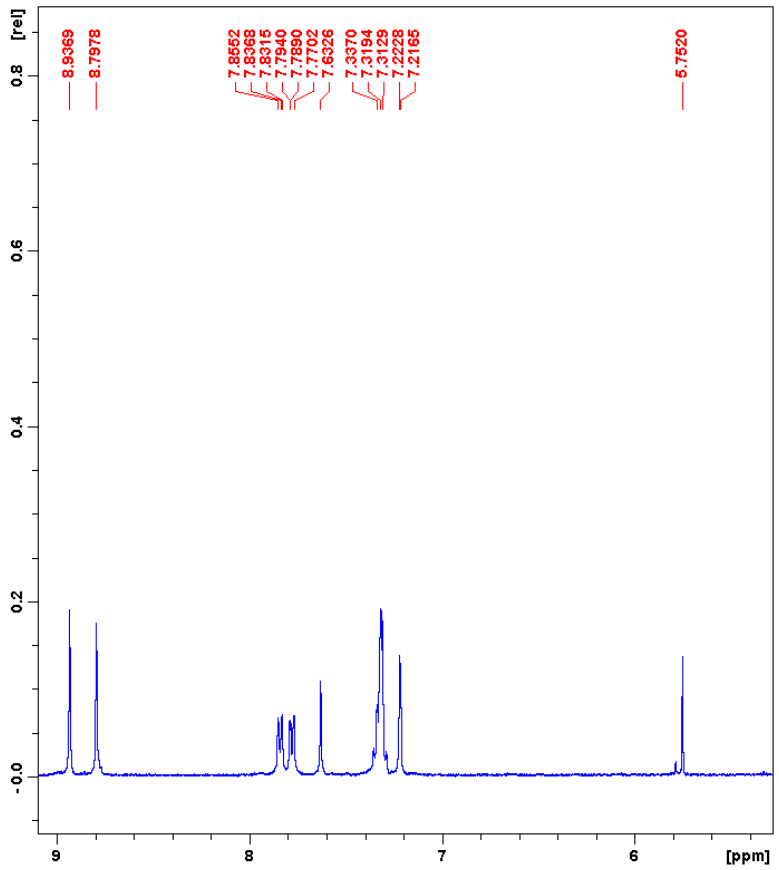


Note that the two peaks in the region 1900–2000 m.u.´s relate to 1971.4 $(M+H)^+$ (calcd 1971.4) and 1928.4 $(M–C_3H_6)^+$ (calcd. 1928.4). The peak at 510.7 does not contain Pd (cf., isotope pattern) and is possibly related to the matrix used (dctb).

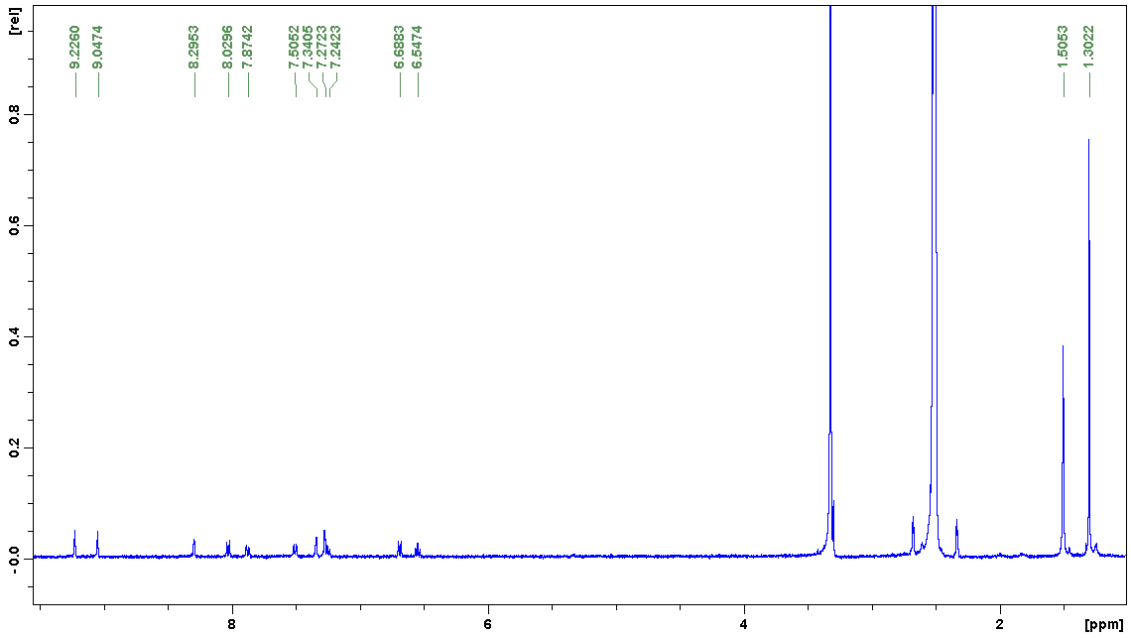
^{1}H NMR (DMSO-d_6) of complex **8**:



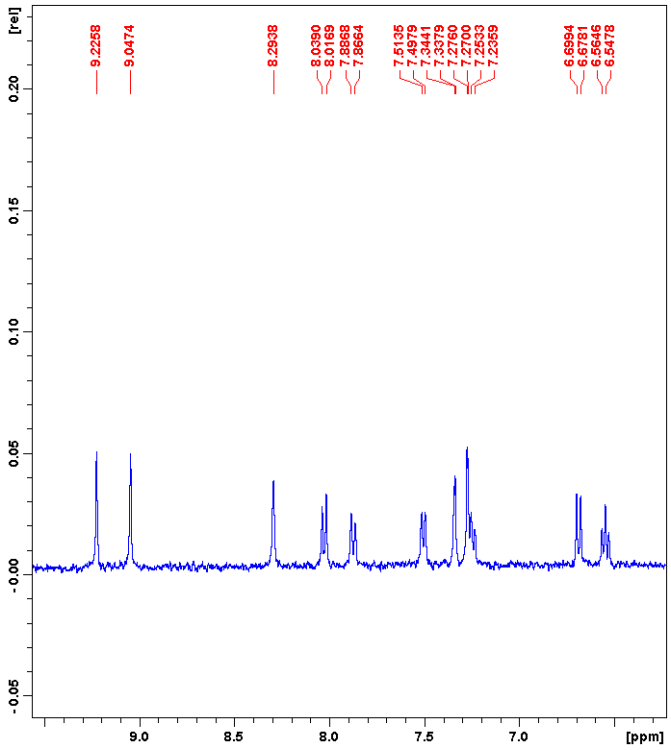
Extension of region between 5-9 ppm:



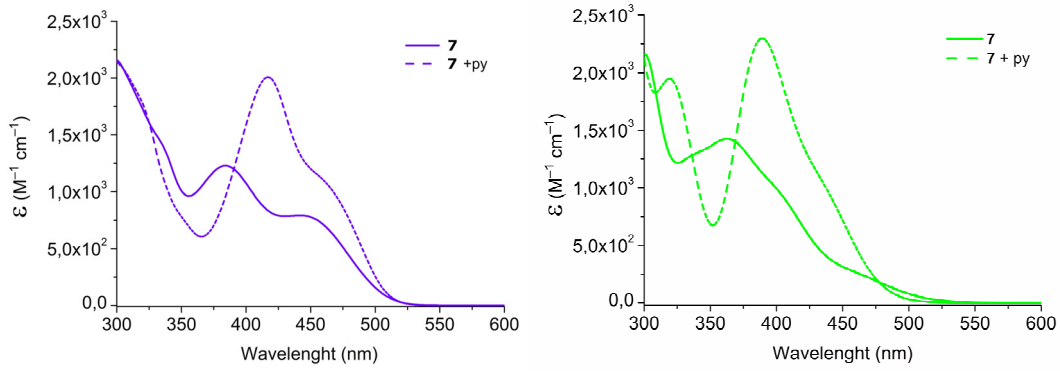
^{1}H NMR (DMSO-d_6) of complex **9**:



Extension of the aromatic region:



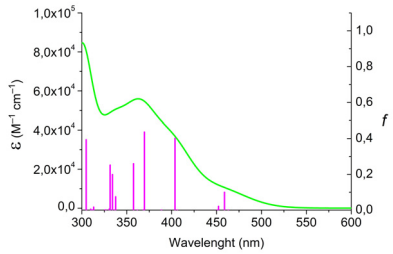
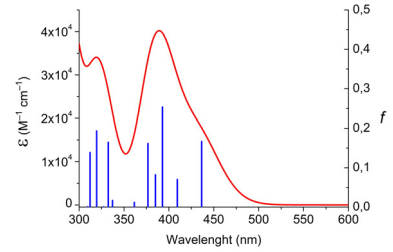
DFT studies on mononuclear complex **7**.



Experimental (left) and simulated (right) UV-Vis Spectra of complex **7** in toluene: the dashed lines represent the traces after addition of pyridine.

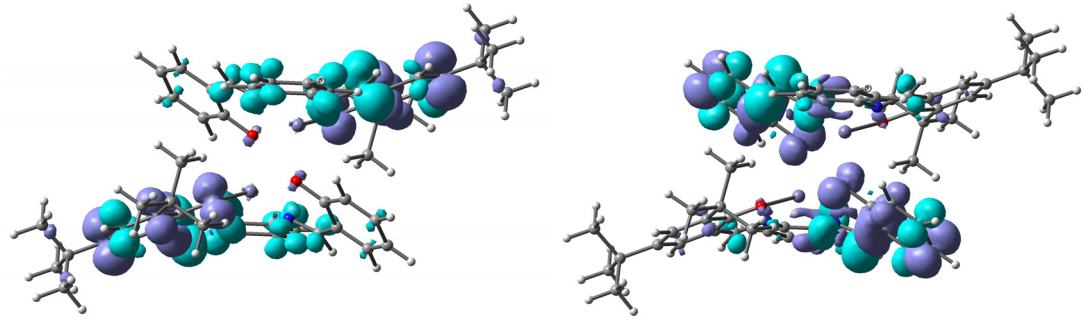
Table S1

a: Related transitions energy values in eV and in nm (in parenthesis).
b: the oscillator strength values (shown also as vertical bars in the images).

Complex	Transition	Energy[a]	*f*[b]	Major contributions
7 dimer 	1	2,6782 (462)	0	H-1→L+1 (10%), HOMO→LUMO (86%)
	2	2,7023 (458)	0,0994	H-1→LUMO (78%), HOMO→L+1 (19%)
	3	2,7420 (452)	0,0211	H-1→LUMO (20%), HOMO→L+1 (78%)
	4	2,7519 (450)	0	H-1→L+1 (88%), HOMO→LUMO (11%)
	5	3,0511 (406)	1E-4	H-1→L+3 (35%), HOMO→L+2 (49%)
	6	3,0709 (403)	0,4009	H-1→L+2 (37%), HOMO→L+3 (44%)
	7	3,1901 (388)	1E-4	H-1→L+2 (48%), HOMO→L+3 (46%)
	8	3,1908 (388)	0	H-1→L+3 (52%), HOMO→L+2 (41%)
	9	3,3539 (369)	0,4357	H-2→LUMO (86%)
	10	3,3651 (368)	1E-4	H-3→LUMO (35%), H-2→L+1 (49%)
7 + py 	1	2,8406 (436)	0,1667	HOMO→LUMO (91%)
	2	3,0282 (409)	0,0701	H-1→LUMO (36%), HOMO→L+1 (56%)
	3	3,1557 (392)	0,2534	H-1→LUMO (43%), HOMO→L+1 (26%), HOMO→L+2 (18%)
	4	3,2201 (385)	0,082	HOMO→L+2 (78%)
	5	3,2915 (376)	0,1614	H-1→L+1 (85%)
	6	3,4298 (361)	0,0119	H-1→L+2 (98%)
	7	3,6761 (337)	0,0168	H-3→LUMO (67%), H-3→L+1 (20%)
	8	3,7289 (332)	0,1645	H-5→LUMO (15%), H-3→L+1 (13%), H-2→LUMO (58%)
	9	3,7885 (327)	5E-4	HOMO→L+3 (99%)
	10	3,8797 (319)	0,1934	H-5→LUMO (19%), H-3→L+1 (33%), H-2→LUMO (33%)

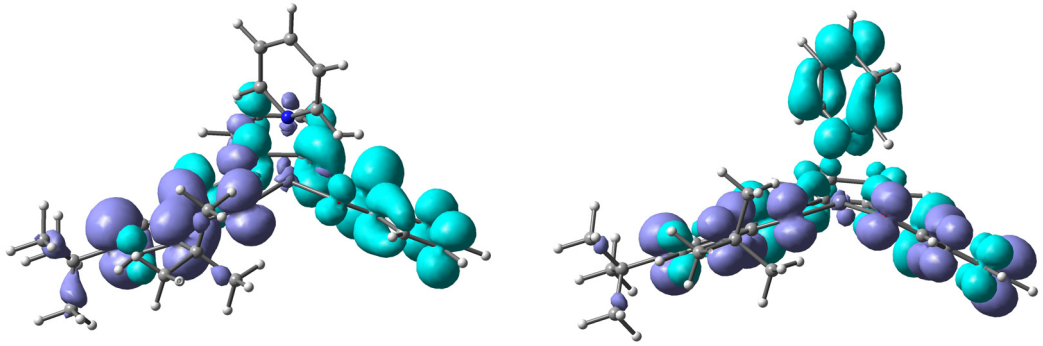
Selected calculated singlet excited-state transitions for complex **7** in toluene.

Electron density difference maps (EDDMs)[1] of transitions 6 (left) and 9 (right) in complex **7** in *dimer* state.



Transition 6, 447 nm Transition 9, 384 nm

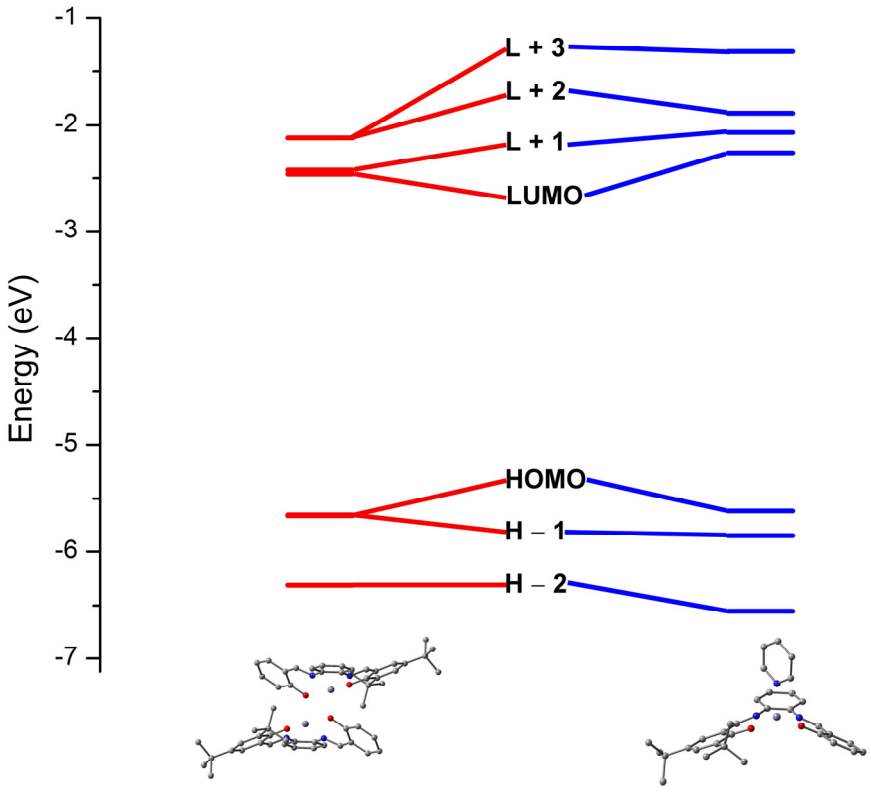
Electron density difference maps (EDDMs) of transitions 1 (left) and 3 (right) in complex **7** in monomer state with pyridine coordinating in the axial position.



Transition 1, 458 nm Transition 3, 417 nm

[1] The electron density migrates from the violet-coloured lobes to the blue-coloured ones.

Frontier orbitals diagram of complex **11** in dimer state (red) and in monomer state.

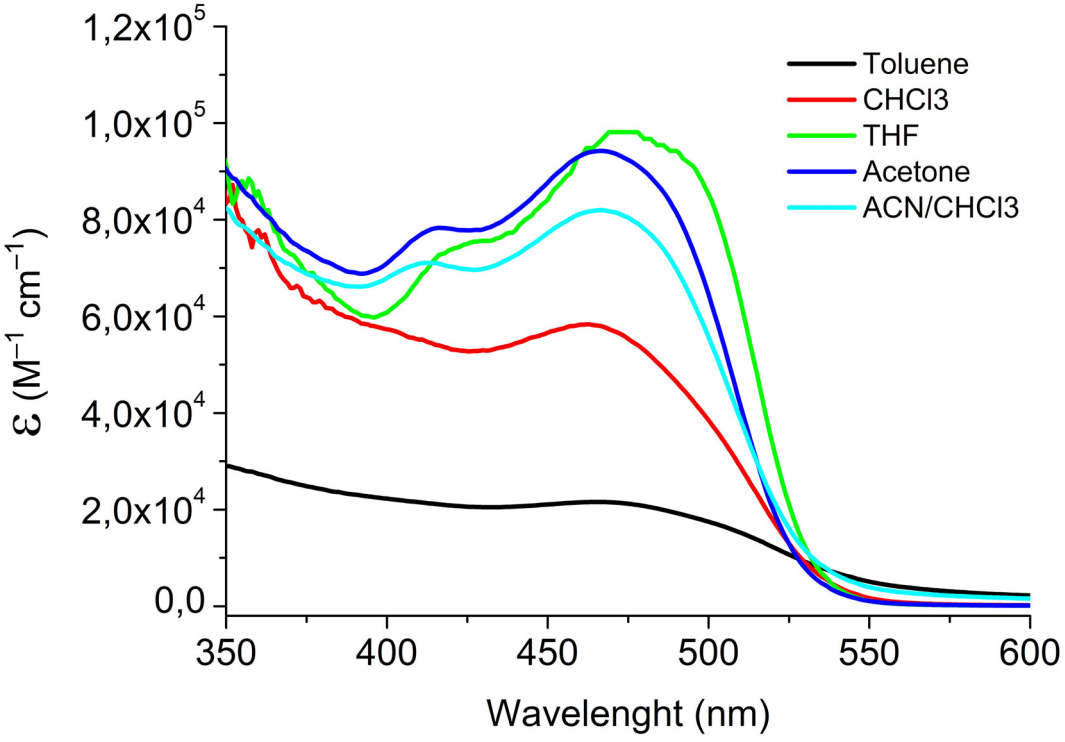


The results from the DFT study carried out for complex **7** helps to understand the hyperchromic shift upon disruption of the dimeric assembly: transitions 1 (458 nm) and 3 (417 nm) become more probable in the monomeric complex, see page S13.

Calculated distances/angles for **3**·$(pyr)_4$ using DFT.

Distances (Å)	
Zn–N(py)	2.195
Zn–O(N_2O_2 pocket)	1.983
Zn–N(N_2O_2 pocket)	2.155
Zn–Zn(long side)	11.683
Zn–Zn(short side)	8.407
Angles (deg)	
N(N_2O_2 pocket)–Zn–O(N_2O_2 pocket)	88.4º
N(N_2O_2 pocket)–Zn–N(N_2O_2 pocket)	77.2º
O(N_2O_2 pocket)–Zn–O(N_2O_2 pocket)	98.7º
O(N_2O_2 pocket)–Zn–N(py)	100.1º
N(N_2O_2 pocket)–Zn–N(py)	101.1º
Dihedral Angles (deg)	
C–C (diaminobenzidine)	32.9º

Influence of solvent on UV-vis spectrum of Zn_4 macrocycle **3**.



Solvent influence (selected region in UV-vis spectrum) in the case of Zn_4 macrocycle **3** (at 1×10^{-5} M). Note that in the case of the more polar media the total absorption increases, indicating a different aggregated state for Zn_4 complex **3**.