crystals

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Supplementary Materials

N,O Chelating Ligands Construct Five-coordinated Zn(II) Exclusive {Zn6} Clusters: Decomposition, Stepwise Assembly and Photoluminescence Study

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Table S1. Crystallographic data of the complex **Zn6**.

Complex	**Zn_6**
Formula	$Zn_6C_{90}H_{90}N_{20}O_{10}\cdot 4(NO_3)\cdot 12(H_2O)\cdot 2(C_2H_3N)$
Weight	2550.38
Crystal System	Monoclinic
Space Group	$P2_1/c$
T (K)	150
a (Å)	14.9791 (2)
b (Å)	14.2965 (2)
c (Å)	25.4993 (3)
α (°)	90
β (°)	99.637(1)
γ (°)	90
V (Å^3)	5383.58(1)
Z	2
F (000)	2636
D_{calcd} (g·cm^{-3})	1.573
μ (mm^{-1})	2.27
Reflection collected	25439
Unique Reflection	9742
R_{int}	0.029
$^aR_1[I \geq 2\sigma(I)]$	0.063
$^bwR_2$(all data)	0.186
GOF	1.03

$^aR_1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$, $^bwR_2=[\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Table S2. Selected bond lengths (Å) and angles (°) of **Zn6**.

Zn2—O1^i	**2.260 (2)**	**Zn1—O1^i**	**2.251 (2)**
Zn2—O2	1.984 (2)	Zn1—O1	1.985 (2)
Zn2—O3	1.977 (2)	Zn1—O2	1.980 (2)
Zn2—N1^i	2.001 (3)	Zn1—O4^i	2.065 (2)
Zn2—N4	2.082 (3)	Zn1—N6^i	2.041 (3)
Zn3—O4	2.062 (2)	O1—Zn2^i	2.260 (2)
Zn3—O3	2.001 (2)	O1—Zn1^i	2.251 (2)
Zn3—O5	2.327 (3)	O4—Zn1^i	2.065 (2)
Zn3—N7	2.014 (3)	N6—Zn1^i	2.041 (3)
Zn3—N10	1.988 (3)	N1—Zn2^i	2.001 (3)
O2—Zn2—O1^i	77.84 (8)	N10—Zn3—O5	74.94 (11)
O2—Zn2—N1^i	115.72 (10)	N10—Zn3—N7	123.98 (11)
O2—Zn2—N4	80.98 (10)	O1—Zn1—O1^i	79.42 (9)
O3—Zn2—O1^i	85.05 (8)	O1—Zn1—O4^i	101.12 (9)
O3—Zn2—O2	128.55 (9)	O1—Zn1—N6^i	136.84 (10)
O3—Zn2—N1^i	107.31 (10)	O2—Zn1—O1	107.14 (9)
O3—Zn2—N4	104.73 (10)	O2—Zn1—O1^i	78.13 (9)
N1^i—Zn2—O1^i	78.10 (9)	O2—Zn1—O4^i	96.36 (9)
N1^i—Zn2—N4	116.00 (11)	O2—Zn1—N6^i	111.20 (10)
N4—Zn2—O1^i	158.28 (10)	O4^i—Zn1—O1^i	174.32 (8)
O4—Zn3—O5	176.19 (9)	N6^i—Zn1—O1^i	89.64 (9)
O3—Zn3—O4	94.19 (9)	N6^i—Zn1—O4^i	93.69 (10)
O3—Zn3—O5	87.48 (9)	Zn1—O1—Zn2^i	103.36 (9)
O3—Zn3—N7	105.39 (10)	Zn1^i—O1—Zn2^i	92.58 (8)
N7—Zn3—O4	83.02 (10)	Zn1—O1—Zn1^i	100.58 (9)
N7—Zn3—O5	99.85 (11)	Zn1—O2—Zn2	110.67 (10)
N10—Zn3—O4	101.40 (10)	Zn3—O4—Zn1^i	102.55 (10)
N10—Zn3—O3	129.42 (10)		

Table S3. *SHAPE* analysis of the Zn^{II} ion in **Zn6**.

		Ideal structures
Zn1	30.584	Pentagon
	16.414	Vacant octahedron
	5.093	**Trigonal bipyramid**
	9.251	Spherical square pyramid
	19.237	Johnson trigonal bipyramid J12
Zn2	28.879	Pentagon
	5.557	Vacant octahedron
	2.879	**Trigonal bipyramid**
	3.916	Spherical square pyramid
	4.271	Johnson trigonal bipyramid J12
Zn3	28.869	Pentagon
	5.658	Vacant octahedron
	1.760	**Trigonal bipyramid**
	4.611	Spherical square pyramid
	2.982	Johnson trigonal bipyramid J12

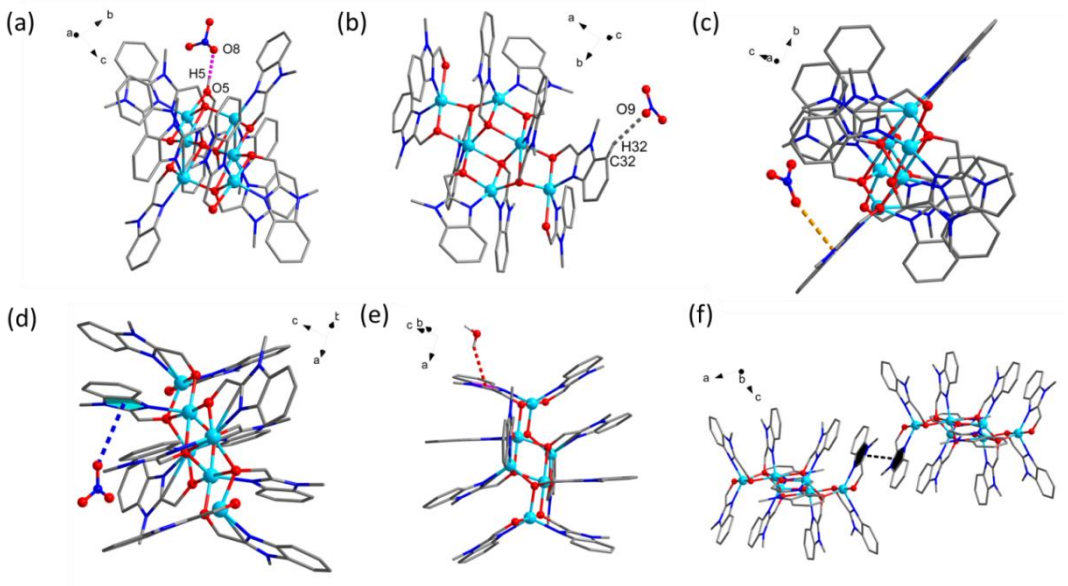


Figure S1. The intramolecular and intermolecular weak interaction of the cluster **Zn6**.

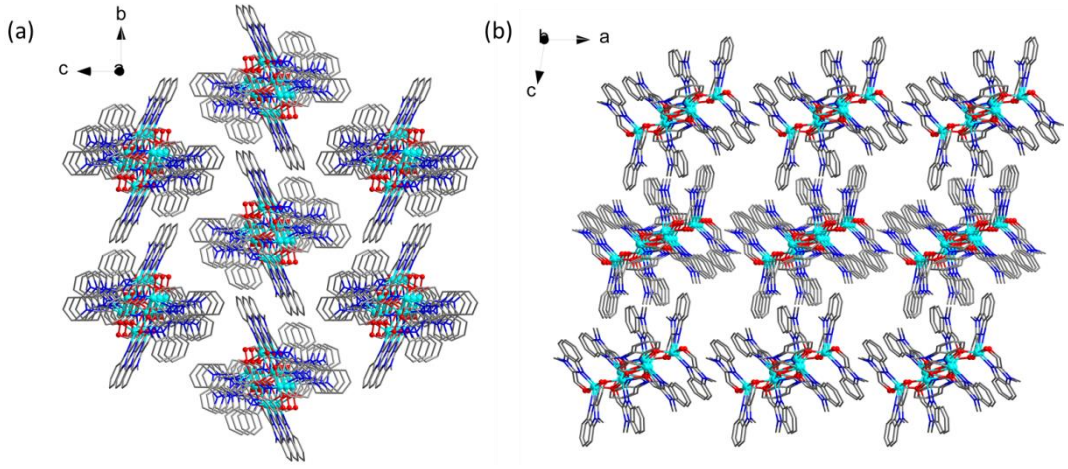


Figure S2. Intermolecular stacking diagram of cluster **Zn6**.

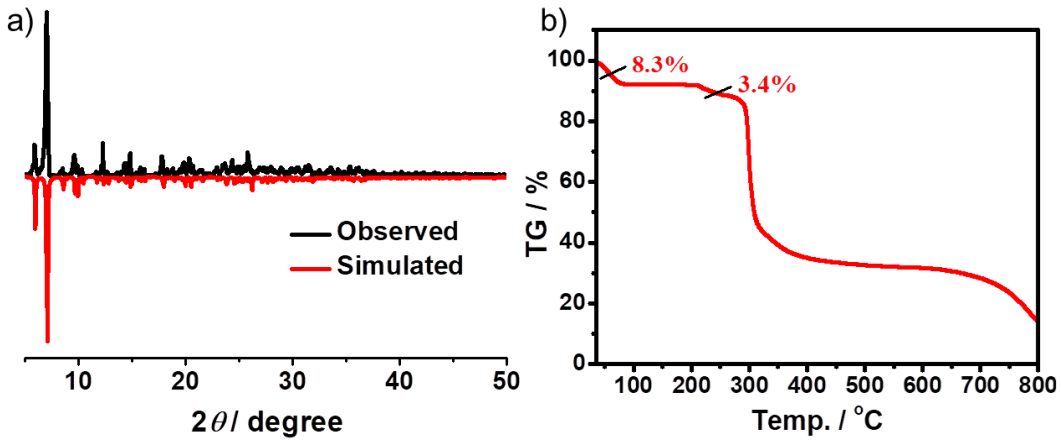


Figure S3. Cluster **Zn6** experiments and fitting PXRD patterns (a) and thermogravimetric analysis (b).

Table S4. Intramolecular and intermolecular weak action of **Zn6**.

Hydrogen bonds	Distance [a], Å	Distance [b], Å	Angle,°
O_5-H_5···O_8	1.81	2.65	168
C_{32}-H_{32}···O_9	2.60	3.49	161
N-O···π	Distance [c], Å	Distance [d], Å	Angle,°
N_{12}-O_9···PhC_3N_2	3.44	4.45	154
N_{12}-O_{10}···PhC_3N_2	3.34	4.45	157
O-H···π	Distance [e], Å	Distance [f], Å	Angle,°
O_{17}-H_{17B}···PhC_3N_2	2.6	3.42	150
π···π	Distance [g], Å	Distance [h], Å	
PhC_3N_2···PhC_3N_2	3.80	3.47	

[a] is the distance from the donor to the acceptor on the donor; [b] is the distance from the donor to the acceptor; [c] is the distance from the O on the donor to the center of the plane; [d] is the distance from the donor N to the center of the plane; [e] is the distance from the H on the donor to the center of the plane; [f] is the distance from the donor to the center of the plane; [g] is the distance from the H on the donor to the center of the plane; [h] is the distance from the donor to the center of the plane.

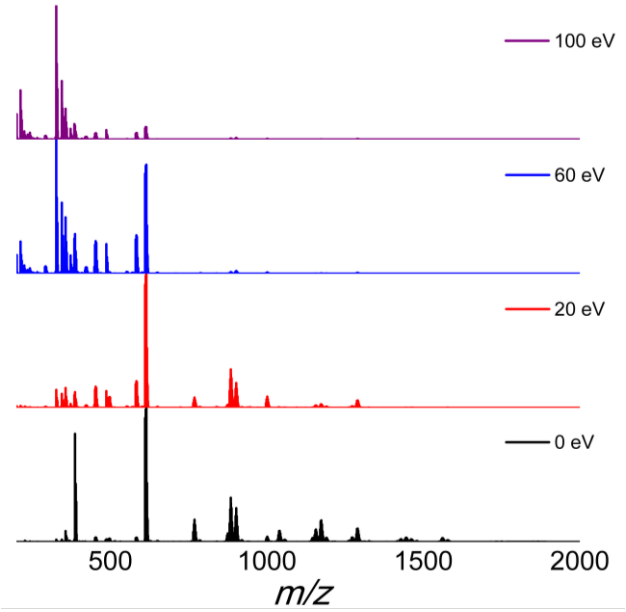


Figure S4. HRESI-MS diagram of cluster **Zn6** under different ion source voltage conditions (Positive mode).

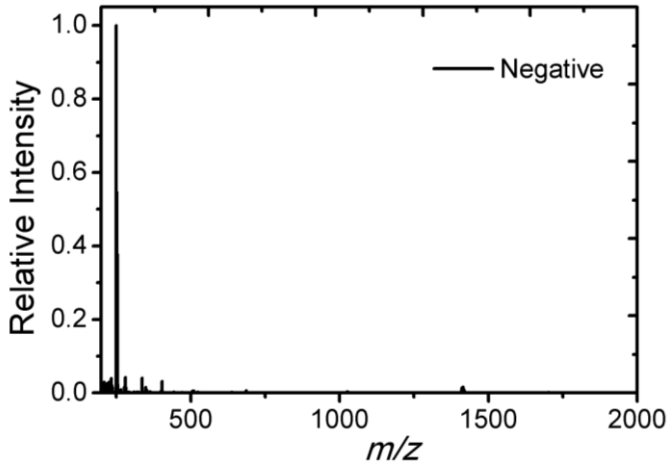
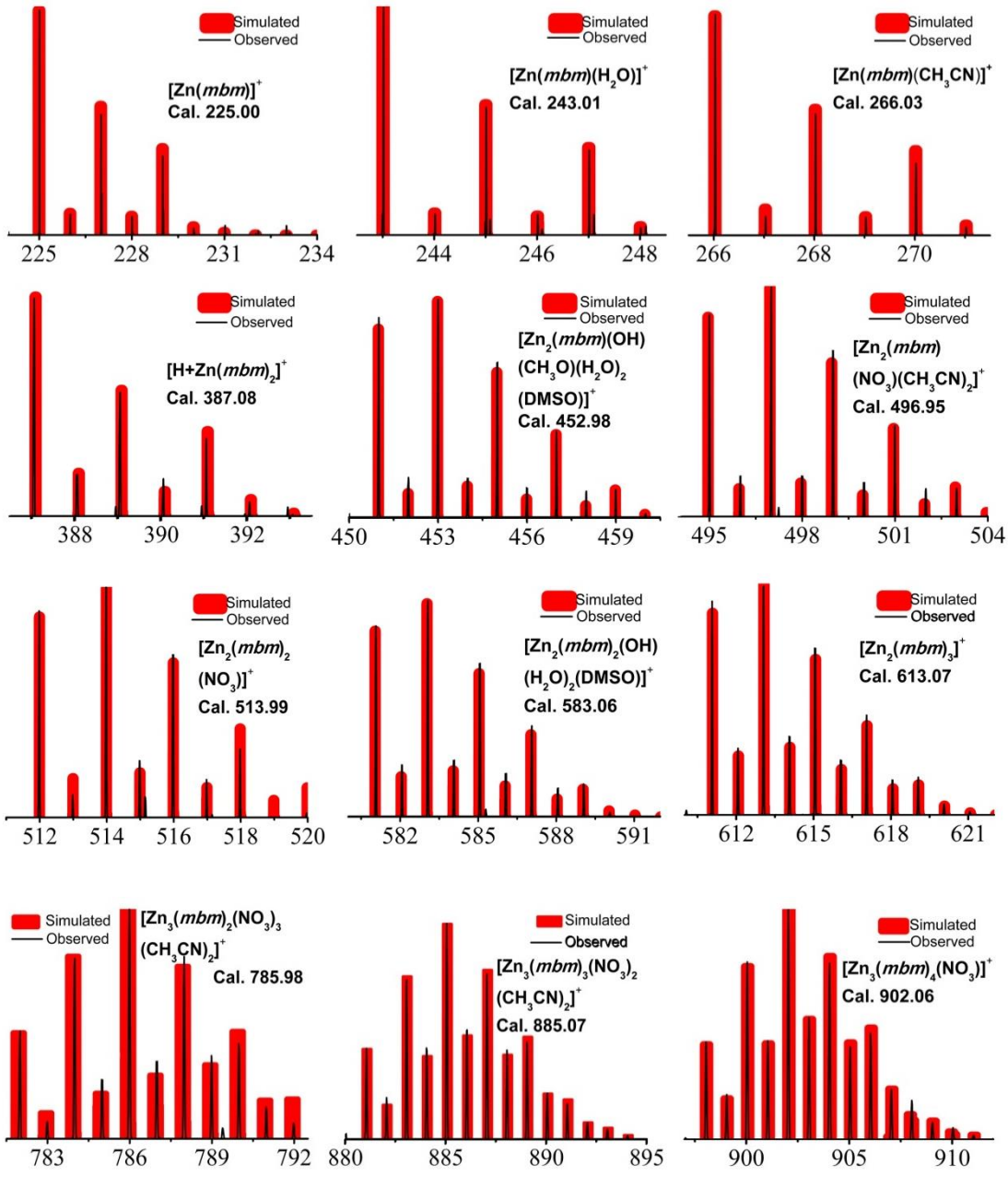


Figure S5. HRESI-MS spectrum of cluster **Zn6** at 0 eV (Negative mode).

Table S5. Analysis of molecular ion peaks of cluster **Zn6** in high resolution electrospray mass spectrometry (HRESI-MS) with different ion source voltages.

Obs. m/z	Formula(Calc. m/z)	Intensity (%)			
		0 eV	20 eV	60 eV	100 eV
Positive mode					
	[Zn_1]				
225.00	[Zn(*mbm*)]$^+$ (225.00)	-	-	6.17	6.20
243.01	[Zn(*mbm*)(H_2O)]$^+$(243.01)	0.46	0.40	4.13	4.98
266.03	[Zn(*mbm*)(CH_3CN)]$^+$(266.03)	0.17	0.15	1.06	1.16
387.08	[HZn(*mbm*)$_2$]$^+$(387.08)	80.77	11.75	29.24	11.58
	[Zn_2]				
453.01	[Zn_2(*mbm*)(OH)(CH_3O)(H_2O)$_2$(DMSO)]$^+$ (452.98)	3.32	15.76	24.20	4.70
497.00	[Zn_2(*mbm*)(NO_3)$_2$(CH_3CN)$_2$]$^+$ (496.95)	2.49	8.12	0.96	-
513.99	[Zn_2(*mbm*)$_2$(NO_3)]$^+$ (513.99)	0.50	0.20	-	-
583.06	[Zn_2(*mbm*)$_2$(OH)(H_2O)$_2$(DMSO)]$^+$(583.06)	3.23	19.78	28.70	4.84
613.07	[Zn_2(*mbm*)$_3$]$^+$ (613.07)	100	100	80.53	9.28
	[Zn_3]				
785.98	[Zn_3(*mbm*)$_2$(NO_3)$_3$(CH_3CN)$_2$]$^+$ (785.98)	1.23	0.68	-	-
885.07	[Zn_3(*mbm*)$_3$(NO_3)$_2$(CH_3CN)$_2$]$^+$ (885.07)	32.88	28.71	1.20	0.81
902.06	[Zn_3(*mbm*)$_4$(NO_3)]$^+$ (902.06)	25.11	18.50	2.03	1.20
1001.14	[Zn_3(*mbm*)$_5$]$^+$ (1001.14)	3.93	8.40	0.92	0.50
	[Zn_4]				
1174.05	[Zn_4(*mbm*)$_5$(NO_3)(C_2H_5O)]$^+$ (1174.09)	16.16	2.60	0.23	0.14
1191.04	[Zn_4(*mbm*)$_5$(NO_3)$_2$]$^+$ (1191.04)	3.06	0.89	0.09	-
1290.13	[Zn_4(*mbm*)$_6$(NO_3)]$^+$ (1290.13)	9.92	5.47	0.54	-
	[Zn_5]				
1461.04	[Zn_5(*mbm*)$_5$(NO_3)$_4$(CH_3CN)$_2$]$^+$ (1461.00)	1.97	0.12	-	-
1480.03	[Zn_5(*mbm*)$_6$(NO_3)$_3$]$^+$ (1480.03)	0.71	0.02	-	-
1579.11	[Zn_5(*mbm*)$_7$(NO_3)$_2$]$^+$ (1579.11)	1.30	0.12	-	-
	[Zn_6]				
1866.10	[Zn_6(*mbm*)$_8$(NO_3)$_3$]$^+$ (1866.10)	0.22	-	-	-
Negative mode					
249.89	[Zn(NO_3)$_3$]$^-$ (249.89)	100			
	[Zn_1]				

348.98	$[Zn(mbm)(NO_3)_2]^-$ (348.98)	1.55
	$[Zn_2]$	
493.89	$[Zn_2(mbm)(NO_3)_3(OH)]^-$ (493.89)	0.13
507.91	$[Zn_2(mbm)(NO_3)_3(CH_3O)]^-$ (507.91)	0.60
637.96	$[Zn_2(mbm)_2(NO_3)_3]^-$ (637.96)	0.19
737.05	$[Zn_2(mbm)_3(NO_3)_2]^-$ (737.05)	0.02
	$[Zn_3]$	
926.95	$[Zn_3(mbm)_3(NO_3)_4]^-$ (926.95)	0.06
1026.03	$[Zn_3(mbm)_4(NO_3)_3]^-$ (1026.03)	0.41
	$[Zn_4]$	
1270.04	$[Zn_4(mbm)_5(NO_3)_3(OH)]^-$ (1270.04)	0.05
1284.05	$[Zn_4(mbm)_5(NO_3)_3(CH_3O)]^-$ (1284.05)	0.15
1315.02	$[Zn_4(mbm)_5(NO_3)_4]^-$ (1315.02)	0.11
1414.11	$[Zn_4(mbm)_6(NO_3)_3]^-$ (1414.10)	1.62
	$[Zn_5]$	
1573.04	$[Zn_5(mbm)_6(NO_3)_4(CH_3O)]^-$ (1573.04)	0.06
1604.01	$[Zn_5(mbm)_6(NO_3)_5]^-$ (1604.01)	0.03
1703.09	$[Zn_5(mbm)_7(NO_3)_4]^-$ (1703.09)	0.19



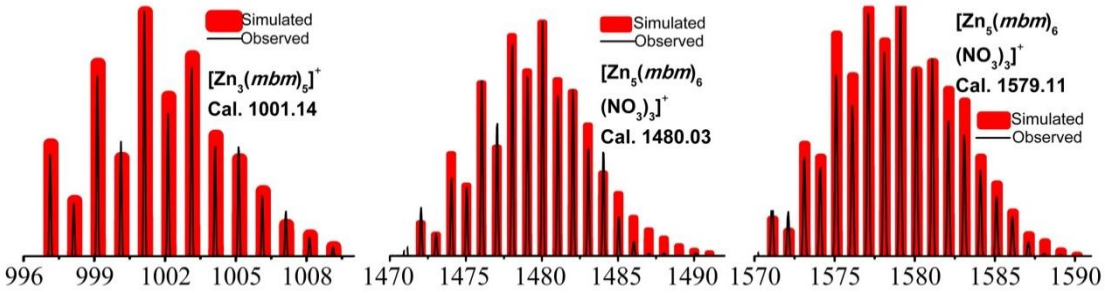
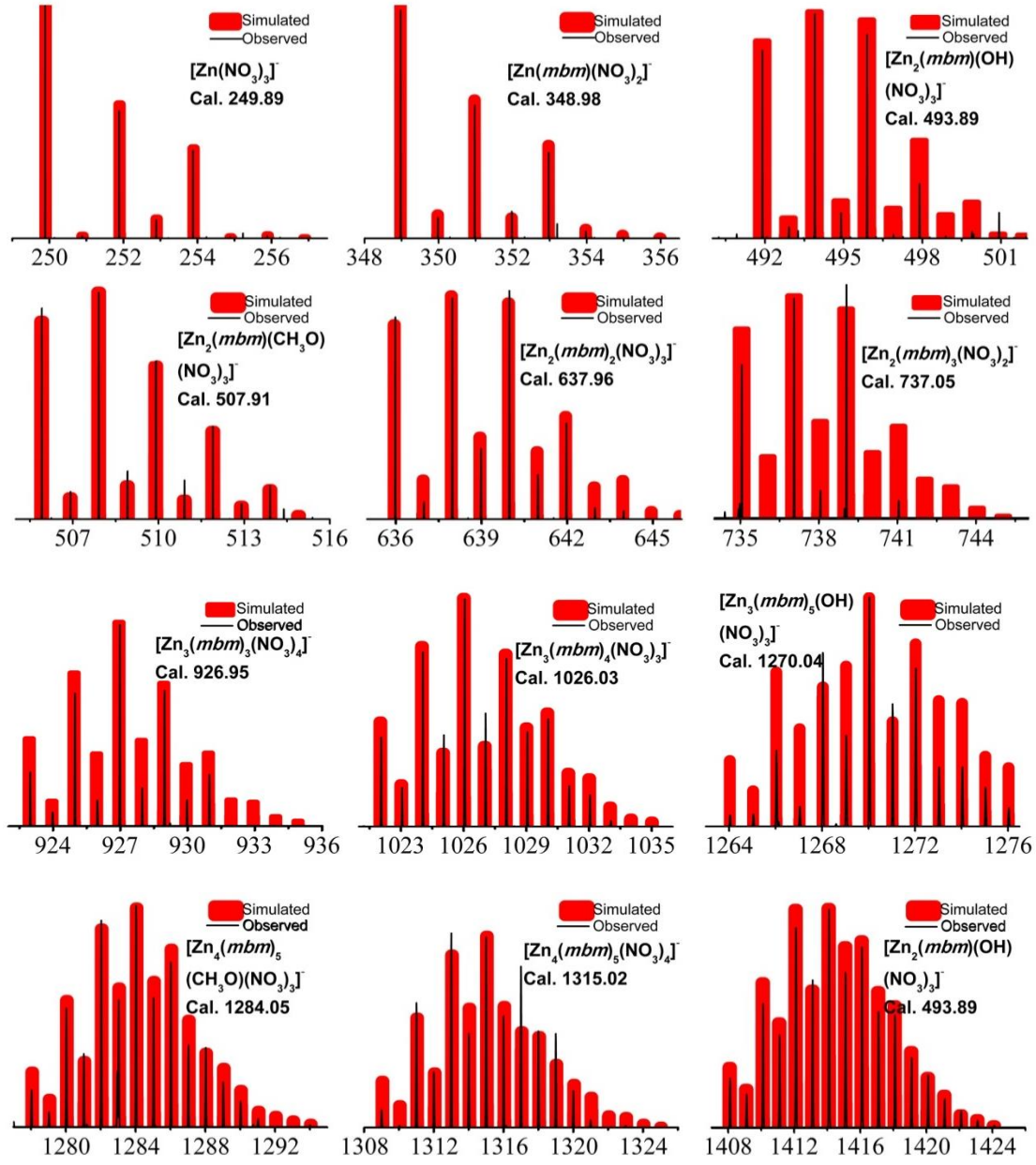


Figure S6. The superposed simulated and observed spectra of several species for **Zn6** (Positive mode).



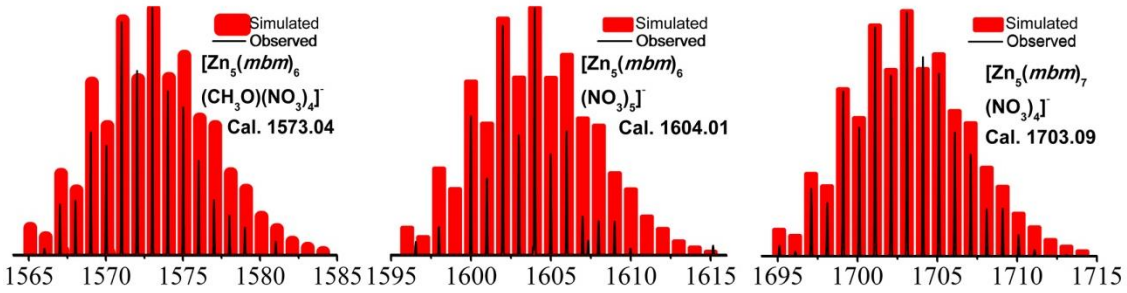


Figure S7. The superposed simulated and observed spectra of several species for **Zn6** (Negative mode).

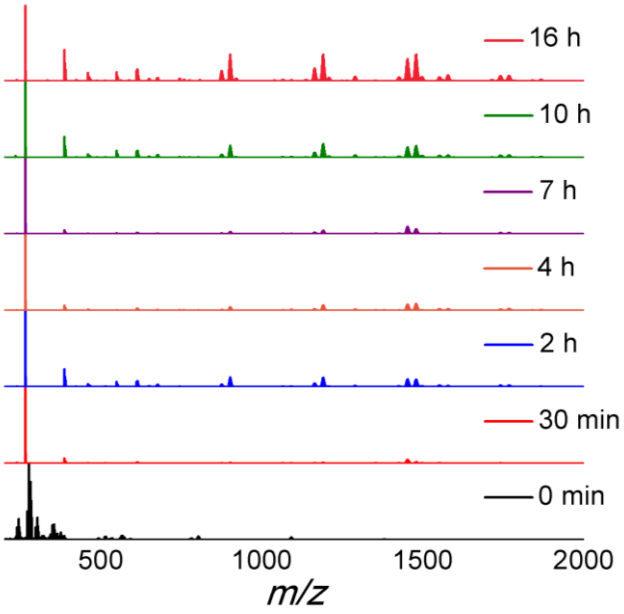


Figure S8. The HRESI-MS spectrum of the reaction process of the cluster **Zn6** in different time periods (Positive mode).

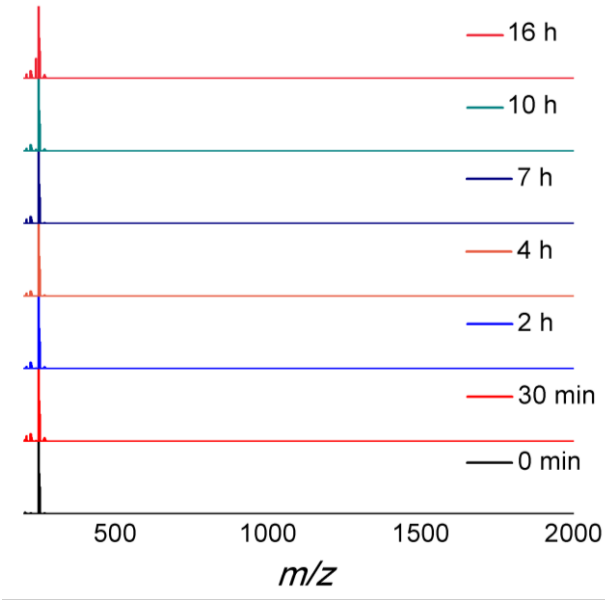
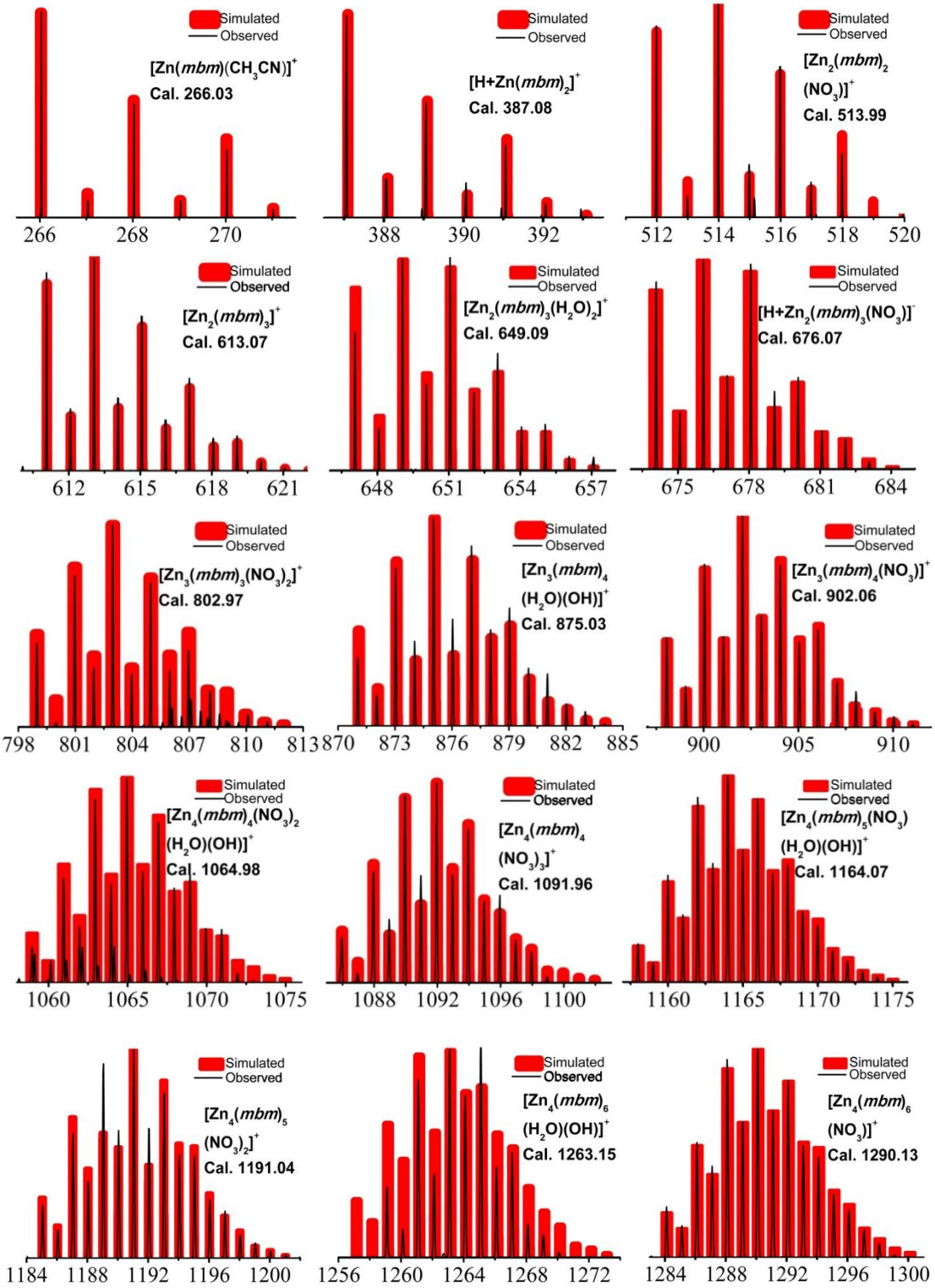


Figure S9. The HRESI-MS spectrum of the reaction process of the cluster **Zn6** in different time periods (Negative mode).



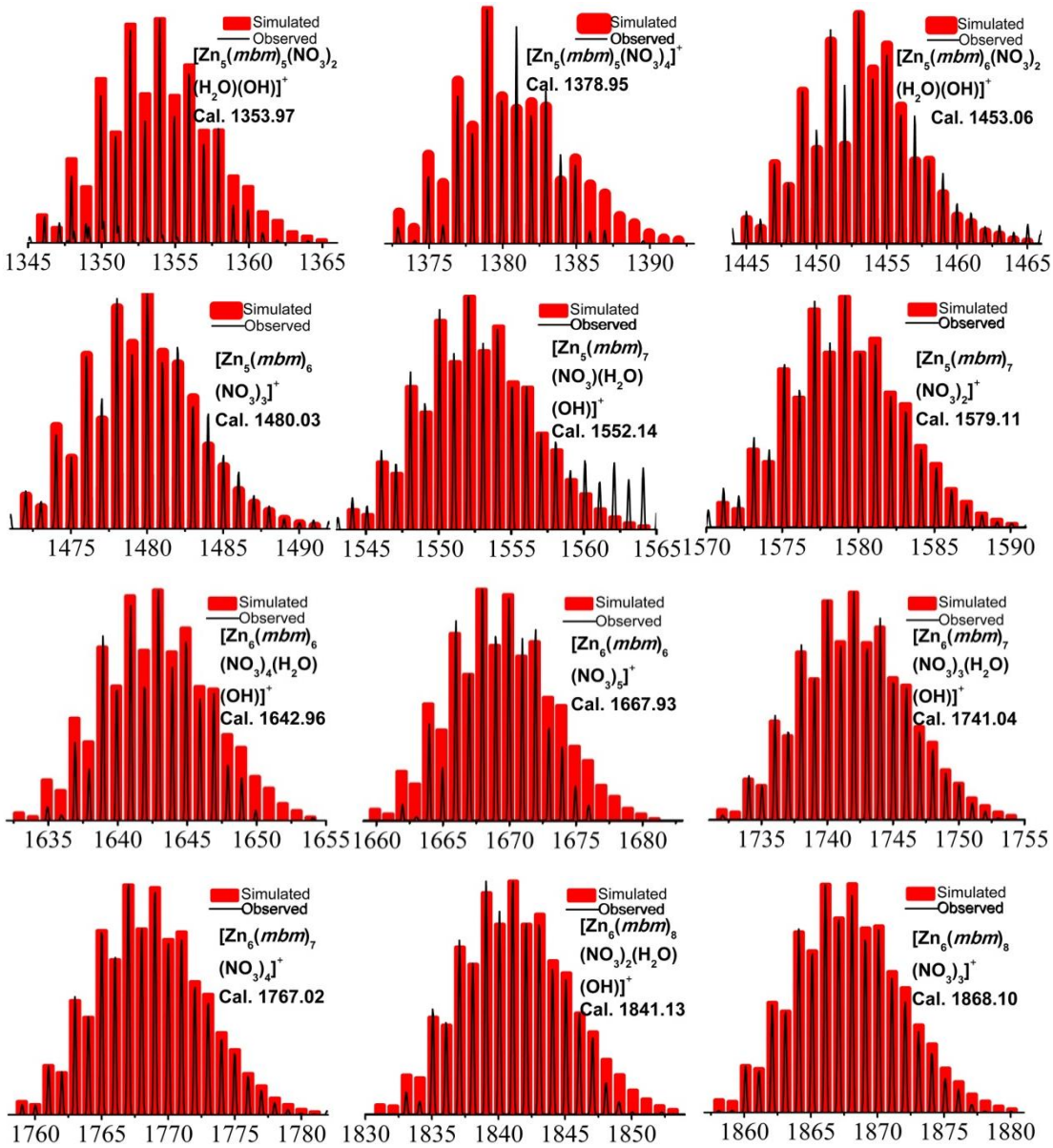


Figure S10. The superposed simulated and observed spectra of several species in the time-dependent ESI-MS of **Zn6** (Positive mode).

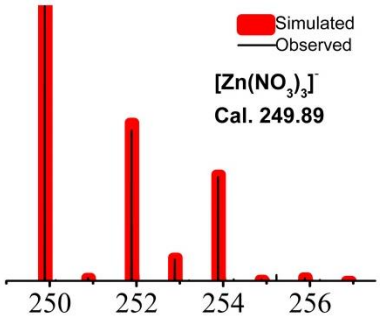


Figure S11. The superposed simulated and observed spectra of several species in the time-dependent ESI-MS of **Zn6** (Negative mode).

Table S6. The HRESI-MS fragment of the cluster **Zn6** formation process was analyzed at different time periods.

Obs. *m/z*	Formula(Calc. *m/z*)	Relative Intensity (%)						
		0 h	**0.5 h**	**2 h**	**4 h**	**7 h**	**10 h**	**16 h**
Positive mode								
		[Zn]						
266.03	$[Zn(mbm)(CH_3CN)]^+$ (266.03)	3.25	100	100	100	100	100	100
387.08	$[HZn(mbm)_2]^+$ (387.08)	5.00	6.48	23.53	6.67	5.04	27.21	41.08
		[Zn_2]						
513.99	$[Zn_2(mbm)_2(NO_3)]^+$ (513.99)	4.60	0.60	0.80	0.46	0.27	0.84	1.02
613.07	$[Zn_2(mbm)_3]^+$ (613.07)	-	1.38	7.93	2.86	1.83	9.25	15.55
649.04	$[Zn_2(mbm)_3(H_2O)_2]^+$ (649.09)	-	0.31	1.46	2.89	0.36	1.58	3.07
676.06	$[H+Zn_2(mbm)_3(NO_3)]^+$ (676.07)		0.58	3.29	1.01	0.89	3.63	4.32
		[Zn_3]						
802.97	$[Zn_3(mbm)_3(NO_3)_2]^+$ (802.97)	4.65	0.53	0.66	0.59	0.35	0.67	0.67
875.03	$[Zn_3(mbm)_4(H_2O)(OH)]^+$ (875.08)	-	0.60	3.57	1.18	1.12	4.22	13.67
902.06	$[Zn_3(mbm)_4(NO_3)]^+$ (902.10)	-	1.09	12.60	4.70	3.19	16.07	35.02
		[Zn_4]						
1064.94	$[Zn_4(mbm)_4(NO_3)_2(H_2O)(OH)]^+$(1064.98)	0.47	0.80	1.06	0.80	0.77	1.15	2.17
1091.96	$[Zn_4(mbm)_4(NO_3)_3]^+$ (1091.96)	3.56	0.61	1.23	1.38	0.76	1.33	1.57
1164.02	$[Zn_4(mbm)_5(NO_3)(H_2O)(OH)]^+$(1164.07)	-	0.71	4.86	1.99	2.21	6.81	16.76
1191.04	$[Zn_4(mbm)_5(NO_3)_2]^+$ (1191.04)	-	1.17	12.18	6.90	4.82	17.98	35.15
1263.10	$[Zn_4(mbm)_6(H_2O)(OH)]^+$ (1263.15)	-	-	0.25	0.22	0.05	0.37	0.84
1290.12	$[Zn_4(mbm)_6(NO_3)]^+$ (1290.13)	-	-	1.79	1.63	0.50	3.18	5.96
		[Zn_5]						
1353.92	$[Zn_5(mbm)_5(NO_3)_3(H_2O)(OH)]^+$(1353.97)	-	0.72	0.62	0.84	0.91	0.66	1.06
1378.95	$[Zn_5(mbm)_5(NO_3)_4]^+$ (1378.95)	-	0.29	0.44	0.68	0.41	0.52	0.62
1453.01	$[Zn_5(mbm)_6(NO_3)_2(H_2O)(OH)]^+$(1453.06)	-	4.74	10.33	8.02	9.59	13.62	29.38
1480.03	$[Zn_5(mbm)_6(NO_3)_3]^+$ (1480.03)	-	1.90	9.82	8.84	6.55	15.31	34.89
1552.09	$[Zn_5(mbm)_7(NO_3)(H_2O)(OH)]^+$ (1552.14)	-	0.94	2.09	2.21	0.94	2.82	5.23
1579.11	$[Zn_5(mbm)_7(NO_3)_2]^+$ (1579.11)	-	0.32	1.69	2.27	0.71	3.11	7.85
		[Zn_6]						
1642.91	$[Zn_6(mbm)_6(NO_3)_4(H_2O)(OH)]^+$(1642.96)	-	0.27	0.23	0.36	0.39	0.26	0.53
1667.93	$[Zn_6(mbm)_6(NO_3)_5]^+$ (1667.93)	-	-	-	0.27	0.19	0.17	0.14
1741.99	$[Zn_6(mbm)_7(NO_3)_3(H_2O)(OH)]^+$(1742.04)	-	0.66	2.06	1.56	1.87	2.84	6.76
1767.01	$[Zn_6(mbm)_7(NO_3)_4]^+$ (1767.02)	-	0.47	2.26	2.33	1.79	3.40	7.35
1841.08	$[Zn_6(mbm)_8(NO_3)_2(H_2O)(OH)]^+$(1841.13)	-	0.15	0.58	0.59	0.38	0.71	1.26
1868.10	$[Zn_6(mbm)_8(NO_3)_3]^+$ (1868.10)	-	-	0.98	1.16	0.54	1.33	2.04
Negative mode								
249.89	$[Zn(NO_3)_3]^-$ (249.89)	100	100	100	100	100	100	100

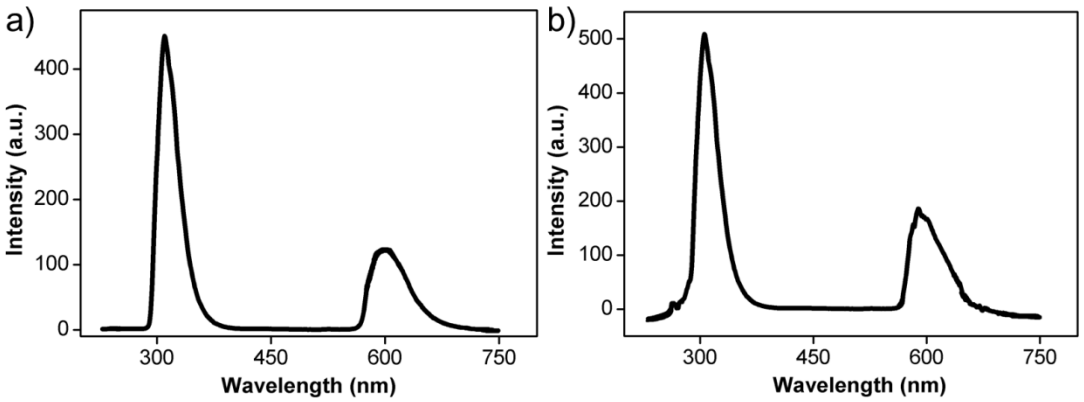


Figure S12. The emission peak (Em) obtained by exciting the DMF solution of the complex **Zn6** with excitation (Ex) wavelengths of 290 nm (a) and 267 nm (b), respectively.