Electronic Supporting Information

A novel 2,6-bis(benzoxazolyl)phenol macrocyclic chemosensor with enhanced fluorophore properties by photoinduced intramolecular proton transfer

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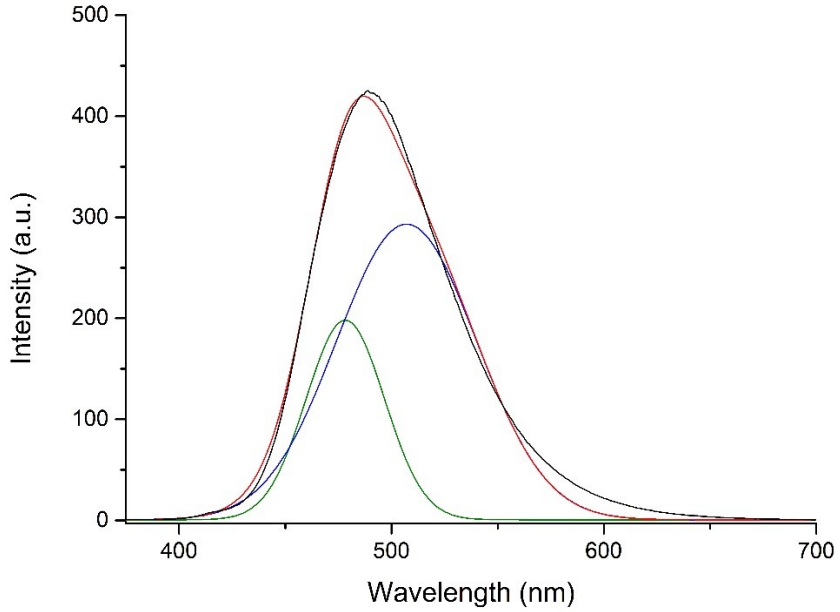

Figure S1. Deconvolution of the emission band at pH=9. The figure reports the experimental emission band recorded at pH=9 (black line), the deconvoluted keto (blue line) and deprotonation emission bands (green line), together with the cumulative fit of the two deconvoluted bands (red line).

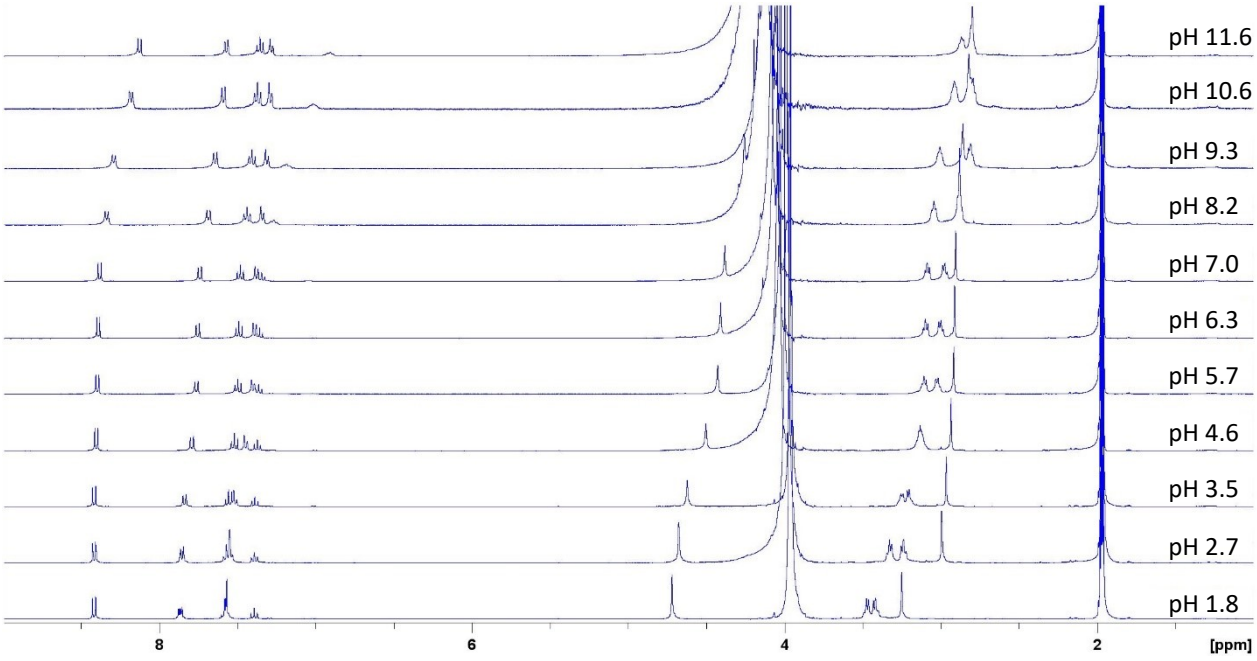

Figure S2. ^{1}H-NMR spectra of **L** recorded at different pH values in D_2O/acetonitrile-d_6 40/60 at 298 K.

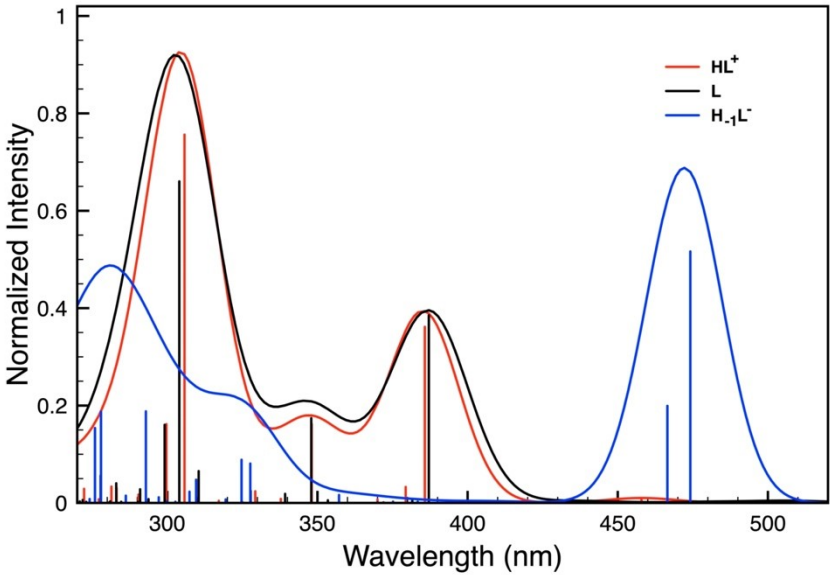

Figure S3. Theoretical UV-Visible absorption spectra of the most stable species of $H_{-1}\mathbf{L}^-$ (blue line), **L** (black line) and $H\mathbf{L}^+$ (red line), obtained by TD-DFT calculations.

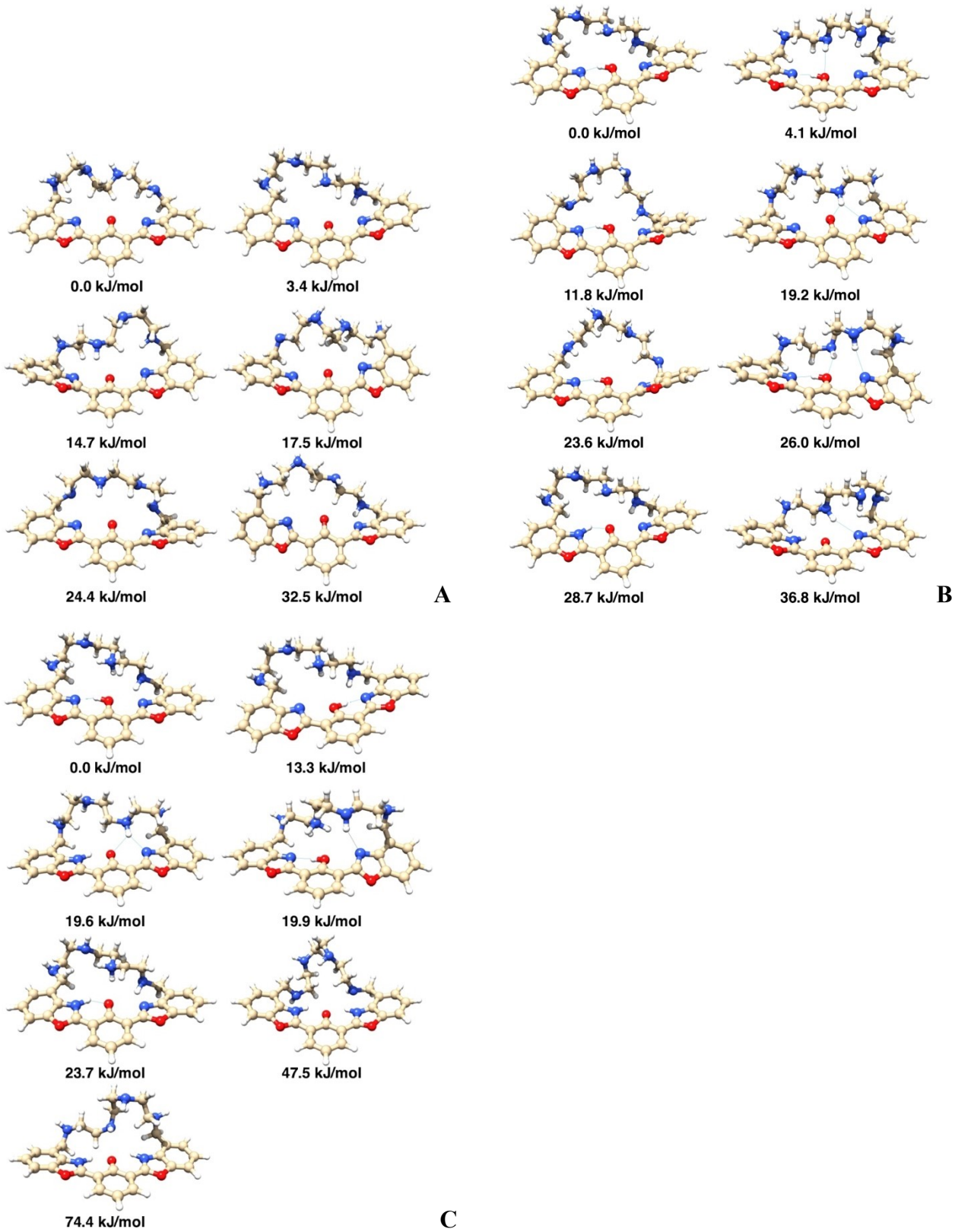

Figure S4. Conformers and tautomers found for species the $H_{-1}\mathbf{L}^-$ (A), **L** (B) and $H\mathbf{L}^+$ (C), obtained by DFT calculations

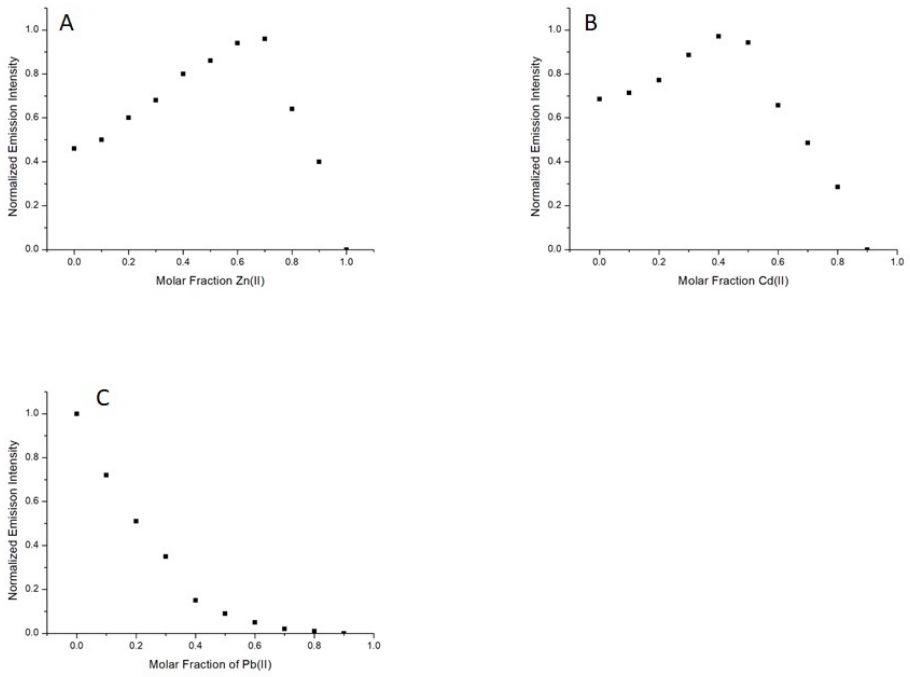

Figure S5. Job-Plots of **L** with Zn(II) (A, Emission at 463 nm), Cd(II) (B, Emission at 463 nm) and Pb(II) (C, Emission at 507 nm). Conditions: aqueous solution at pH = 7.0 (Tris-HCl 0.001 mol dm^{-3}) at 298 K, [**L**] = $1.0 \cdot 10^{-5}$ mol dm^{-3}.

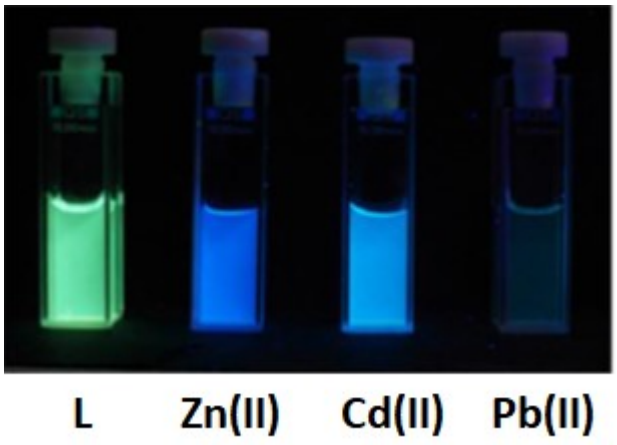

Figure S6. Color changes from green to blue after the addition of Zn(II) and Cd(II) and quenching of the fluorescence upon addition of Pb(II) to an aqueous solution of **L** (10^{-5} mol dm^{-3}, Tris-HCl 10^{-3} mol dm^{-3}, pH = 7.0, lighting with 360 nm UV lamp).

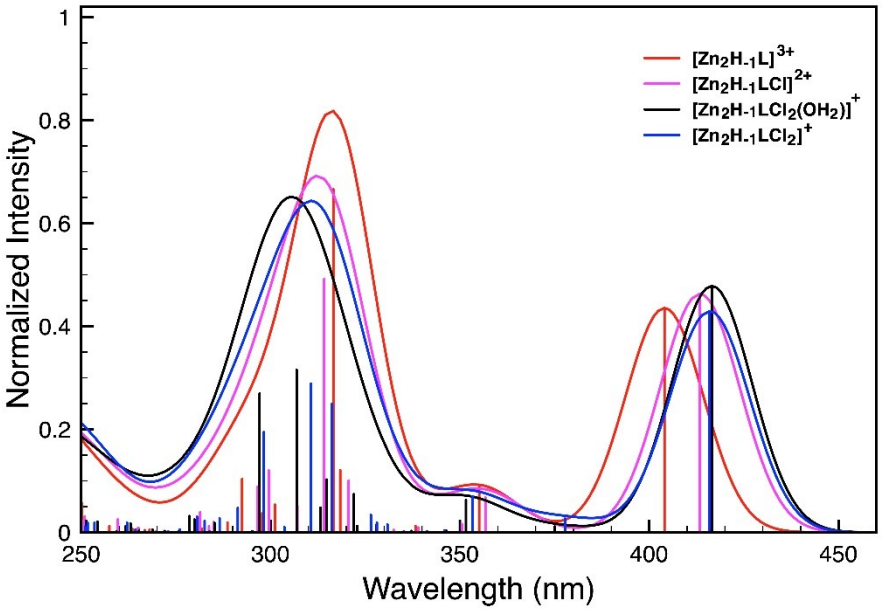

Figure S7. Theoretical UV-Visible absorption spectra of the most stable species of the four considered dinuclear zinc(II) complexes of **L**, including also Cl^- and H_2O, as indicated, obtained by TD-DFT calculations.

Table S1. Chemical shifts of the protons of **L** as a function of pH (ppm) in D_2O/acetonitrile-d_6 40/60 at 298 K.

pH	H1	H3	H2	H4	H9	H5	H6	H7	H8
1.8	3.25	3.42	3.48	4.72	7.39	7.59	7.58	7.87	8.42
2.7	2.99	3.24	3.33	4.68	7.39	7.57	7.57	7.86	8.42
3.5	2.97	3.21	3.25	4.62	7.39	7.52	7.56	7.84	8.42
4.6	2.93	3.13	3.13	4.50	7.37	7.45	7.52	7.79	8.40
5.7	2.92	3.11	3.02	4.43	7.36	7.40	7.50	7.76	8.40
6.3	2.92	3.10	3.00	4.41	7.36	7.39	7.49	7.75	8.39
7.0	2.90	3.10	2.98	4.38	7.35	7.38	7.48	7.74	8.38
8.2	2.88	3.05	2.88	4.26	7.26	7.34	7.44	7.69	8.34
9.3	2.86	3.01	2.81	4.16	7.19	7.31	7.41	7.64	8.29
10.6	2.82	2.91	2.79	-	7.02	7.29	7.37	7.59	8.18
11.6	2.80	2.87	2.79	4.08	6.91	7.28	7.36	7.57	8.13

NMR spectra of synthetic intermediates and of the final product

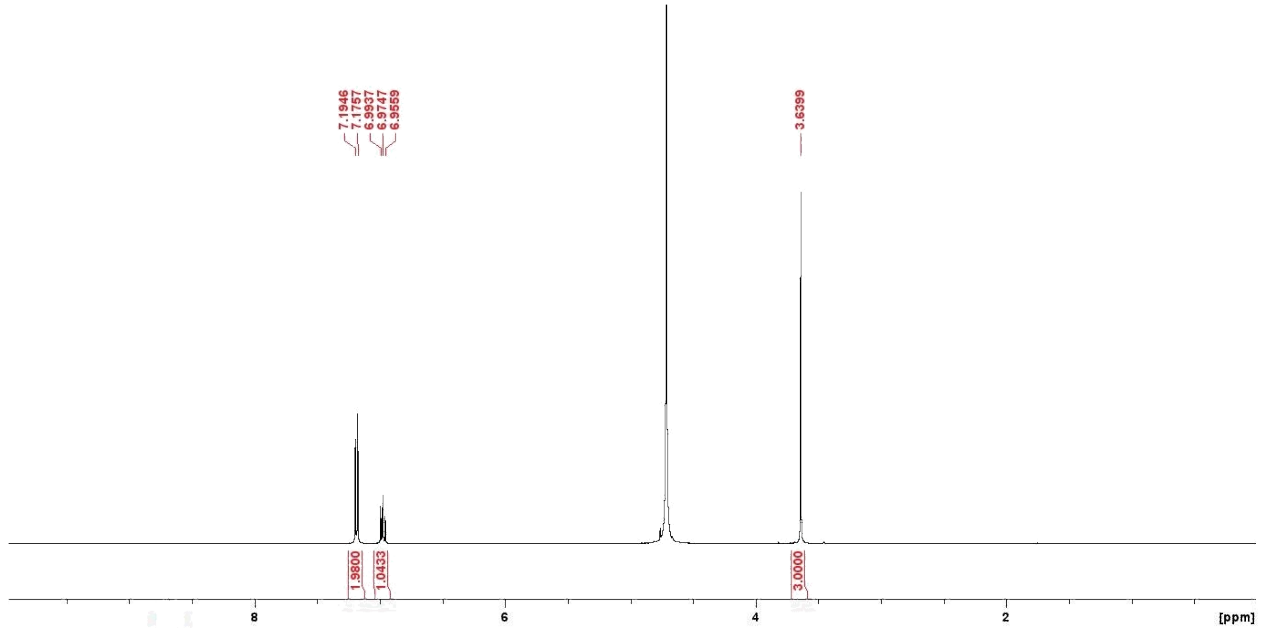

Figure S8. ^{1}H-NMR of 2-Methoxyisophtalic acid **(2)**, D_2O, 400 MHz.

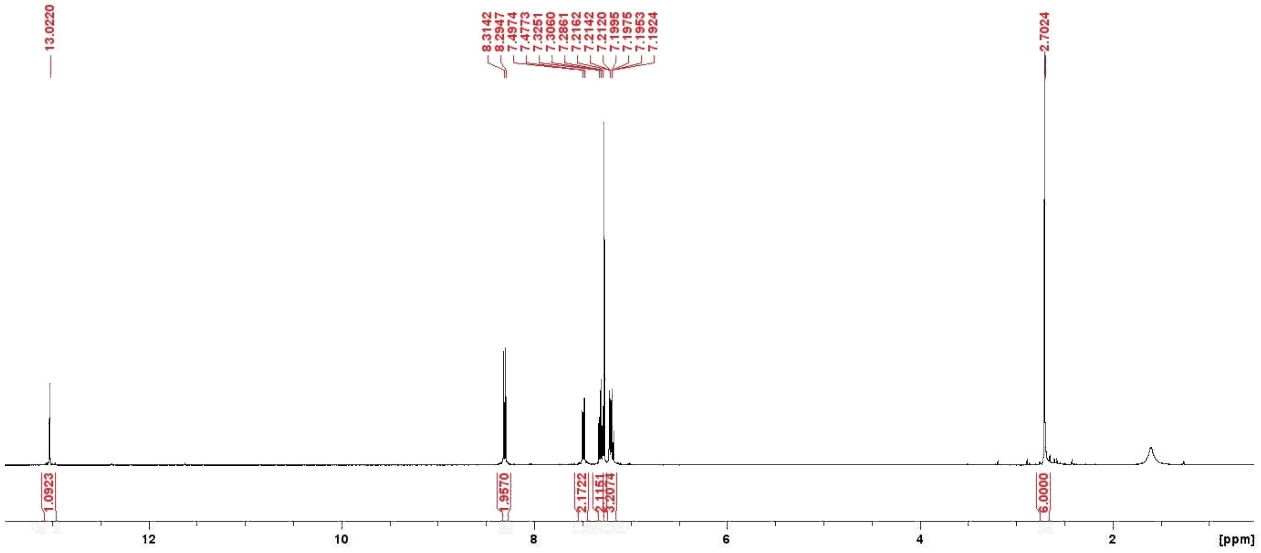

Figure S9. ^{1}H-NMR of 2,6-bis(4-methyl-2-ossazolyl)phenol **(4)**, $CDCl_3$, 400 MHz.

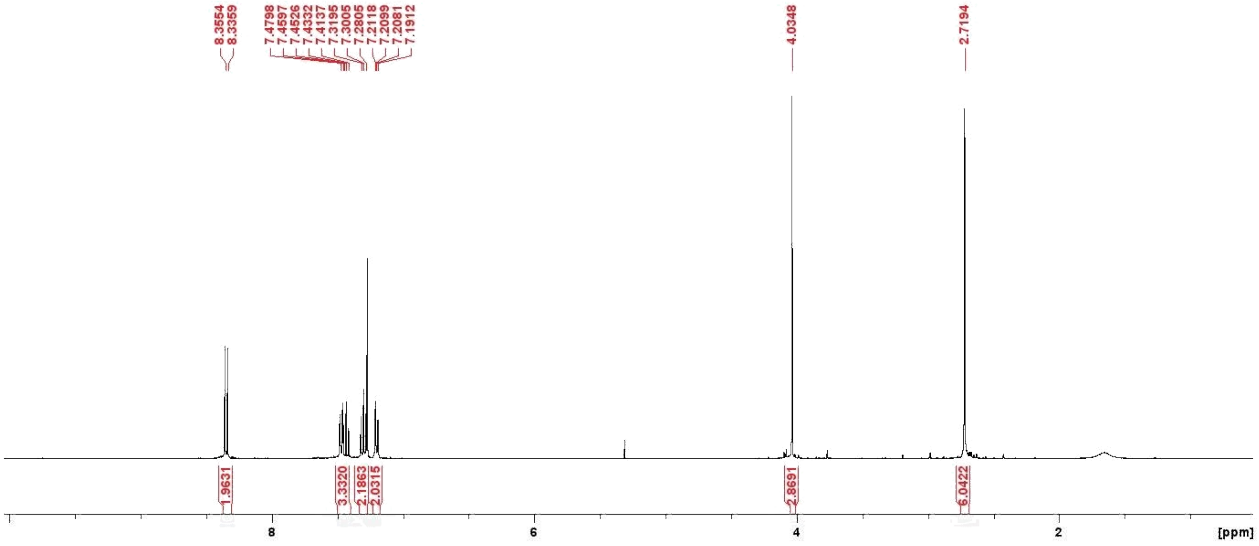

Figure S10. ^{1}H-NMR of 2,6-bis(4-methyl-2-ossazolyl)anisole **(5)**, $CDCl_3$, 400 MHz.

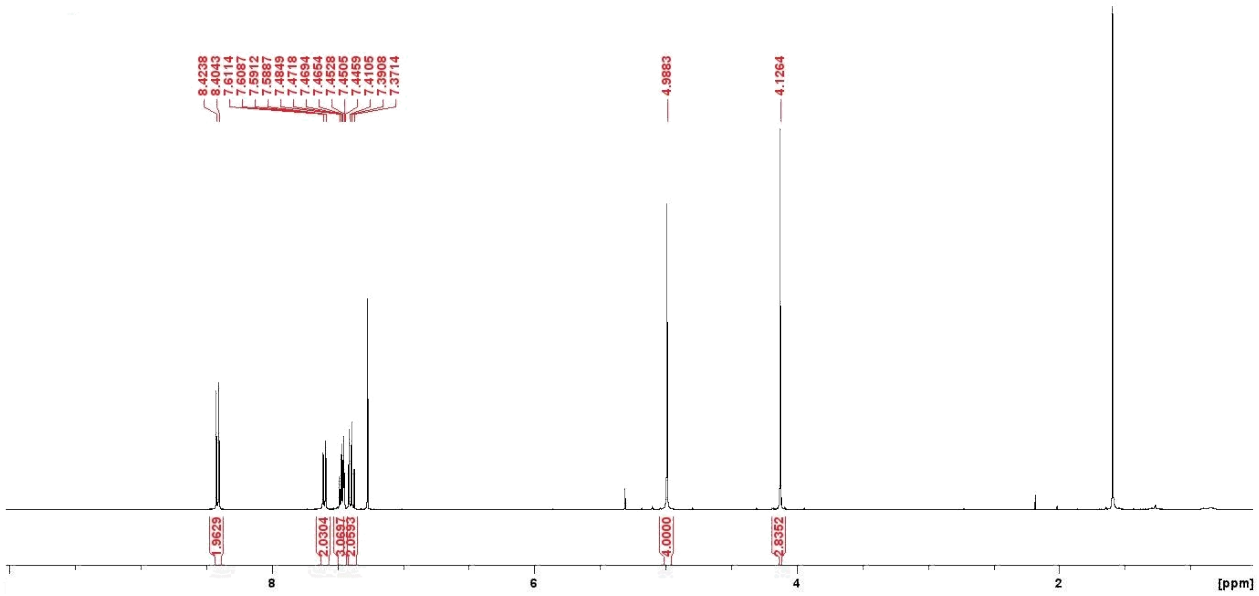

Figure S11. ^{1}H-NMR of 2,6-bis(4-bromomethyl-2-ossazolyl)anisole **(6)**, $CDCl_3$, 400 MHz.

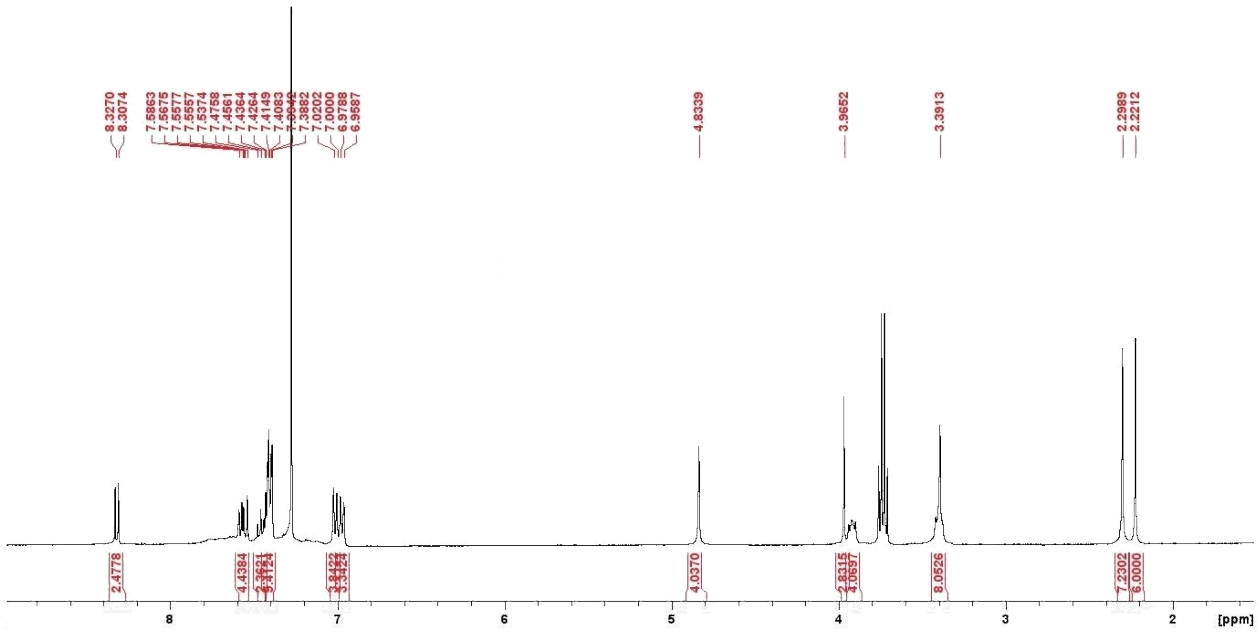

Figure S12. ^{1}H-NMR of 34-methoxy-11,14,17,20-tetratosylhexacyclo[28.3.1.1(2,5).1(26,29).0(9,4).0(22,27)]-35,36-dioxa-3,11,14,17,20,28-hexaaza-2,4,6,8,22,24,26,28,30,32,1(34)-tetratricontaendecaene **(8)**, $CDCl_3$, 400 MHz.

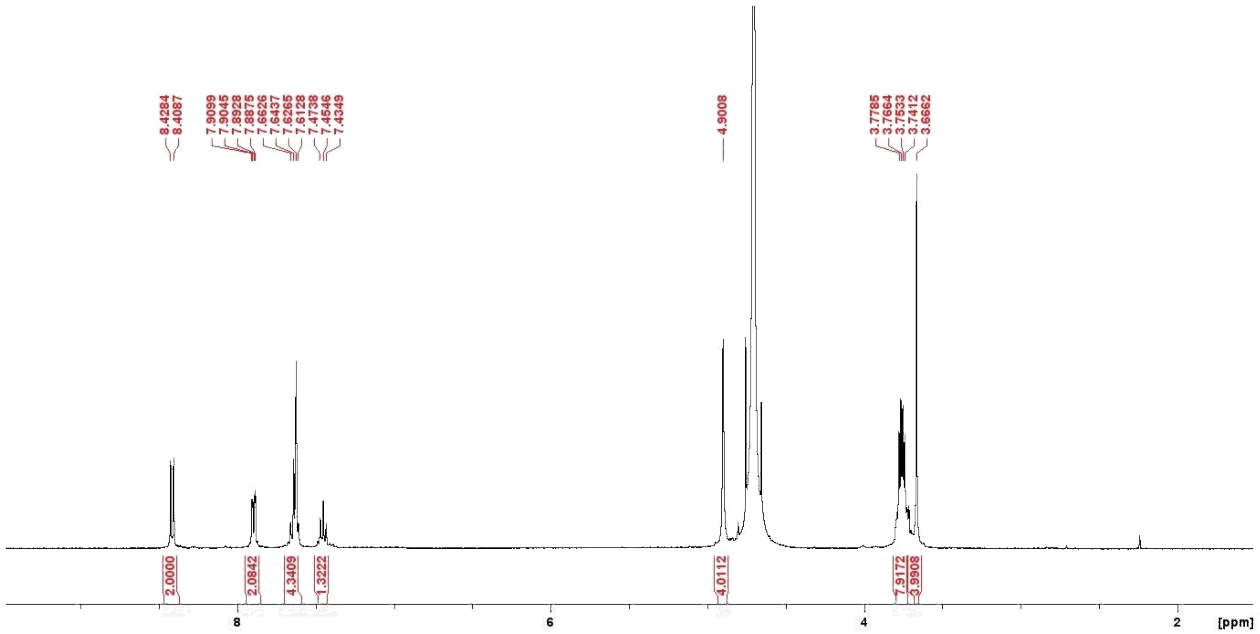

Figure S13. ^{1}H-NMR of hexacyclo[28.3.1.1(2,5).1(26,29).0(9,4).0(22,27)]-35,36-dioxa-3,11,14,17,20,28-hexaaza-2,4,6,8,22,24,26,28,30,32,1(34)-tetratricontaendecaen-34-ol tetraperchlorate **($L \cdot 4HClO_4$)**, D_2O, 400 MHz.

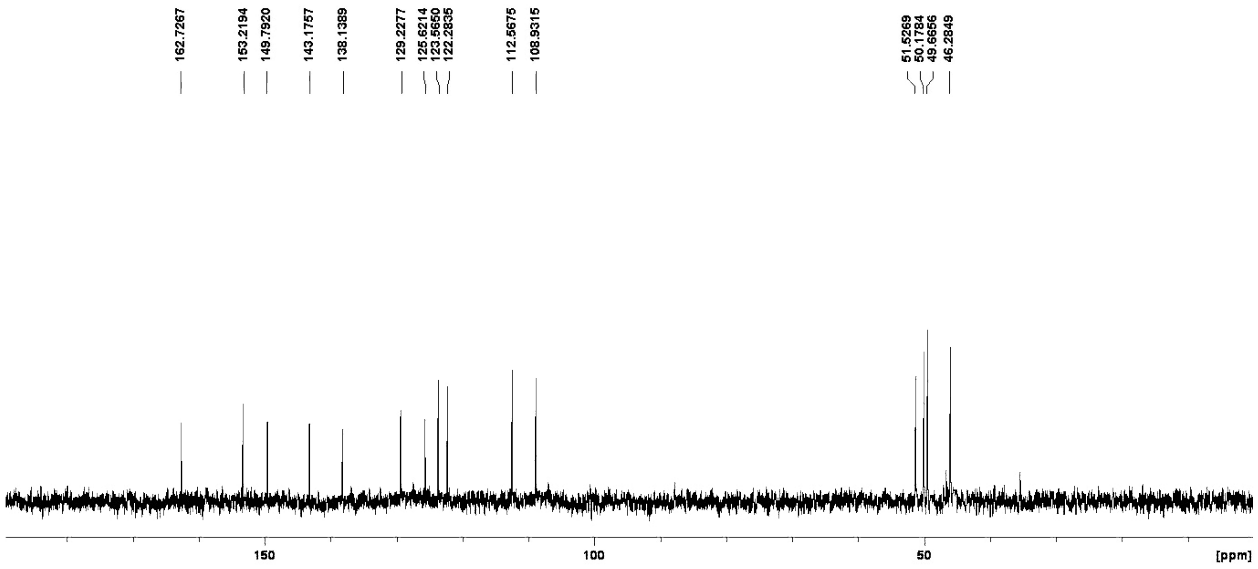

Figure S14. ^{13}C-NMR of hexacyclo[28.3.1.1(2,5).1(26,29).0(9,4).0(22,27)]-35,36-dioxa-3,11,14,17,20,28-hexaaza-2,4,6,8,22,24,26,28,30,32,1(34)-tetratricontaendecaen-34-ol tetraperchlorate **(L·4HClO$_4$)** D_2O, 100 MHz.