Tuning the Photophysical Properties of Lanthanide(III)/Zinc(II) 'Encapsulated Sandwich' Metallacrowns Emitting in the Near-Infrared Range†

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Table of content

NMR spectra

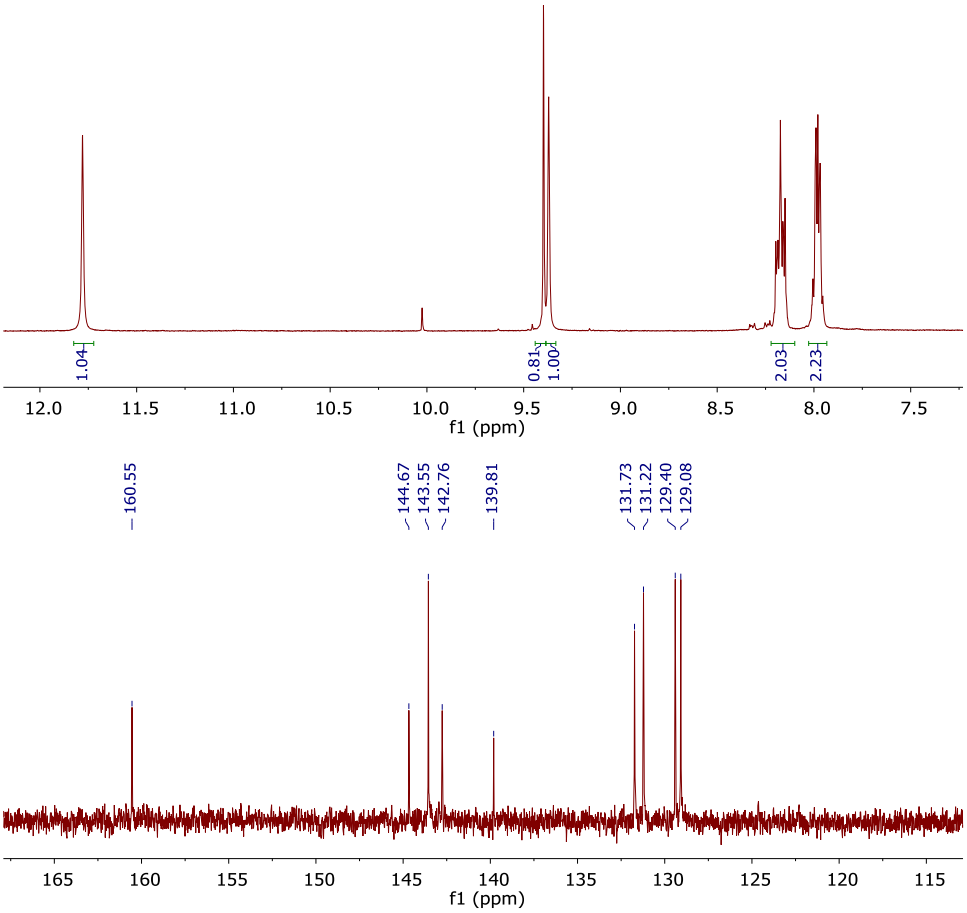


Figure S1. ^{1}H- and ^{13}C NMR spectra of H_2quinoHA collected in DMSO-d_6.

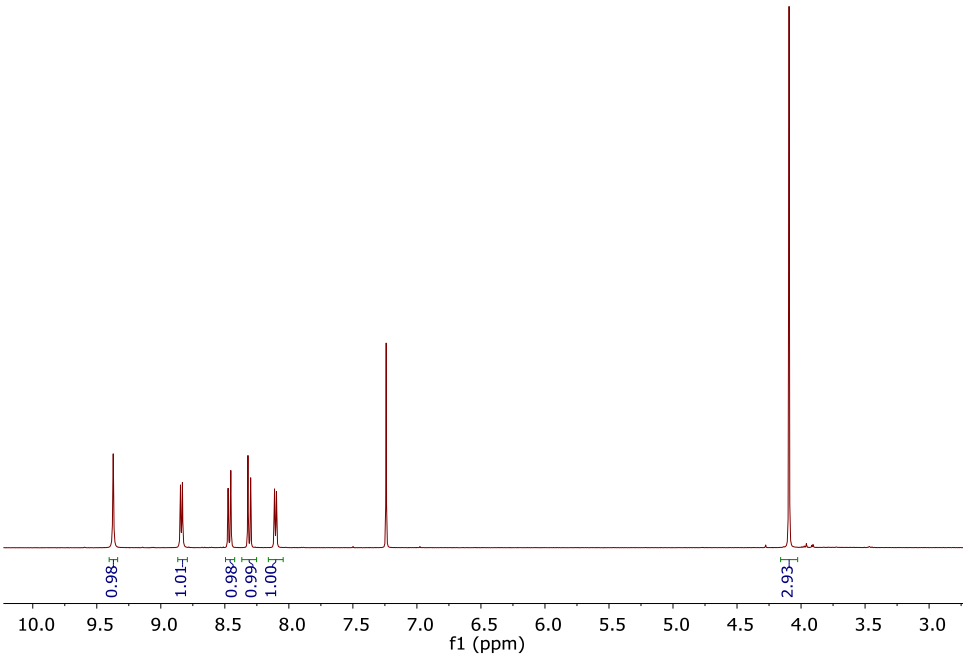


Figure S2. ^{1}HNMR spectrum of methyl naphthyridine-2-carboxylate collected in $CDCl_3$.

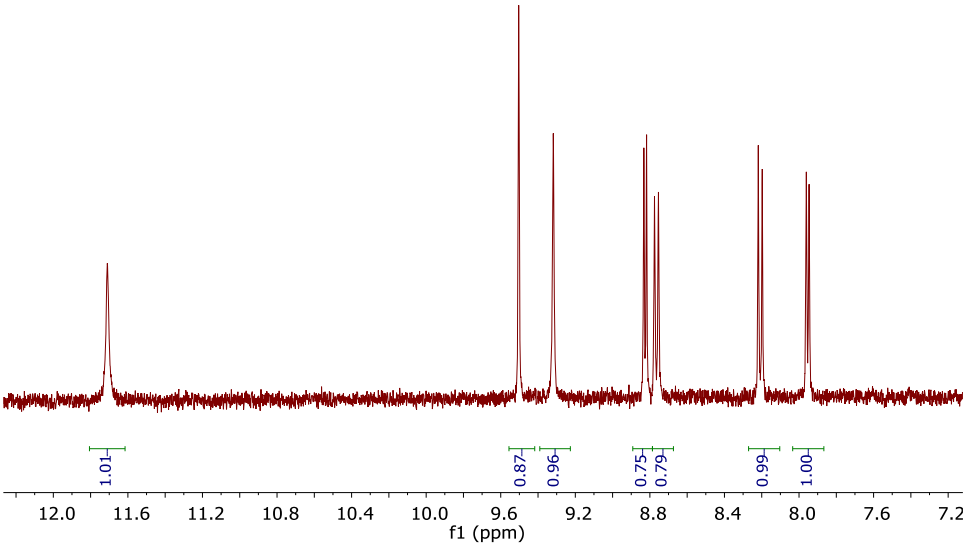


Figure S3. ^{1}HNMR spectrum of H_2napHA collected in DMSO-d_6.

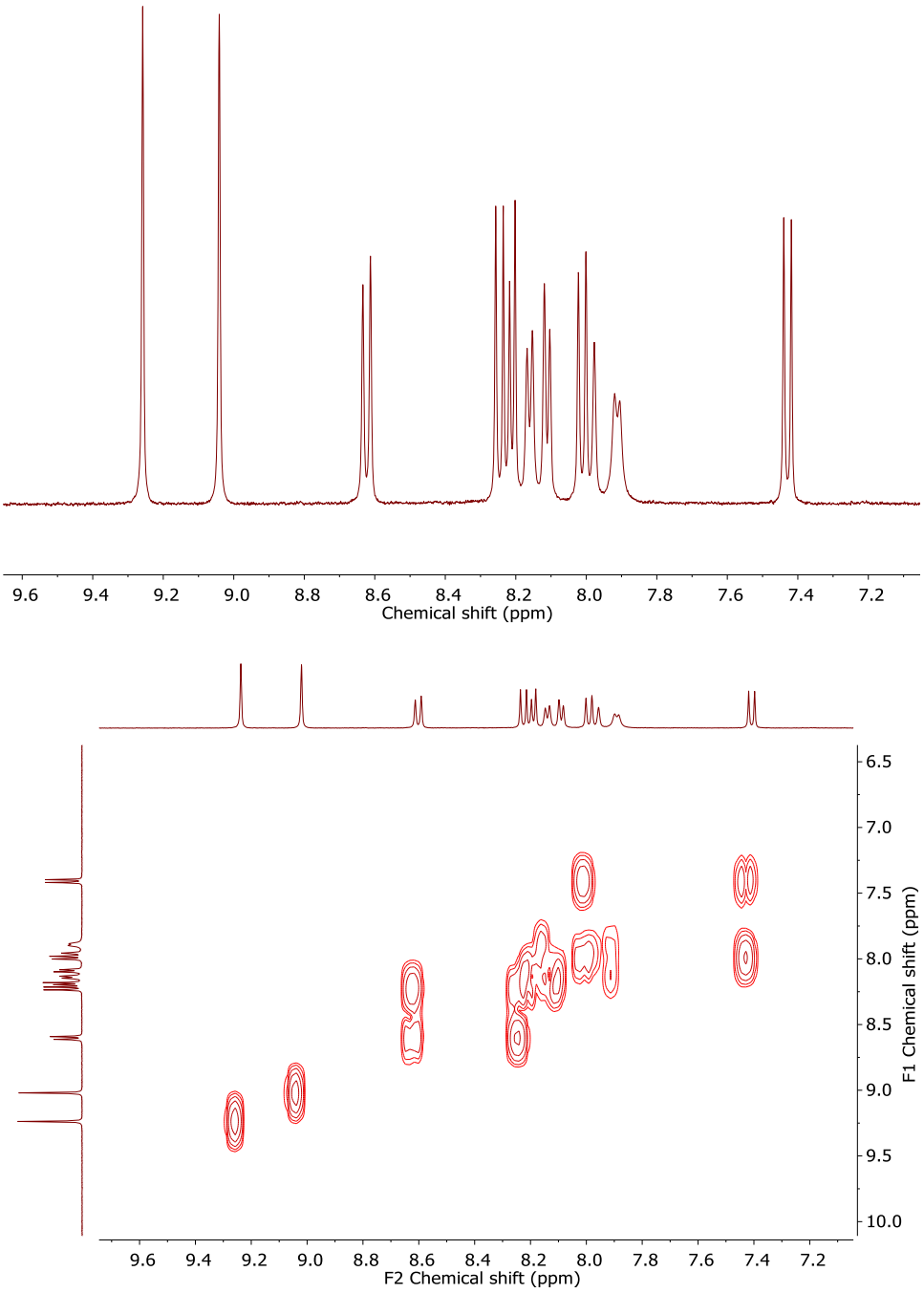
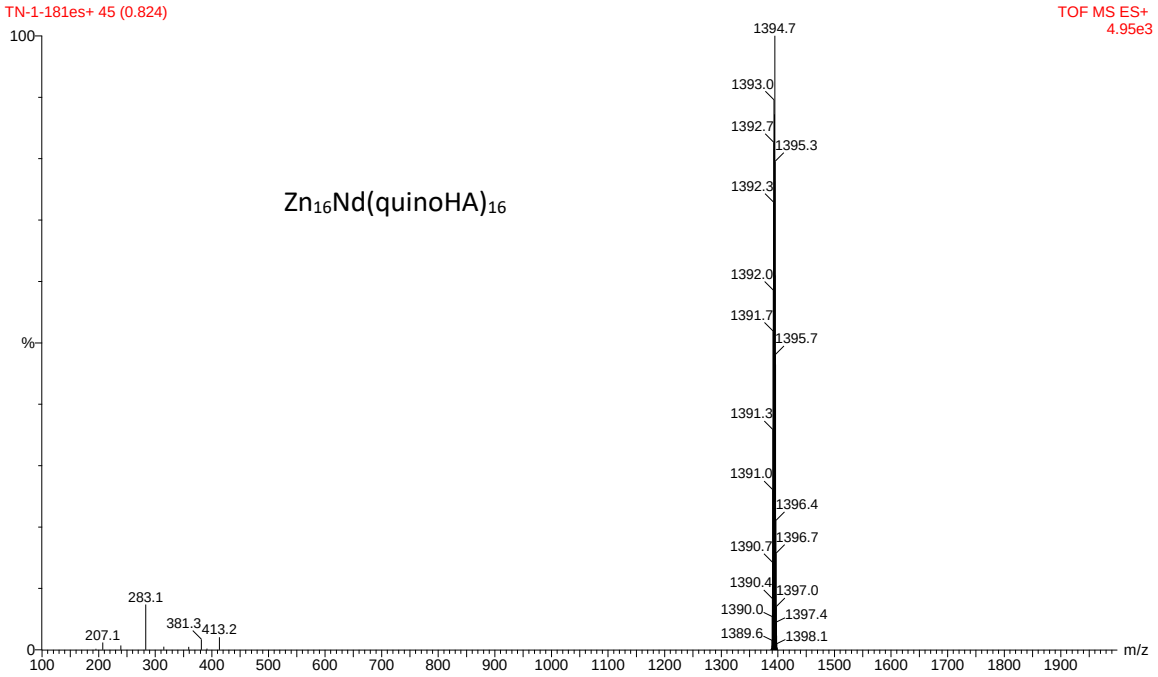
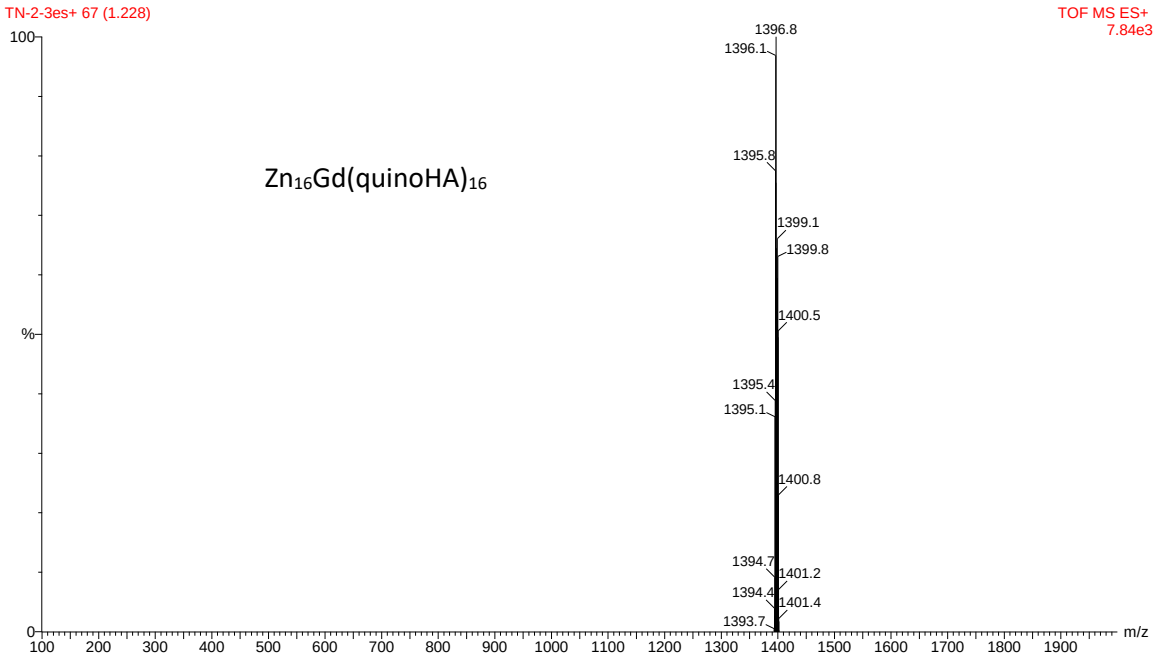
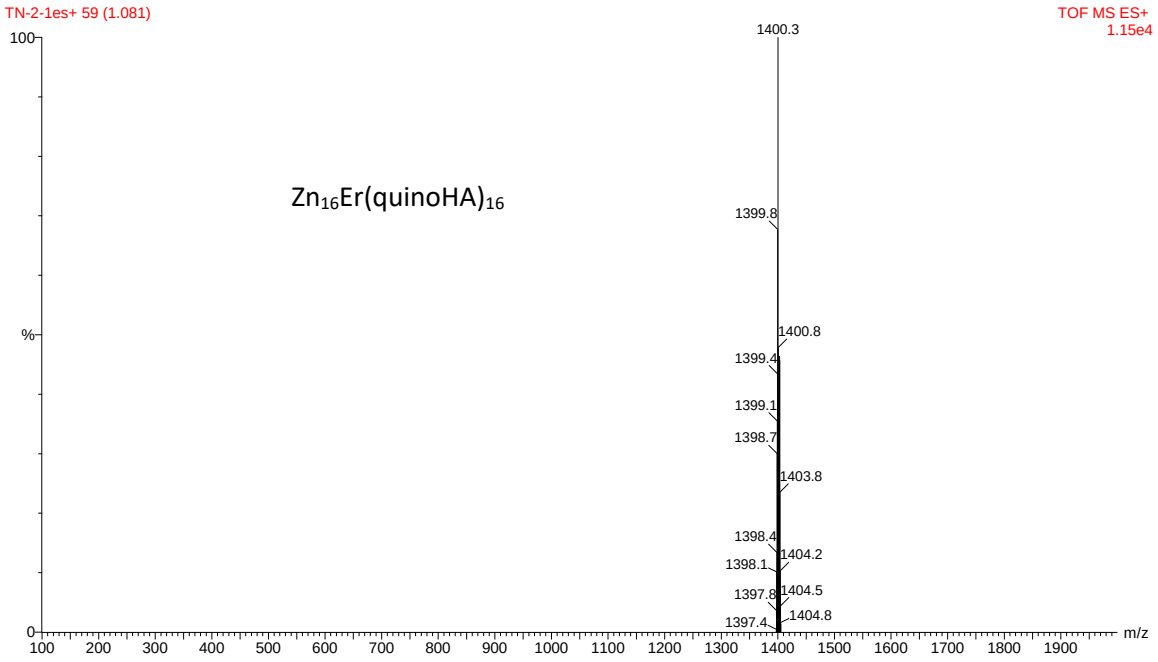


Figure S4. ^{1}H- and COSY-NMR spectra of $Zn_{16}Y(napHA)_{16}$ collected in CD_3OD.

Mass spectra



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%
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1399.8
1400.8
1399.4
1399.1
1398.7
1403.8
1398.4
1404.2
1398.1
1404.5
1397.8
1404.8
1397.4
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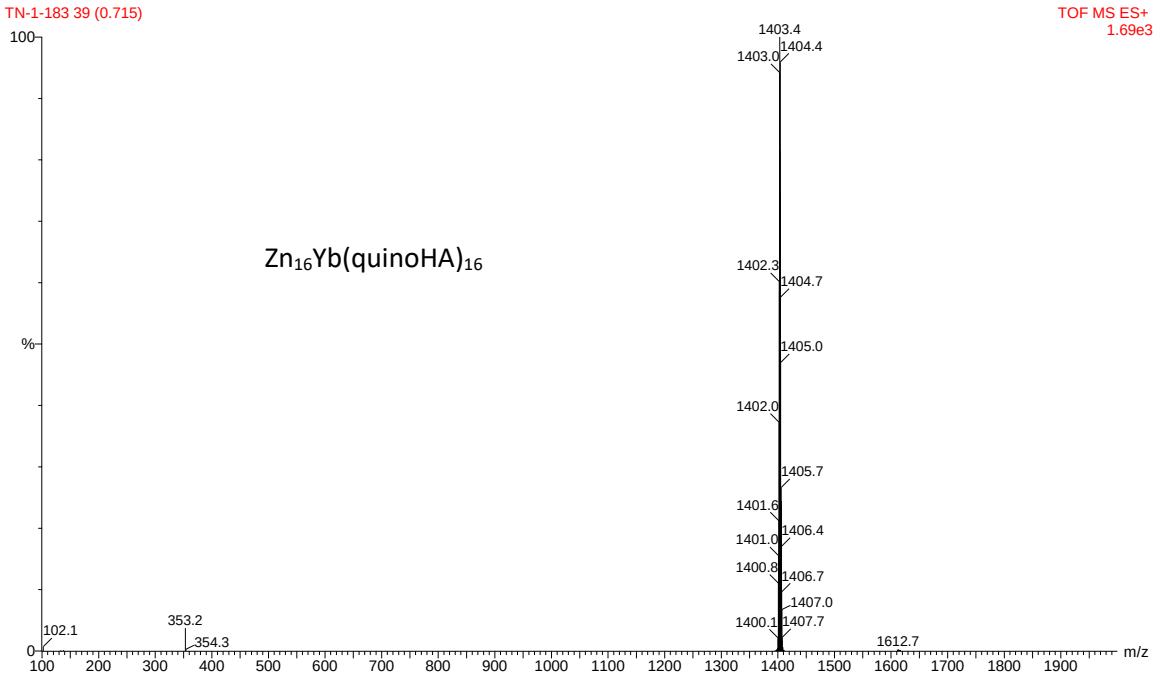
m/z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%
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1404.4
1403.0
1402.3
1404.7
1405.0
1402.0
1405.7
1401.6
1406.4
1401.0
1400.8
1406.7
1407.0
1400.1
1407.7
102.1
353.2
354.3
1612.7
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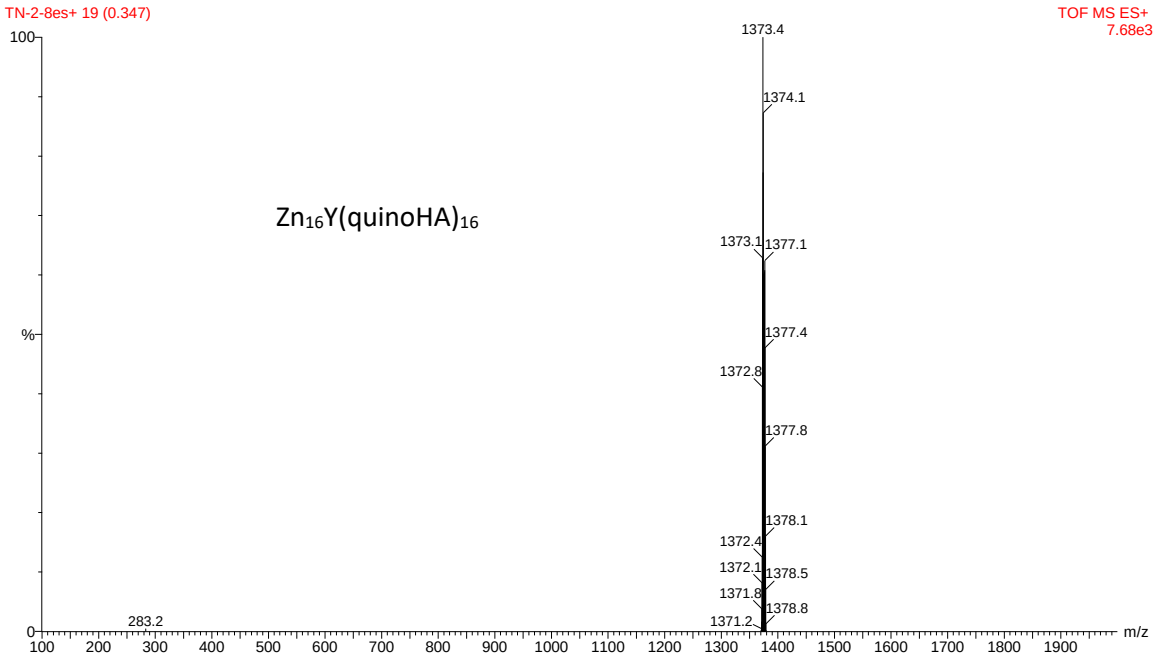
m/z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%
0
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1374.1
1373.1
1377.1
1377.4
1372.8
1377.8
1378.1
1372.4
1372.1
1378.5
1371.8
1378.8
1371.2
283.2
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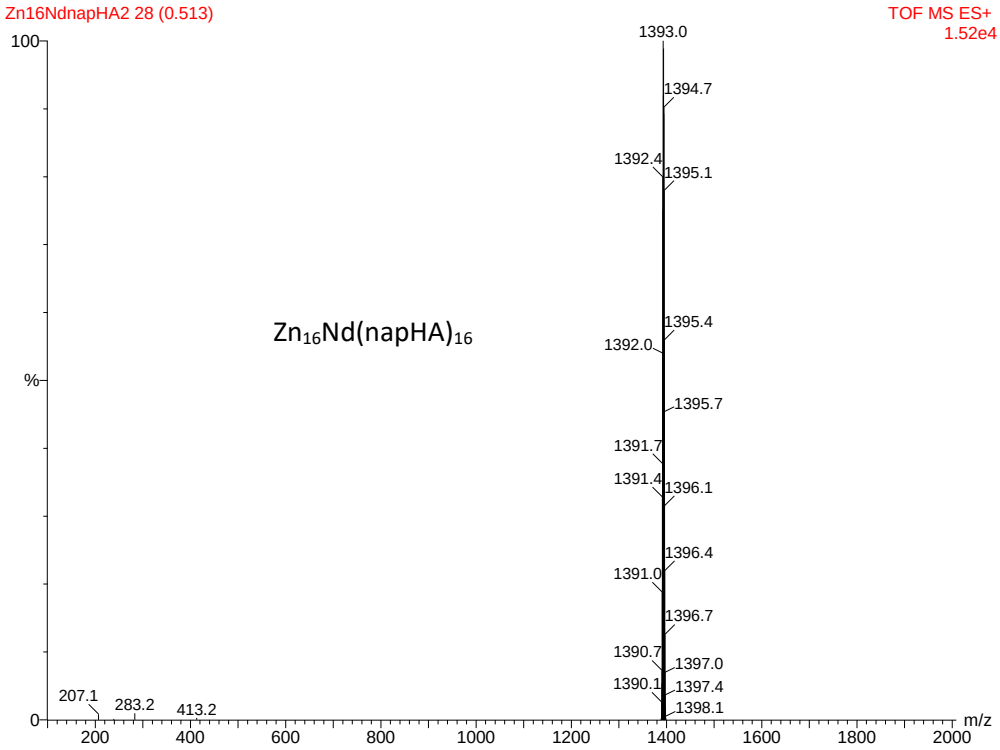
m/z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1.52e4
100
%
0
$Zn_{16}Nd(napHA)_{16}$
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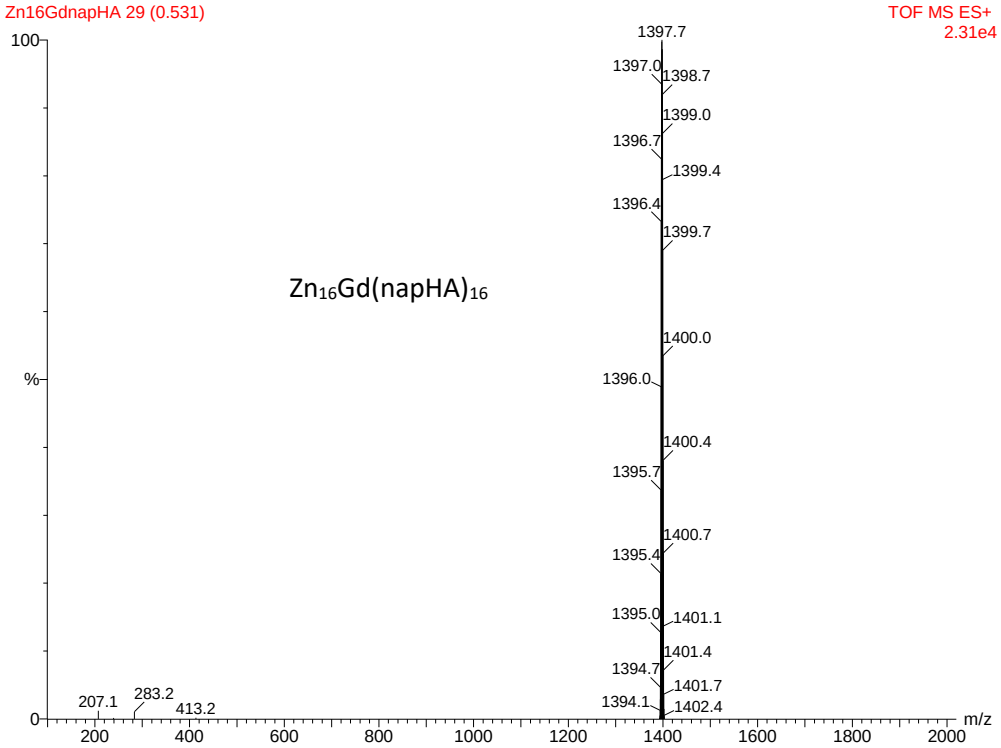
1394.7
1392.4
1395.1
1395.4
1392.0
1395.7
1391.7
1391.4
1396.1
1396.4
1391.0
1396.7
1390.7
1397.0
1390.1
1397.4
1398.1
207.1
283.2
413.2
200 400 600 800 1000 1200 1400 1600 1800 2000
m/z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%
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$Zn_{16}Gd(napHA)_{16}$
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1398.7
1399.0
1396.7
1399.4
1396.4
1399.7
1400.0
1396.0
1400.4
1395.7
1400.7
1395.4
1395.0
1401.1
1401.4
1394.7
1401.7
1394.1
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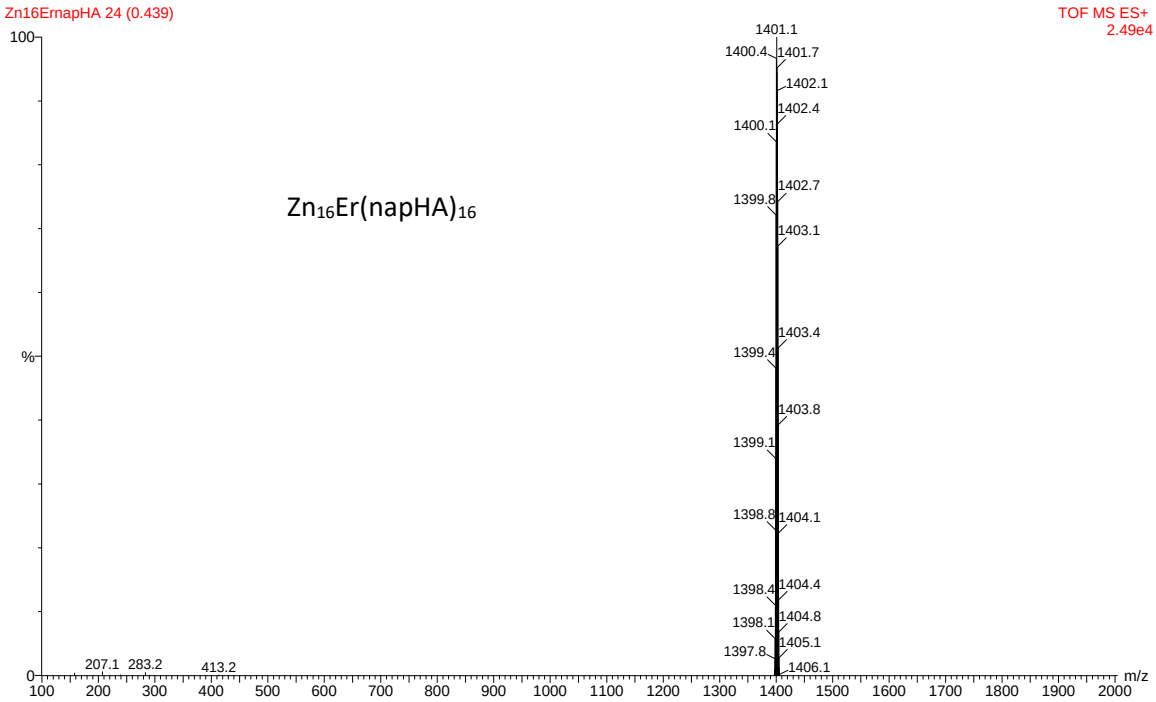
283.2
413.2
200
400
600
800
1000
1200
1400
1600
1800
2000
m/z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%
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$Zn_{16}Er(napHA)_{16}$
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1400.4
1401.7
1402.1
1402.4
1400.1
1402.7
1399.8
1403.1
1403.4
1399.4
1403.8
1399.1
1398.8
1404.1
1398.4
1404.4
1398.1
1404.8
1397.8
1405.1
1406.1
207.1
283.2
413.2
100
200
300
400
500
600
700
800
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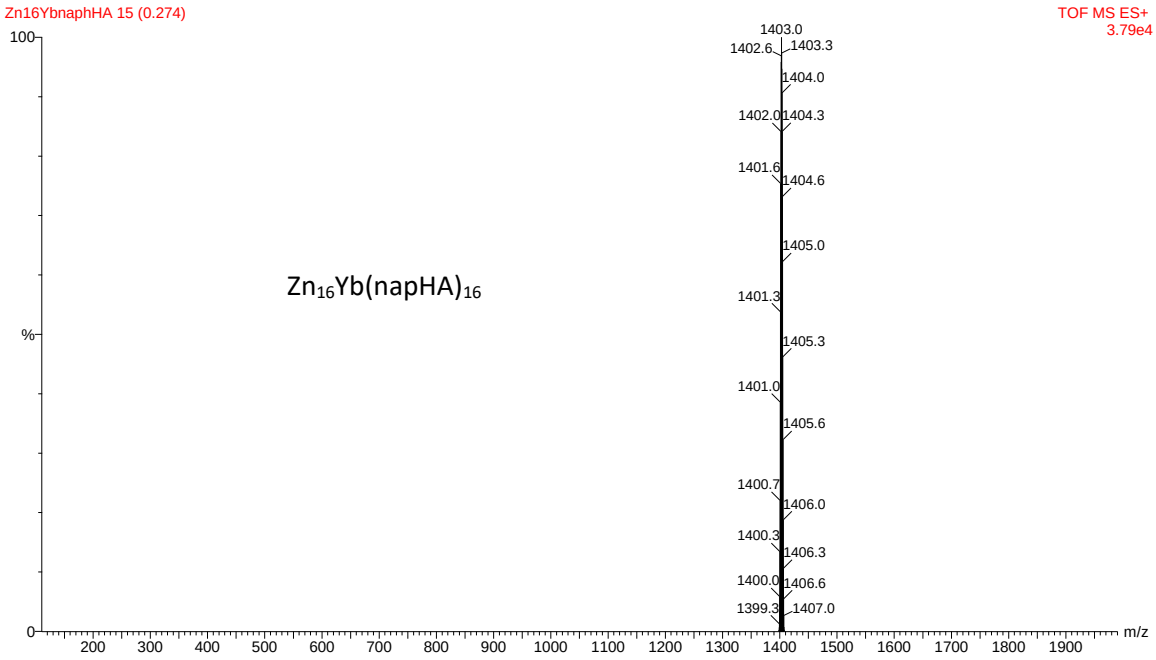
1800
1900
2000
m/z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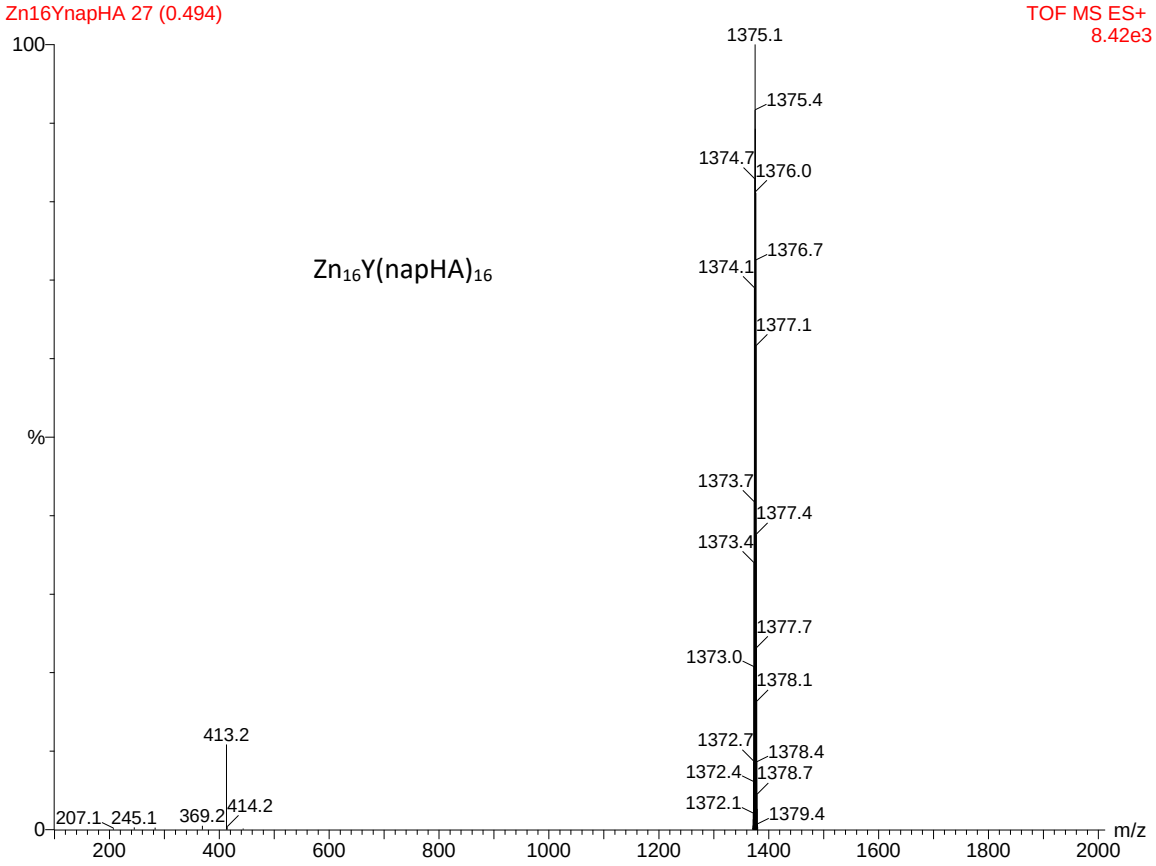
TOF MS ES+
3.79e4
100
%
0
$Zn_{16}Yb(napHA)_{16}$
1403.0
1402.6
1403.3
1404.0
1402.0
1404.3
1401.6
1404.6
1405.0
1401.3
1405.3
1401.0
1405.6
1400.7
1406.0
1400.3
1406.3
1400.0
1406.6
1399.3
1407.0
200 300 400 500 600 700 800 900 1000 1100 1200 1300 1400 1500 1600 1700 1800 1900
m/z


Zn16YnapHA 27 (0.494)
TOF MS ES+
8.42e3
100
%
0
$Zn_{16}Y(napHA)_{16}$
1375.1
1375.4
1374.7
1376.0
1376.7
1374.1
1377.1
1373.7
1377.4
1373.4
1377.7
1373.0
1378.1
413.2
1372.7
1378.4
1372.4
1378.7
207.1
245.1
369.2
414.2
1372.1
1379.4
200 400 600 800 1000 1200 1400 1600 1800 2000
m/z

X-Ray crystallography

Table S1. Crystal data and structure refinement for $Zn_{16}Nd(quinoHA)_{16}$.

Identification code	tn1177a_sq
Empirical formula	$C_{187}H_{120}F_9N_{62}NdO_{57.50}S_3Zn_{16}$
Formula weight	5612.78
Temperature	85(2) K
Wavelength	1.54184 Å
Crystal system, space group	Tetragonal, *P*4/*ncc*
Unit cell dimensions	*a* = 29.7978(4) Å α = 90°
	b = 29.7978(4) Å β = 90°
	c = 27.5410(19) Å γ = 90°
Volume	24453.9(18) $Å^3$
Z, Calculated density	4, 1.502 Mg/m^3
Absorption coefficient	4.114 mm^{-1}
F(000)	11056
Crystal size	0.200×0.190×0.140 mm
Theta range for data collection	2.966 to 74.076 deg.
Limiting indices	$-37 \le h \le 35$, $-37 \le k \le 37$, $-34 \le l \le 33$
Reflections collected / unique	472686 / 12397 [*R*(int) = 0.0525]
Completeness to θ = 67.684	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.66737
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	12397 / 123 / 839
Goodness-of-fit on F^2	1.050
Final *R* indices [$I>2\sigma(I)$]	R_1 = 0.0550, wR_2 = 0.1902
R indices (all data)	R_1 = 0.0572, wR_2 = 0.1943
Extinction coefficient	n/a
Largest diff. peak and hole	1.334 and -0.881 e.$Å^{-3}$

Table S2. Crystal data and structure refinement for $Zn_{16}Yb(quinoHA)_{16}$.

Identification code	tn1183_sq
Empirical formula	$C_{187}H_{124.50}F_9N_{56}O_{47}S_3Yb\ Zn_{16}$
Formula weight	5394.06
Temperature	85(2) K
Wavelength	1.54178 Å
Crystal system, space group	Tetragonal, *P*4/*ncc*
Unit cell dimensions	*a* = 30.0778(4) Å α = 90°
	b = 30.0778(4) Å β = 90°
	c = 26.9277(19) Å γ = 90°
Volume	24360.8(18) $Å^3$
Z, Calculated density	4, 1.471 Mg/m^3
Absorption coefficient	3.315 mm^{-1}
F(000)	10774
Crystal size	0.120×0.110×0.080 mm
Theta range for data collection	2.938 to 68.245 deg.
Limiting indices	$-36 \le h \le 36$, $-36 \le k \le 36$, $-32 \le l \le 32$
Reflections collected / unique	386106 / 11168 [*R*(int) = 0.0946]
Completeness to θ = 67.684	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8747 and 0.4461
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	11168 / 93 / 779
Goodness-of-fit on F^2	1.045
Final *R* indices [$I>2\sigma(I)$]	R_1 = 0.0687, wR_2 = 0.2087
R indices (all data)	R_1 = 0.0768, wR_2 = 0.2193
Extinction coefficient	0.00019(2)
Largest diff. peak and hole	1.426 and -1.017 e.$Å^{-3}$

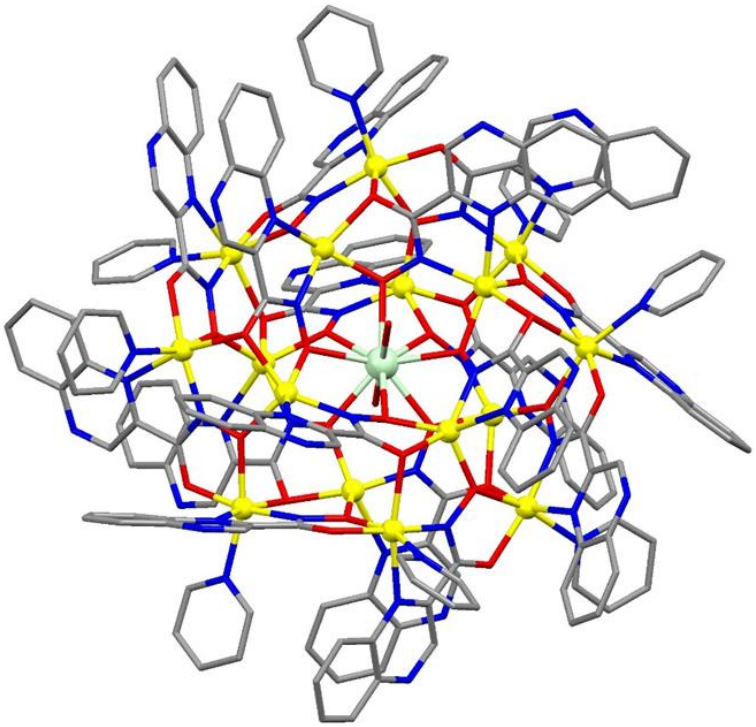


Figure S5. Crystal structure of $Zn_{16}Nd(quinoHA)_{16}$ obtained by single-crystal X-ray diffraction. Color code: Light green, Nd; Yellow, Zn; Red, O; Blue, N; Grey, C. H atoms and solvent molecules have been omitted for clarity.

Photophysical data

Absorption spectra

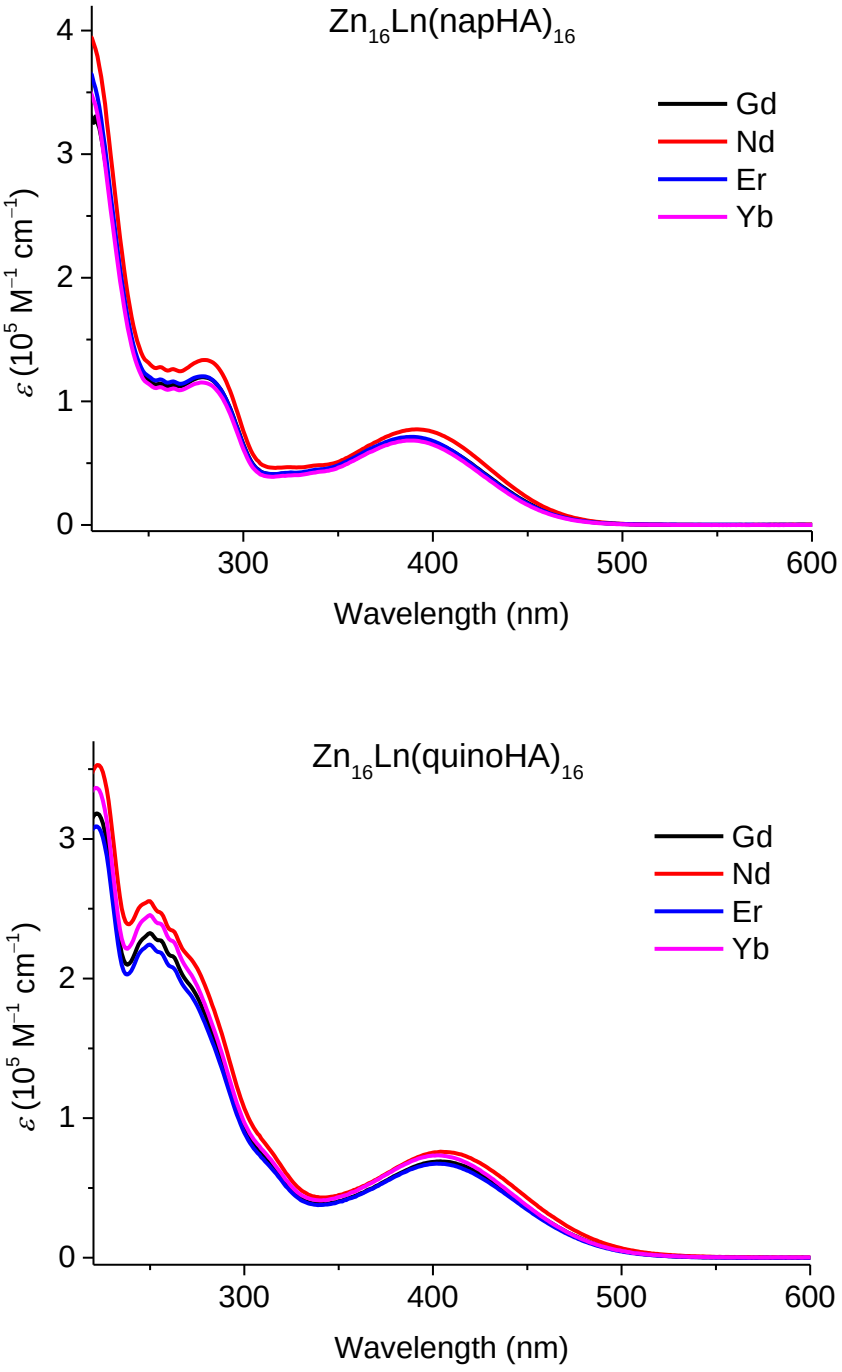


Figure S6. Absorption spectra of $Zn_{16}Ln(HA)_{16}$ (Ln = Nd, Gd, Er, Yb; HA = $quinoHA^{2-}$, $napHA^{2-}$) measured in CH_3OH at room temperature.

Table S3. Maxima of the low-energy intra-ligand charge transfer band observed in the absorption spectra of $Zn_{16}Yb(HA)_{16}$ MCs and corresponding molar absorption coefficients.

Metallacrown	Solvent	Wavelength (nm)	ε (M^{-1} cm^{-1})
$Zn_{16}Ln(picHA)_{16}$	MeOH	330	68590
$Zn_{16}Ln(pyzHA)_{16}$	H_2O	360	48010
$Zn_{16}Ln(quinHA)_{16}$	MeOH	380	53480
$Zn_{16}Ln(quinoHA)_{16}$	MeOH	402	73370
$Zn_{16}Ln(napHA)_{16}$	MeOH	387	68290

Energy levels and phosphorescence spectra

Table S4. Energies of singlet, triplet and ILCT states in $Zn_{16}Ln(HA)_{16}$.

Metallacrown	Singlet (cm^{-1}) [a]	Triplet (cm^{-1}) [a]	ILCT (cm^{-1}) [b]	Ref.
$Zn_{16}Ln(picHA)_{16}$	31250	24690	25000	This work
$Zn_{16}Ln(pyzHA)_{16}$	28570	25035	22220	This work
$Zn_{16}Ln(quinHA)_{16}$	29850	21000	21560	[1]
$Zn_{16}Ln(quinoHA)_{16}$	26320	24150	19685	This work
$Zn_{16}Ln(napHA)_{16}$	22370	25510	20830	This work

[a] Determined at the edge of absorption spectra of the corresponding hydroxamic acids. [b] Determined as 0-0 transition either from the Gaussian decomposition or as an onset of the phosphorescence spectra of $Zn_{16}Gd(HA)_{16}$ (Figure S7). [c] Determined at the edge of absorption spectra of $Zn_{16}Ln(HA)_{16}$.

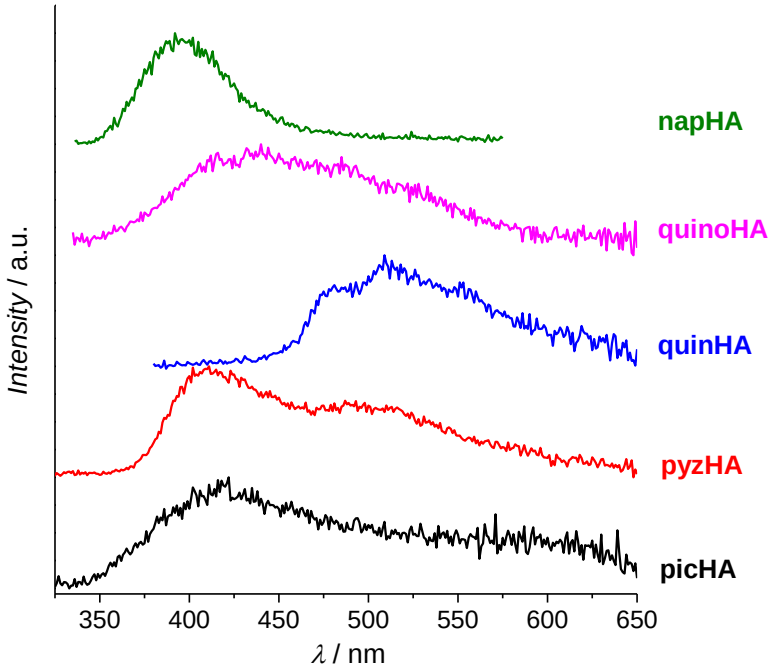


Figure S7. Phosphorescence spectra (λ_{ex} = 290-320 nm) of $Zn_{16}Gd(HA)_{16}$ collected in the solid state at 77 K upon applying a 100-200 μs delay after the excitation flash.

References

1. E. R. Trivedi, S. V. Eliseeva, J. Jankolovits, M. M. Olmstead, S. Petoud and V. L. Pecoraro, *J. Am. Chem. Soc.*, 2014, **136**, 1526-1534.