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Supporting Information

Lower Energy Excitation of Water Soluble Near-Infrared Emitting Mixed-Ligand Metallacrowns

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Experimental Details

Measurements of absolute quantum yields

Quantum yields were determined with a Fluorolog 3 spectrofluorimeter based on the modified de Mello et al. method[1] using an integration sphere (GMP SA). More specifically, the following parameters were acquired: (1) L_a, the integrated intensity of light exiting the sphere when the empty capillary is illuminated at the excitation wavelength (Rayleigh scattering band); (2) L_c, the same integrated intensity at the excitation wavelength when the sample is introduced into the sphere; these two measurements often involve the use of attenuators (transmission 0.01–10 %); (3) E_c, the integrated intensity of the emission spectrum.[2] The absolute quantum yield (Q_{Ln}^L) was then calculated by the following equation:

$$Q_{Ln}^L = \frac{E_c}{[L_a(\lambda_{exc}) - L_c(\lambda_{exc})]F_{att}(\lambda_{exc})}$$

whereby $F_{att}(\lambda_{exc})$ is the correction for the attenuators used. To ensure careful correction the instrument was regularly calibrated using quartz tungsten halogen lamp. Each sample was measured several times varying the position of samples. Estimated experimental error for the determination of quantum yields is ~10%.

Susceptibility testing and determination of the minimum inhibitory concentration (MIC)

The NCCLS broth macrodilution method, as outlined in the M27-A document,[3] was used for susceptibility tests of $Zn_{16}Yb(pyzHA)_{16}$ against *C. albicans*. *C. albicans* isolates were stored at -70°C in Sabouraud dextrose broth with glycerol. Each isolate was retrieved from storage and plated twice in succession on Sabouraud dextrose agar before testing. Prior to testing, each isolate was grown on Sabouraud agar (Becton Dickinson, BBL) for 24 h at 35°C. Suspensions were prepared in 0.85% saline to achieve a 0.5 McFarland standard. Two control strains, *C. albicans* ATCC 22019, were tested on each day that susceptibility tests were performed. Stock solutions of fluconazole and voriconazole were serially diluted with RPMI-1640 buffered with 0.164 M morpholinepropanesulfonic acid (MOPS) buffer (Sigma, St. Louis, Mo.), to concentrations ranging from 0.125 µg/mL to 128 µg/mL. Caspofungin, micafungin and anidulafungin were diluted to concentrations between 0.0078 µg/mL and 16 µg/mL. Concentrations were 0.06-64 µg/mL for fluconazole, and 0.008-8 µg/mL for voriconazole. Reagent-grade voriconazole, anidulafungin, and fluconazole powders were obtained from Pfizer, caspofungin was obtained from Merck & Co, and micafungin from Astellas. The stock solution of voriconazole was made by dissolving the powder in dimethyl sulfoxide (DMSO); fluconazole was dissolved in sterile distilled water. All stock solutions were stored at -70°C. The solutions were thawed and diluted to the proper concentrations in RPMI 1640.
Minimum inhibitory concentrations (MICs) of the $Zn_{16}Yb(pyzHA)_{16}$ MC and controls against *E. coli* and *S. aureus* were determined by the broth macrodilution method in accordance with the Clinical and Laboratory Standards Institute (CLSI) M07-A10.[4] Control strains included a methicillin-resistant strain of *Staphylococcus aureus* ATCC BAA 1026 and *Escherichia coli* ATCC 25922.

Note about the characterization of $[Zn_{16}Ln(pyzHA)_x(quinoHA)_{16-x}(py)_8](OTf)_3$ ($Zn_{16}Ln(pyzHA)_x(quinoHA)_{16-x}$)

Elemental analyses and ^1H NMR data for the pure $LnZn_{16}(pyzHA)_{16}$ and $LnZn_{16}(quinoHA)_{16}$ can be found in Refs.[5, 6] Mixed-ligand MCs possess a general formula $LnZn_{16}(pyzHA)_x(quinoHA)_{16-x}$, where x range from 15 to 7 and depends on the nature of the Ln(III) ion used.

Calculations of the polydispersity index (PDI) (from mass-spectral distribution)

$[NdZn_{16}(pyzHA)_x(quinoHA)_{16-x}(py)_8](OTf)_3$: x_{av} = 10.6, Mw_{av} = 4734 g/mol

pyzHA:quinoHA	Intensity	Distribution, %	Mw [g/mol]	$N_iM_i^2$	N_iM_i	N_i
14:2	2	0.7	4564.03	14365772.3	3147.6	0.7
13:3	8	2.8	4614.09	58730555.9	12728.5	2.8
12:4	48	16.6	4664.15	360071093.3	77199.7	16.6
11:5	100	34.5	4714.21	766337100.8	162559.0	34.5
10:6	90	31.0	4764.27	704429026.5	147856.7	31.0
9:7	35	12.1	4814.33	279731747.3	58104.0	12.1
8:8	5	1.7	4864.39	40797051.8	8386.9	1.7
7:9	2	0.7	4914.45	16656426.8	3389.3	0.7
Total		**100.0**		**2241118774.9**	**473371.6**	**100.0**
PDI	**1.00**					

$[ErZn_{16}(pyzHA)_x(quinoHA)_{16-x}(py)_8](OTf)_3$, x_{av} = 12.5, Mw_{av} = 4664 g/mol

pyzHA:quinoHA	Intensity	Distribution, %	Mw [g/mol]	$N_iM_i^2$	N_iM_i	N_i
15:1	10	3.1	4536.99	63926330.0	14090	3.1
14:2	52	16.1	4587.05	339792994.0	74077	16.1
13:3	100	31.1	4637.11	667788483.0	144010	31.1
12:4	95	29.5	4687.17	648170325.4	138286	29.5
11:5	50	15.5	4737.23	348468137.8	73559	15.5
10:6	13	4.0	4787.29	92526674.6	19328	4.0
9:7	2	0.6	4837.35	14534133.6	3005	0.6
Total		**100.0**		**2175207078.2**	**466353.9**	**100.0**
PDI	**1.00**					

$[YbZn_{16}(pyzHA)_x(quinoHA)_{16-x}(py)_8](OTf)_3$, x_{av} = 12.2, Mw_{av} = 4681 g/mol

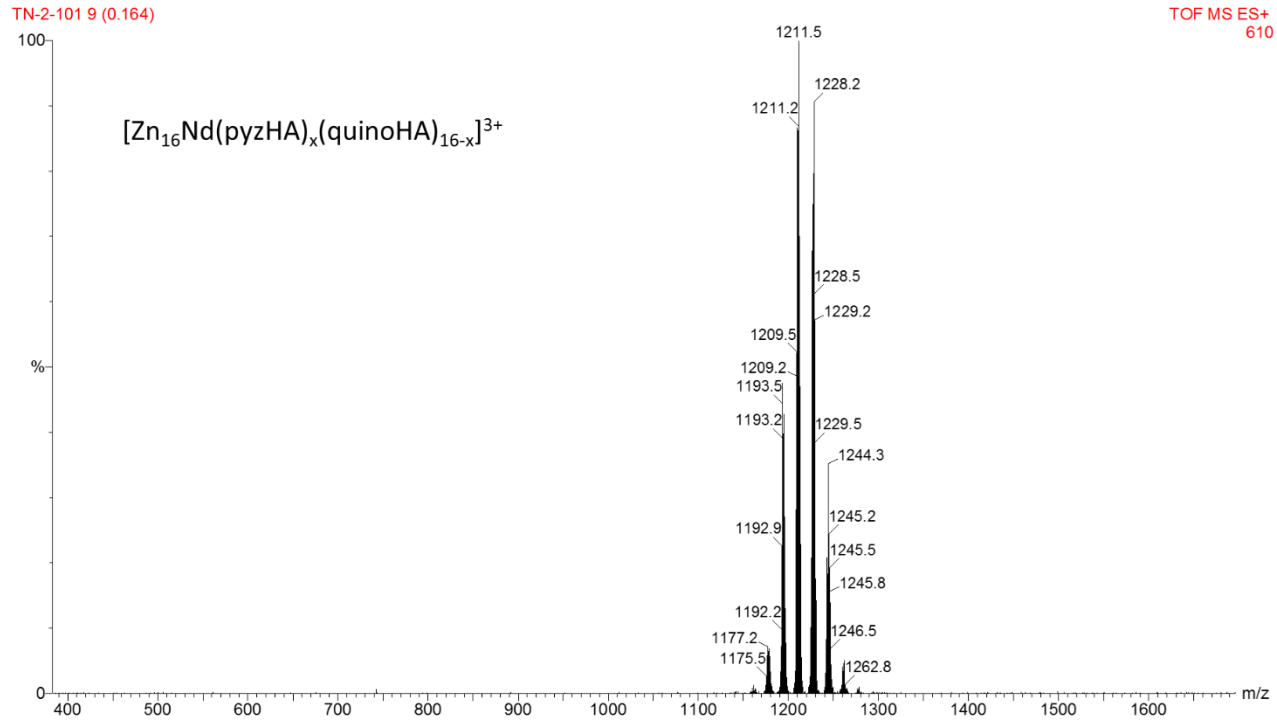
pyzHA:quinoHA	Intensity	Distribution, %	Mw [g/mol]	$N_iM_i^2$	N_iM_i	N_i
15:1	8	2.4	4542.78	49578018.3	10913.6	2.4
14:2	45	13.5	4592.84	285056476.6	62065.4	13.5
13:3	93	27.9	4642.90	602028948.4	129666.6	27.9
12:4	100	30.0	4692.96	661377584.4	140929.7	30.0
11:5	60	18.0	4743.02	405337634.6	85459.8	18.0
10:6	20	6.0	4793.08	137979675.0	28787.3	6.0
9:7	5	1.5	4843.14	35219226.8	7272.0	1.5
8:8	2	0.6	4893.20	14380424.2	2938.9	0.6
Total		**100.0**		**2190957988.3**	**468033.2**	**100.0**
PDI	**1.00**					

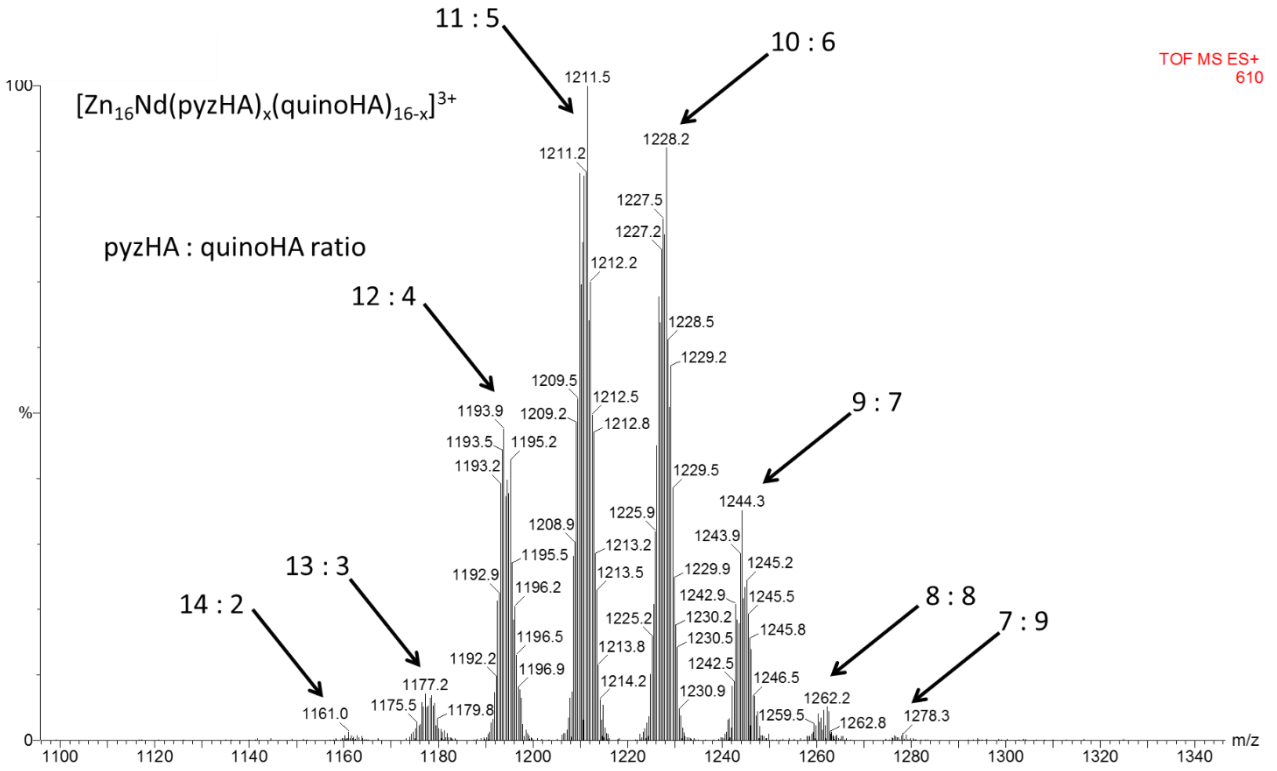
Analysis of absorption spectra

The average composition of the $LnZn_{16}(pyzHA)_x(quinoHA)_{16-x}$ was also estimated by deconvoluting the absorption spectra (Figure 2) since we know the extinction coefficients for the pure $LnZn_{16}(pyzHA)_{16}$ and $LnZn_{16}(quinoHA)_{16}$ MCs. Based on this analysis we obtain the following values:
$[NdZn_{16}(pyzHA)_x(quinoHA)_{16-x}(py)_8](OTf)_3$: Mw_{av} = 4827 g/mol, x_{av} = 8.75;
$[YbZn_{16}(pyzHA)_x(quinoHA)_{16-x}(py)_8](OTf)_3$: Mw_{av} = 4768 g/mol, x_{av} = 10.5.

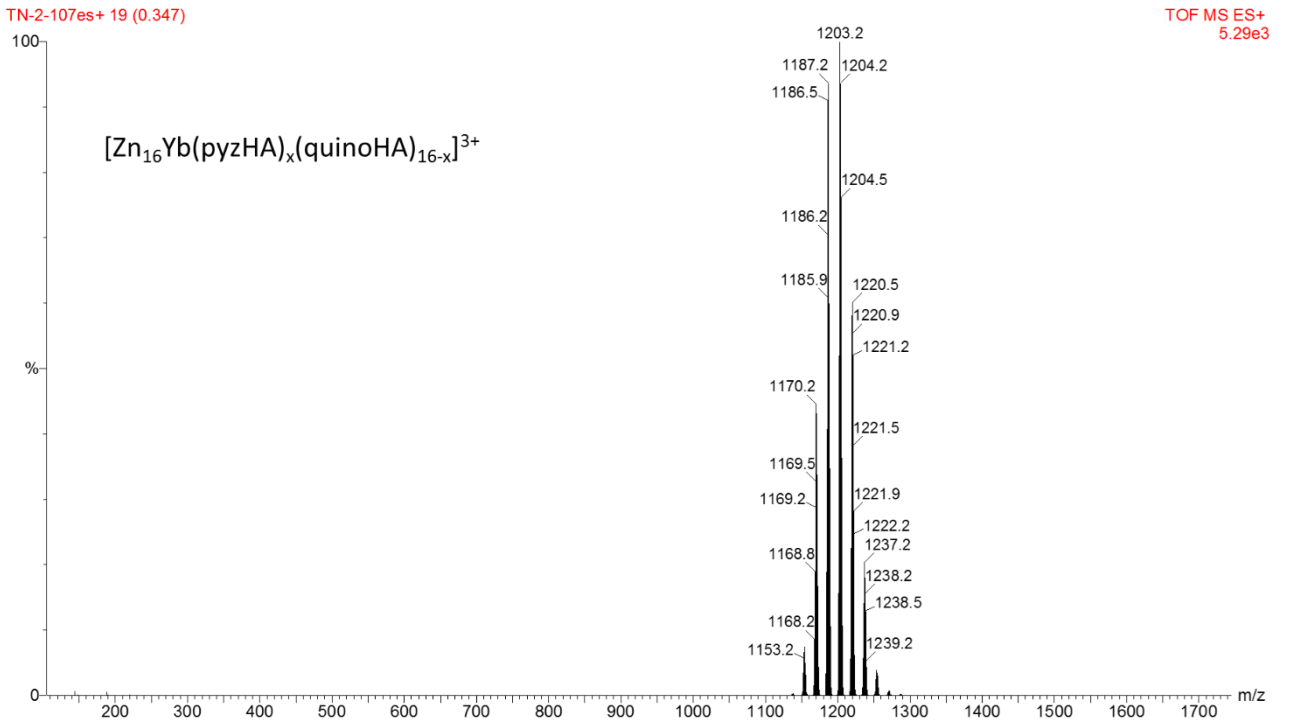
While the values of x_{av} estimated from mass-spectral distribution and absorption spectra are not exactly equivalent, they show the relative enrichment of pyzHA in the Yb(III) MC compared to the Nd(III) analogue. Furthermore, the differences between the values of MW_{av} are <100 (~2%) for both samples: 4734 vs. 4827 g/mol for $NdZn_{16}(pyzHA)_x(quinoHA)_{16-x}$ and 4681 vs. 4768 g/mol for $YbZn_{16}(pyzHA)_x(quinoHA)_{16-x}$. All these observations point to samples with narrow molecular species distribution and high reproducibility.

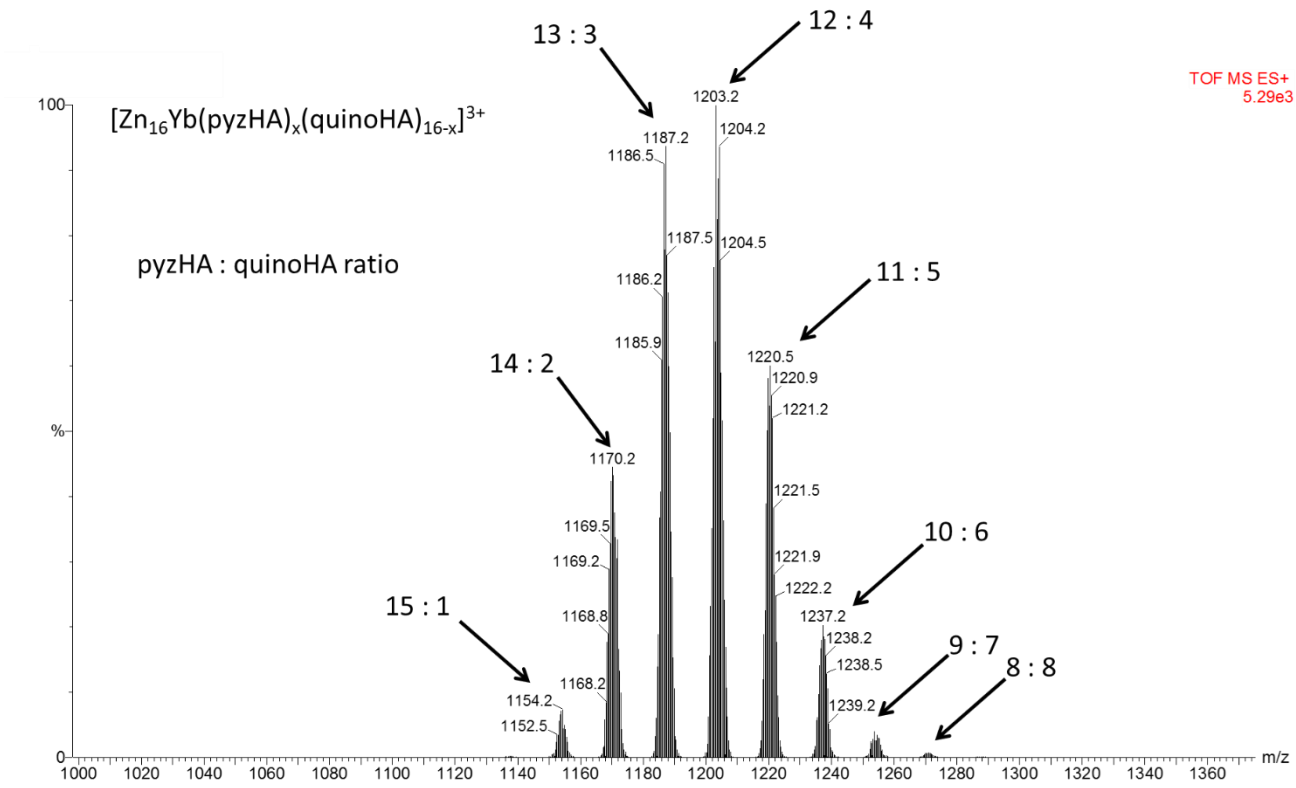
Mass spectra $Zn_{16}Ln(pyzHA)_x(quinoHA)_{16-x}$



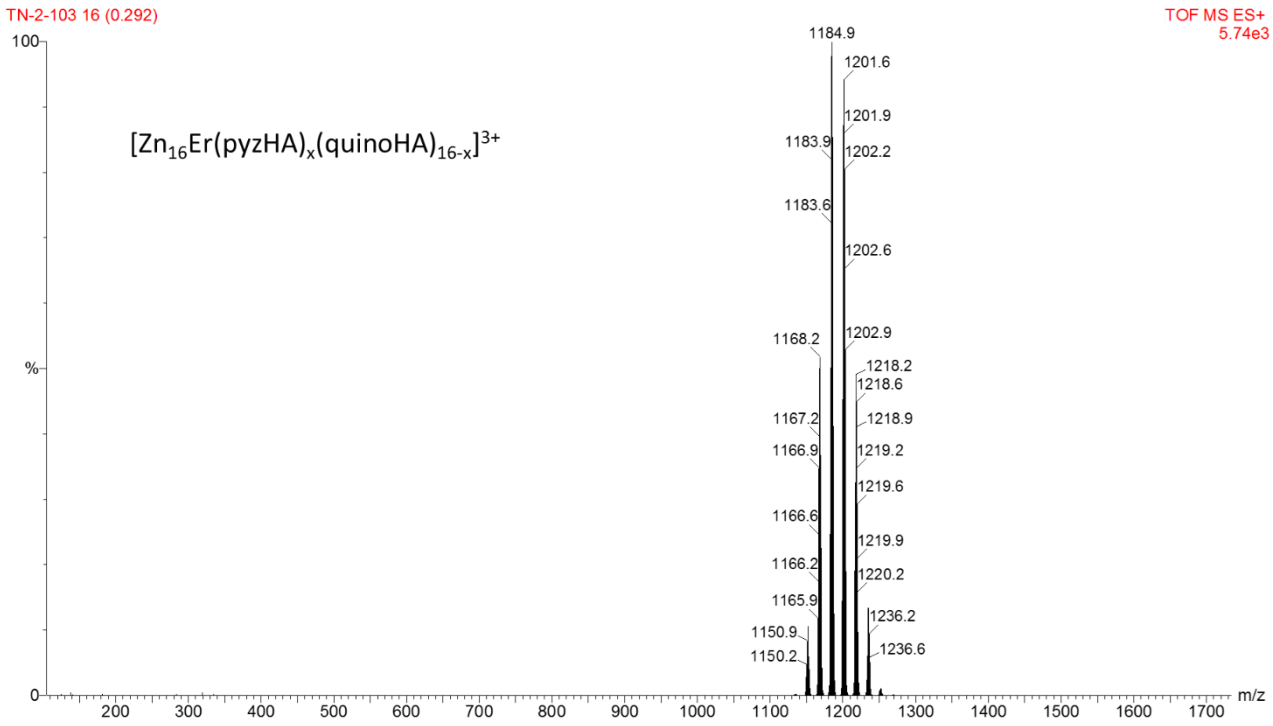


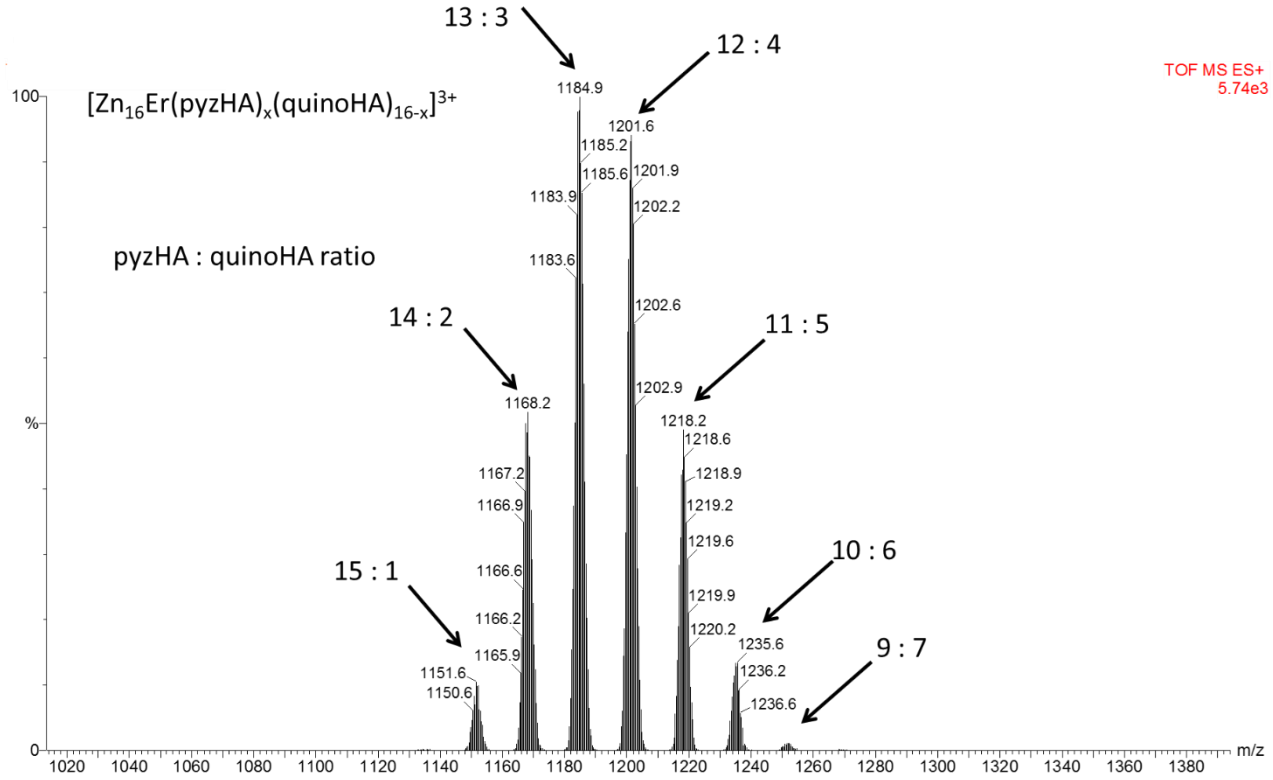
$Zn_{16}Nd(pyzHA)_x(quinoHA)_{16-x}$								
x: (16-*x*)	14:2	13:3	12:4	11:5	10:6	9:7	8:8	7:9
m/z (Cald.)	1161.34	1178.02	1194.73	1211.40	1228.08	1244.77	1261.46	1278.14





$Zn_{16}Yb(pyzHA)_x(quinoHA)_{16-x}$								
x: (16-*x*)	15:1	14:2	13:3	12:4	11:5	10:6	9:7	8:8
m/z (Cald.)	1154.25	1170.94	1187.63	1204.31	1221.00	1237.69	1254.37	1271.06

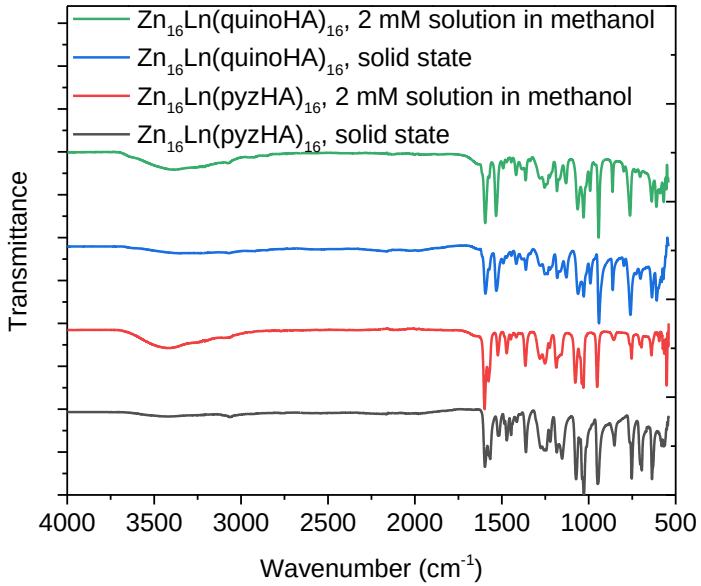


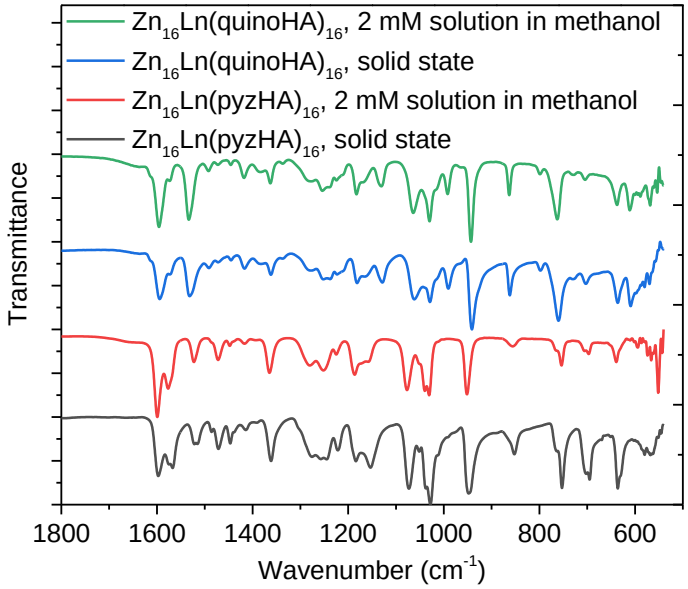


$Zn_{16}Er(pyzHA)_x(quinoHA)_{16-x}$							
x: (16-*x*)	15:1	14:2	13:3	12:4	11:5	10:6	9:7
m/z (Cald.)	1152.32	1169.01	1185.70	1202.38	1219.07	1235.76	1252.44

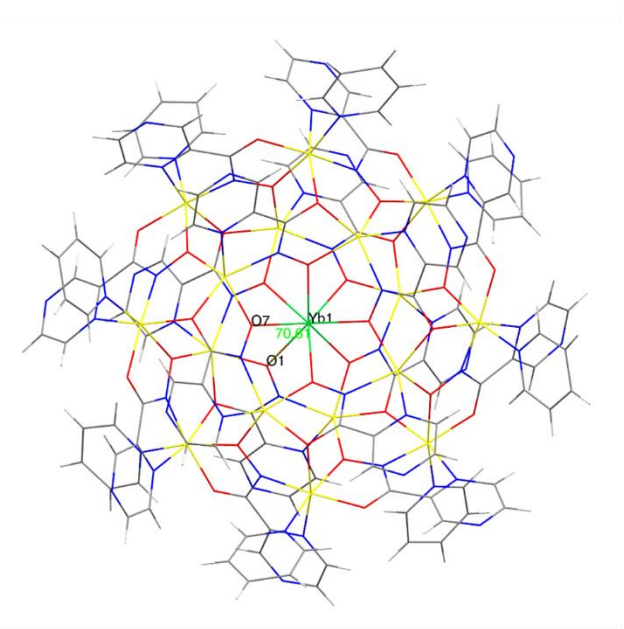
Infrared (IR) spectra of $Zn_{16}Ln(pyzHA)_{16}$ and $Zn_{16}Ln(quinoHA)_{16}$

IR spectra were recorded in the range 500–4000 cm^{-1} on a Thermo-Nicolet IS-50 FT-IR spectrometer in ATR mode for $Zn_{16}Ln(pyzHA)_{16}$ and $Zn_{16}Ln(quinoHA)_{16}$ MCs in the solid state and in 2 mM solutions in methanol. The IR spectra of MCs in solution were corrected for the transmittance of methanol.
The similarity of the IR spectra recorded in the solid state and in solution of MCs confirms stability of the $Zn_{16}Ln(HA)_{16}$ series of compounds in methanol.



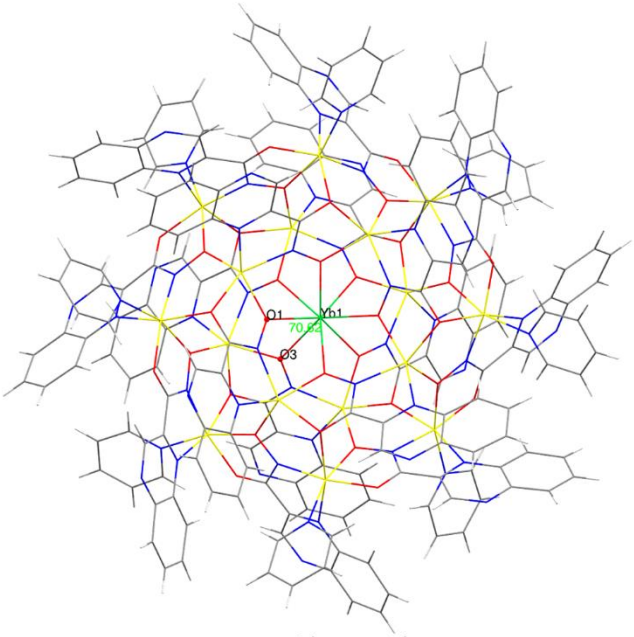


Comparison of $Zn_{16}Ln(pyzHA)_{16}$ and $Zn_{16}Ln(quinoHA)_{16}$ crystal structures (Ln = Yb, Nd)



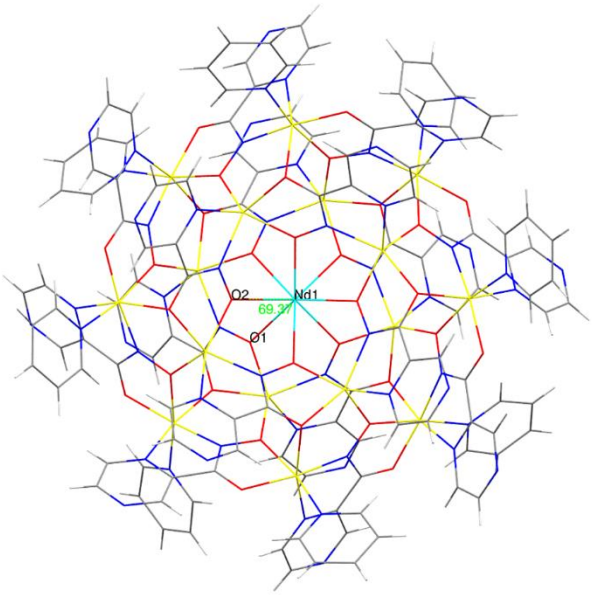
$Zn_{16}Yb(pyzHA)_{16}$

O1-Yb-O7 angle: 70.61°



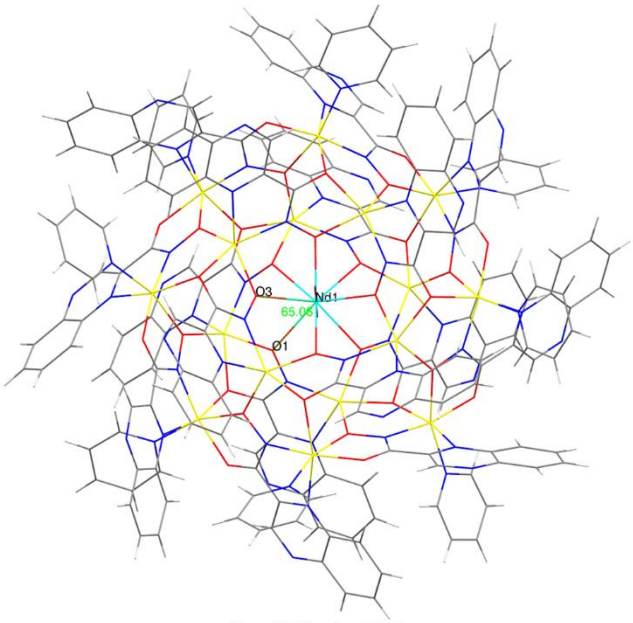
$Zn_{16}Yb(quinoHA)_{16}$

O1-Yb-O3 angle: 70.62°



$Zn_{16}Nd(pyzHA)_{16}$

O1-Nd-O2 angle: 69.37°



$Zn_{16}Nd(quinoHA)_{16}$

O1-Nd-O3 angle: 65.06°

References

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[5] I. Martinić, S. V. Eliseeva, T. N. Nguyen, V. L. Pecoraro, S. Petoud, *J. Am. Chem. Soc.* **2017**, *139*, 8388-8391.

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Author Contributions

T.N.N.: Conceptualization, Synthesis and characterization, Data curation, Writing – review, editing; S.V.E.: Conceptualization, Photophysical data acquisition and analysis, Data curation, Writing – original draft, editing, Funding acquisition; I.M.: Biological experiments and optical imaging; P.L.C.: Supervision, Writing – review, editing; T.L.: IR data collection and analysis of mass-spectral distributions; S.P.: Conceptualization, Funding acquisition, Writing – review, editing; V.L.P.: Conceptualization, Supervision, Funding acquisition, Writing – review, editing.