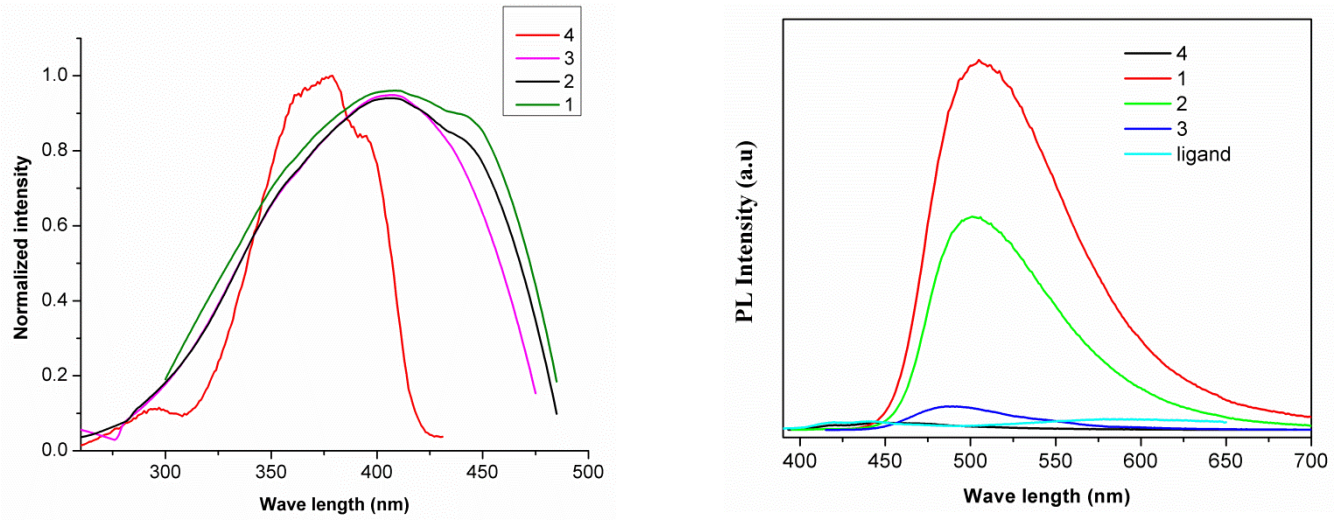
Electronic Supporting Information

A Phosphorus-Based Compartmental Ligand, (S)P[N(Me)N=CH-C_6H_3-*2*-O-*3*-OMe]$_3$ (LH_3), Enables the Assembly of Luminescent Heterobimetallic Linear $\{L_2Zn_2Ln\}^+$ [Ln = Gd, Tb, Nd and Eu] Complexes

Vadapalli Chandrasekhar*,[a,b] Prasenjit Bag,[a] Balasubramanian Murugesapandian,[a] and Mrituanjay D. Pandey[a]

[a]Department of Chemistry, Indian Institute of Technology Kanpur, Kanpur-208016, India,

[b]Tata Institute of Fundamental Research, Centre for Interdisciplinary Sciences, 21 Brundavan Colony, Narsingi, Hyderabad-500075, India



(a) (b)

Fig. S1 Room temperature solid state excitation spectra (a) monitored at 500 nm and emission spectra (b) of **1-4**.

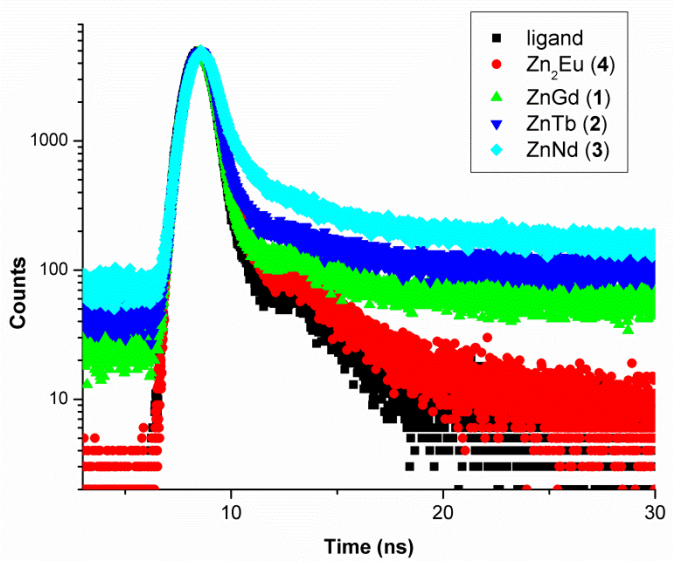
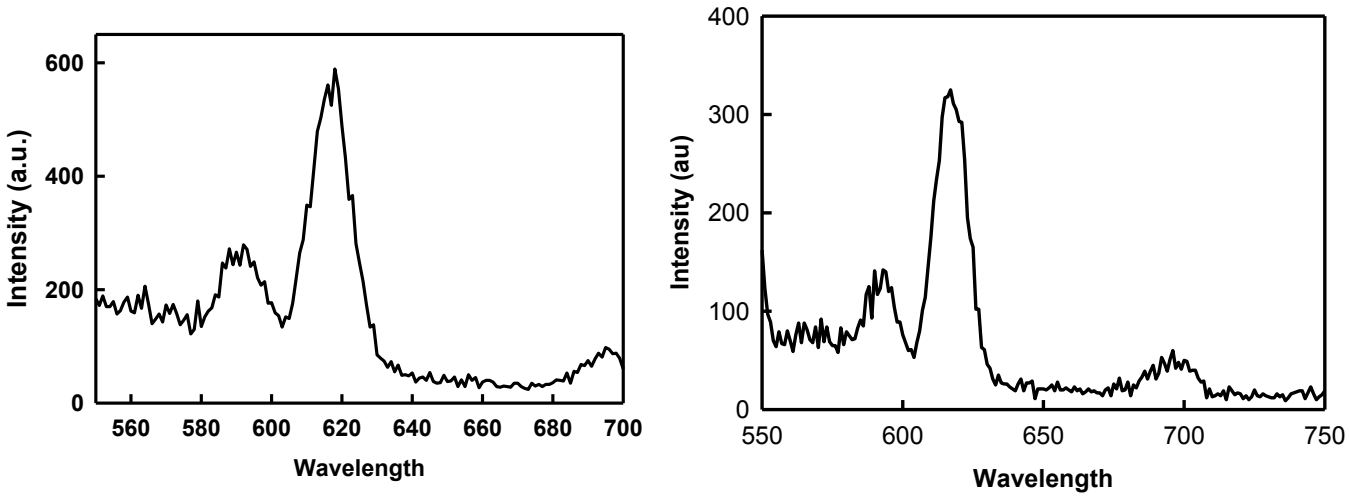


Fig. S2 Fluorescence decay of compounds **1-4,** emission monitored at 500 nm respectively in powder state at 298 K.

Table S1. Fluorescence lifetime measurement parameters of **1-4**.

Compound	500 nm		
	T1 (ns)	T2 (ns)	Chi Sq
Zn_2Gd (**1**)	0.160	0.643	1.19
Zn_2Tb (**2**)	0.175	0.701	1.19
Zn_2Nd(**3**)	0.164	0.656	1.11
Zn_2Eu (**4**)	0.166	0.643	1.14



(a) **(b)**

Fig. S3 Solution state emission spectra of **4** at room temperature [λ_{ex} = 525 (a), 535 (b) nm]

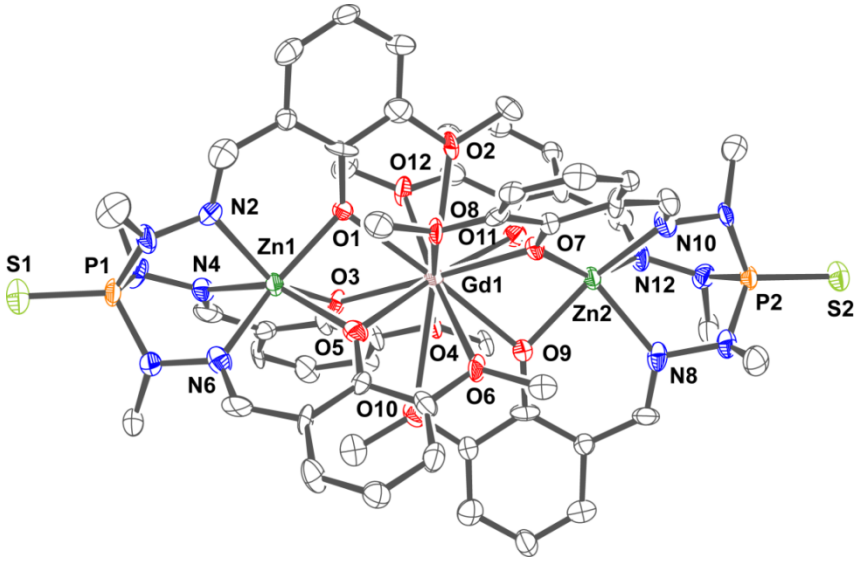


Fig. S4 The molecular structure of **1** (Hydrogen atoms, Solvent molecules and counter anion have been omitted for clarity)

Table S2. Selected Bond distances (Å) and bond angles (°) for compound **1**

Bond Lengths around Zinc (1)		Bond Lengths around Gadolinium(1)		Bond angles	
Zn(1)-O(3)	2.086(5)	Gd(1)-O(9)	2.395(5)	Zn(1)-O(1)-Gd(1)	94.44(18)
Zn(1)-O(5)	2.090(5)	Gd(1)-O(7)	2.398(5)	Zn(1)-O(3)-Gd(1)	94.60(18)
Zn(1)-O(1)	2.095(5)	Gd(1)-O(11)	2.402(5)	Zn(1)-O(5)-Gd(1)	95.25(18)
Zn(1)-N(6)	2.116(6)	Gd(1)-O(5)	2.409(5)	Zn(2)-O(11)-Gd(1)	94.28(18
Zn(1)-N(2)	2.127(6)	Gd(1)-O(1)	2.432(5)	Zn(2)-O(9)-Gd(1)	95.89(18)
Zn(1)-N(4)	2.157(6)	Gd(1)-O(3)	2.435(5)	Zn(2)-O(7)-Gd(1)	94.10(18)
Bond Lengths around Zinc (2)		Gd(1)-O(10)	2.768(5)		
		Gd(1)-O(6)	2.871(5)		
Zn(2)-O(9)	2.070(5)	Gd(1)-O(12)	2.883(5)		

Zn(2)-O(11)	2.123(5)	Gd(1)-O(4)	2.888(5)		
Zn(2)-O(7)	2.134(5)	Gd(1)-O(2)	2.899(5)		
Zn(2)-N(10)	2.134(6)	Gd(1)-O(8)	2.937(5)		
Zn(2)-N(12)	2.141(6)				
Zn(2)-N(8)	2.180(6)				

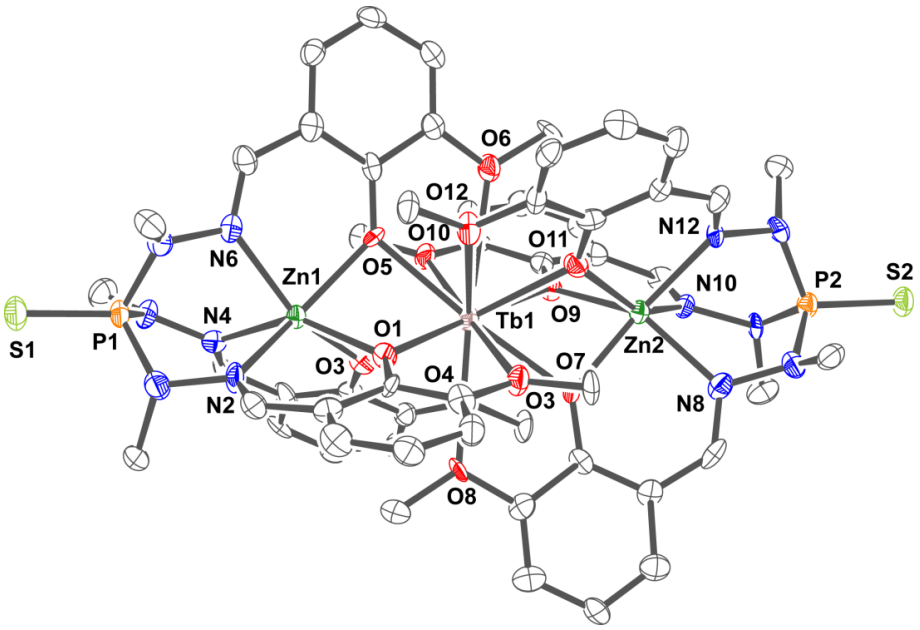


Fig. S5 The molecular structure of **2** (Hydrogen atoms, Solvent molecules and counter anion have been omitted for clarity)

Table S3. Selected Bond distances (Å) and bond angles (°) for compound **2**

Bond Lengths around Zinc (1)		Bond Lengths around Terbium (1)		Bond angles	
Zn(1)-O(3)	2.084(4)	Tb(1)-O(7)	2.371(4)	Zn(1)-O(1)-Tb(1)	95.29(14)

Zn(1)-O(5)	2.087(4)	Tb(1)-O(11)	2.380(4)	Zn(1)-O(3)-Tb(1)	94.68(14)
Zn(1)-O(1)	2.093(4)	Tb(1)-O(9)	2.386(4)	Zn(1)-O(5)-Tb(1)	94.64(15)
Zn(1)-N(2)	2.129(5)	Tb(1)-O(1)	2.388(4)	Zn(2)-O(7)-Tb(1)	96.22(15)
Zn(1)-N(6)	2.134(5)	Tb(1)-O(5)	2.415(4)	Zn(2)-O(11)-Tb(1)	94.04(14)
Zn(1)-N(4)	2.141(5)	Tb(1)-O(3)	2.416(4)	Zn(2)-O(9)-Tb(1)	94.35(14)
Bond Lengths around		Tb(1)-O(8)	2.764(4)		
Zinc (2)		Tb(1)-O(2)	2.871(4)		
Zn(2)-O(7)	2.065(4)	Tb(1)-O(4)	2.885(4)		
Zn(2)-O(9)	2.118(4)	Tb(1)-O(10)	2.901(4)		
Zn(2)-N(12)	2.125(5)	Tb(1)-O(6)	2.920(4)		
Zn(2)-N(10)	2.134(5)				
Zn(2)-O(11)	2.137(4)				
Zn(2)-N(8)	2.188(5)				

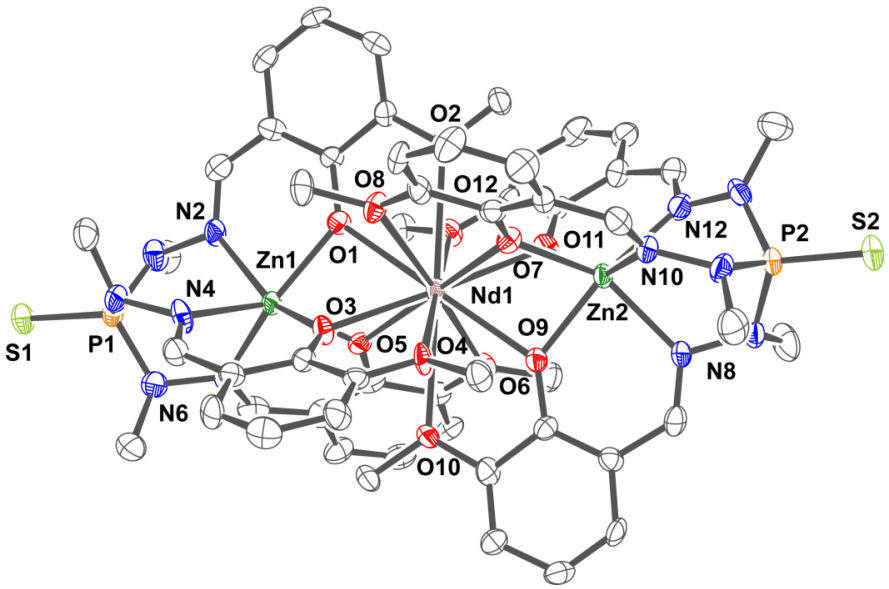


Fig. S6 The molecular structure of **3** (Hydrogen atoms, Solvent molecules and counter anion have been omitted for clarity).

Table S4. Selected Bond distances (Å) and bond angles (°) for compound **3**

Bond Lengths around Zinc (1)		Bond Lengths around Neodymium (1)		Bond angles	
Zn(1)-O(5)	2.082(4)	Nd(1)-O(7)	2.437(4)	Zn(1)-O(3)-Nd(1)	95.88(16)
Zn(1)-O(1)	2.085(4)	Nd(1)-O(3)	2.448(4)	Zn(1)-O(5)-Nd(1)	95.41(16)
Zn(1)-O(3)	2.095(4)	Nd(1)-O(11)	2.454(4)	Zn(2)-O(7)-Nd(1)	95.50(16)
Zn(1)-N(4)	2.108(5)	Nd(1)-O(9)	2.457(4)	Zn(2)-O(9)-Nd(1)	94.46(15)
Zn(1)-N(6)	2.141(6)	Nd(1)-O(5)	2.474(4)	Zn(2)-O(11)-Nd(1)	95.96(16)
Zn(1)-N(2)	2.161(5)	Nd(1)-O(1)	2.488(4)	Zn(1)-O(1)-Nd(1)	94.91(16)
Bond Lengths around Zinc (2)		Nd(1)-O(12)	2.779(4)		
		Nd(1)-O(8)	2.863(4)		
Zn(2)-O(11)	2.071(4)	Nd(1)-O(4)	2.871(4)		
Zn(2)-O(7)	2.109(4)	Nd(1)-O(6)	2.878(4)		
Zn(2)-O(9)	2.126(4)	Nd(1)-O(2)	2.891(4)		
Zn(2)-N(12)	2.136(5)	Nd(1)-O(10)	2.911(4)		
Zn(2)-N(8)	2.143(5)				
Zn(2)-N(10)	2.189(5)				

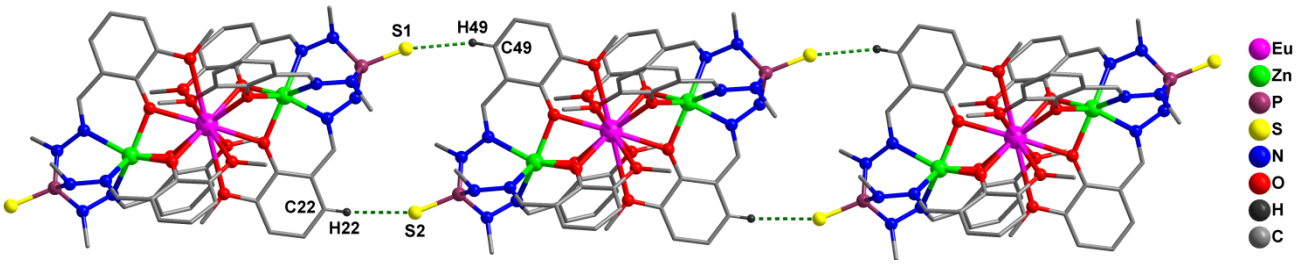


Fig. S7 Formation of one dimensional chain through intermolecular C–H….O interactions in **4**

Table S5. Hydrogen bond parameters for compound **4**

Compound	D–H….A	d(D–H)	d(H….A)	d(D….A)	<(DHA)	Symmetry of A
4	C49–H49….S1	0.929(7)	2.799(2)	3.643(7)	151.39(42)	x, 1+y, z
	C22–H22….S2	0.929(6)	2.795(2)	3.686(7)	160.77(42)	x, 1+y, z

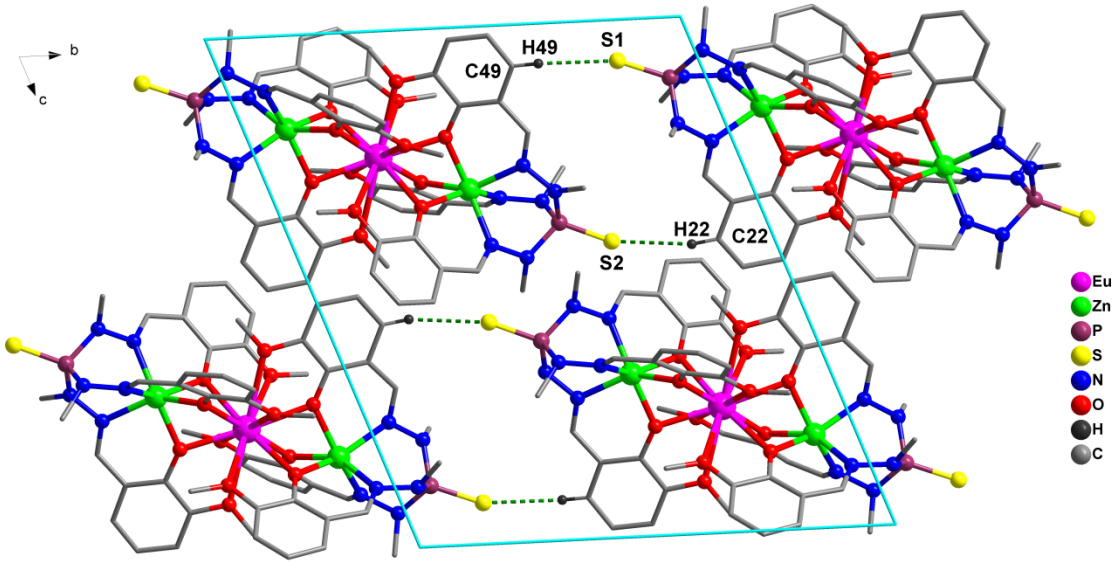


Fig. S8 Packing diagram of compound **4** along crystallographic ‘a’ axis of the unit cell.

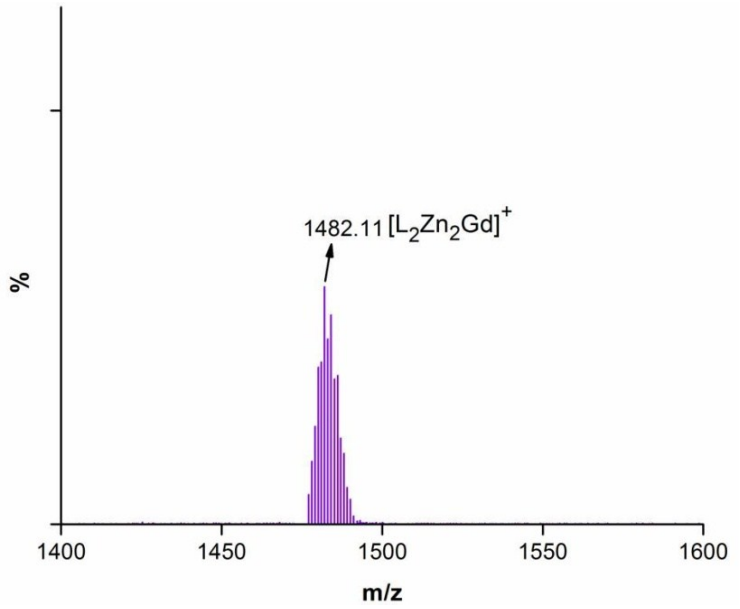


Fig. S9 ESI-MS of compound **1**. (shows the isotopic distribution pattern of molecular ion peak)

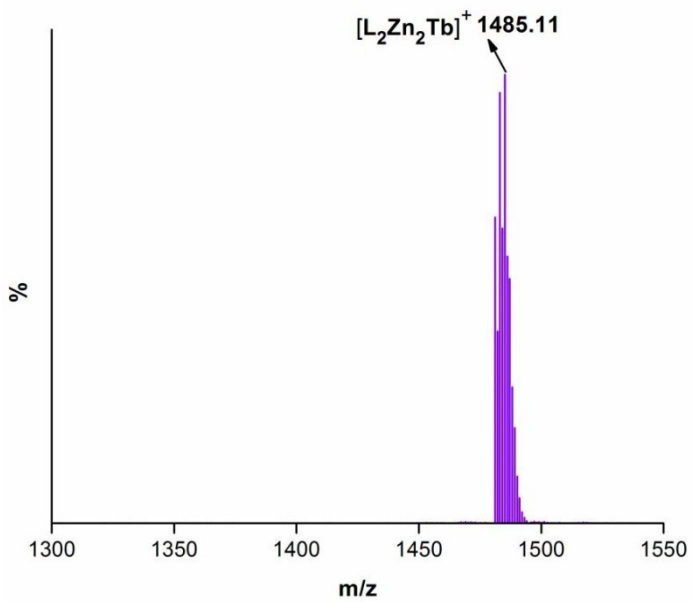


Fig. S10 ESI-MS of compound **2**. (Shows the isotopic distribution pattern of molecular ion peak)

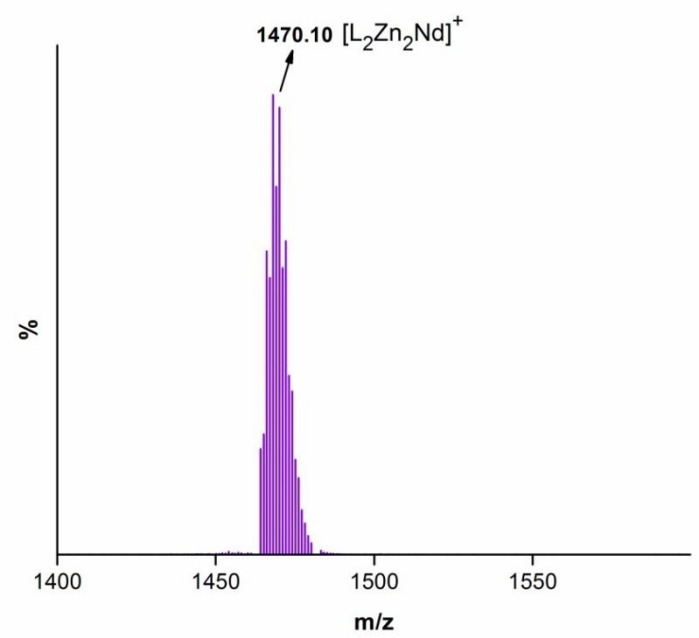


Fig. S11 ESI-MS of compound **3**. (Shows the isotopic distribution pattern of molecular ion peak)

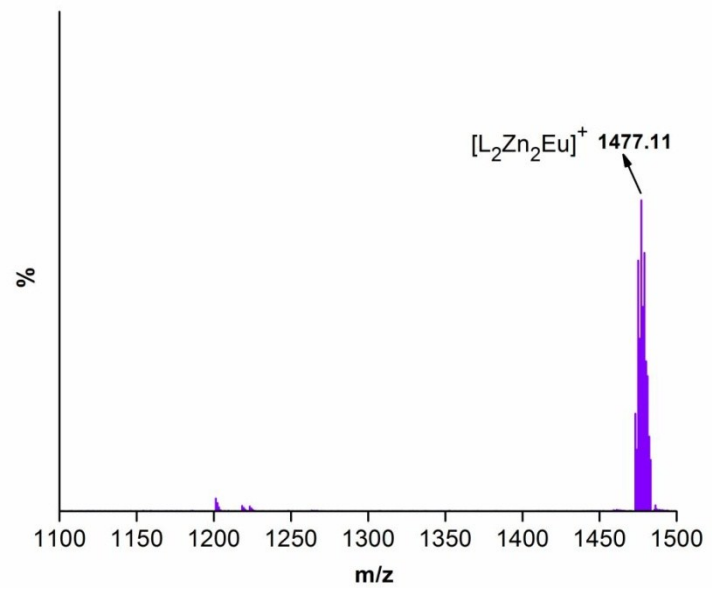


Fig. S12 ESI-MS of compound **4**. (Shows the isotopic distribution pattern of molecular ion peak).

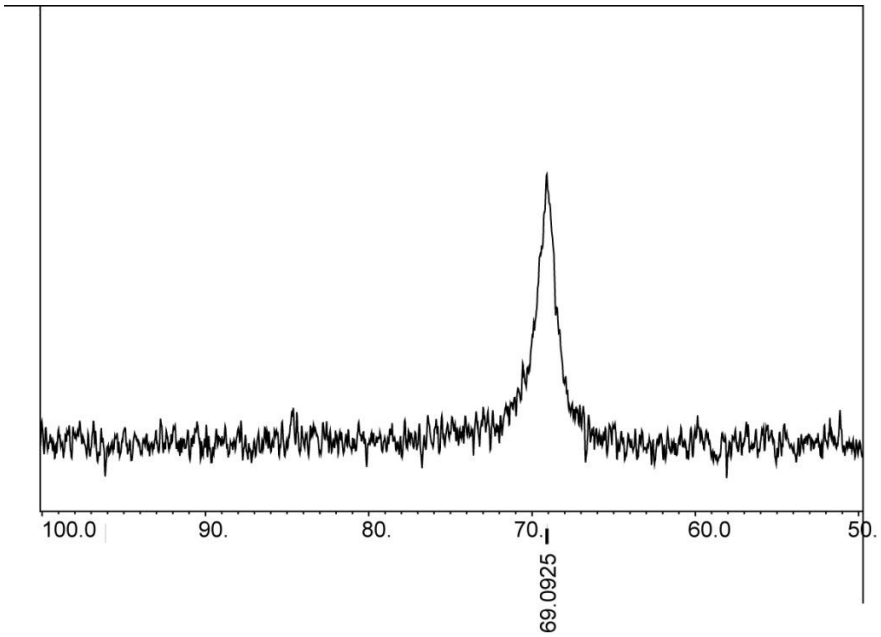


Fig. S13 ^{31}P $\{^{1}H\}$ NMR spectrum of compound **1**

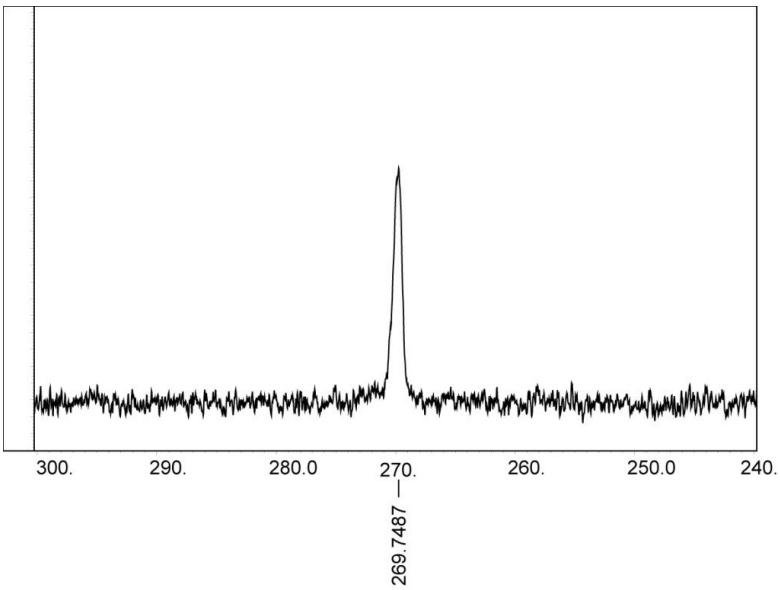


Fig. S14 ^{31}P $\{^{1}H\}$ NMR spectrum of compound **2**

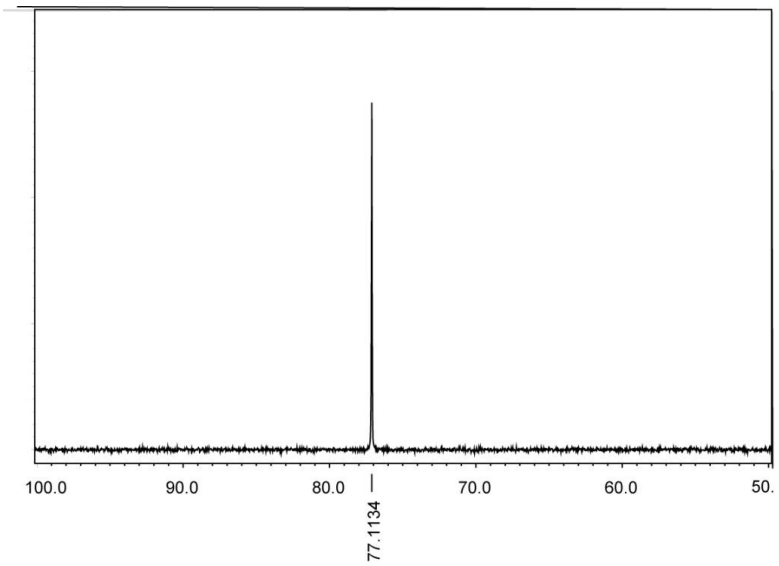


Fig. S15 ^{31}P $\{^{1}H\}$ NMR spectrum of compound **3**

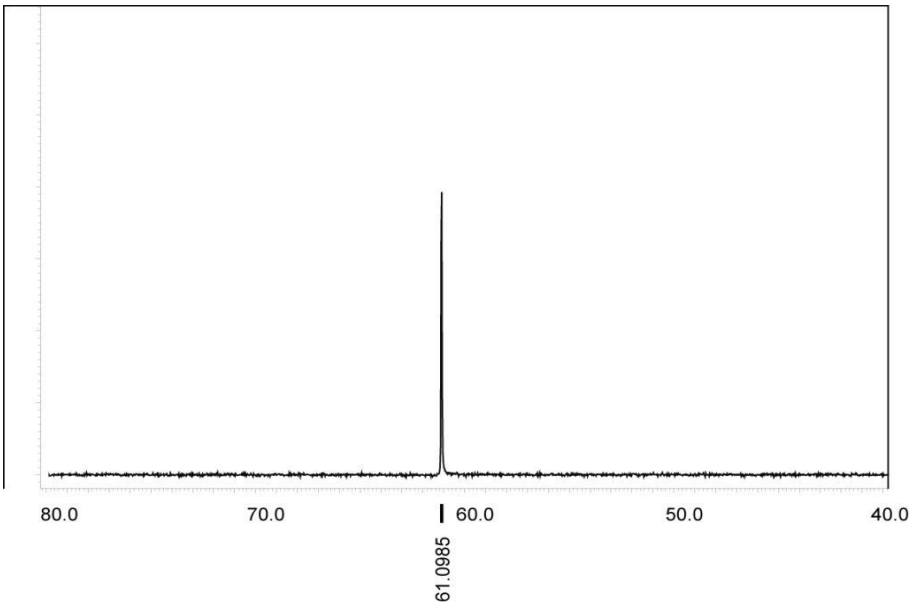


Fig. S16 ^{31}P $\{^{1}H\}$ NMR spectrum of compound **4**.

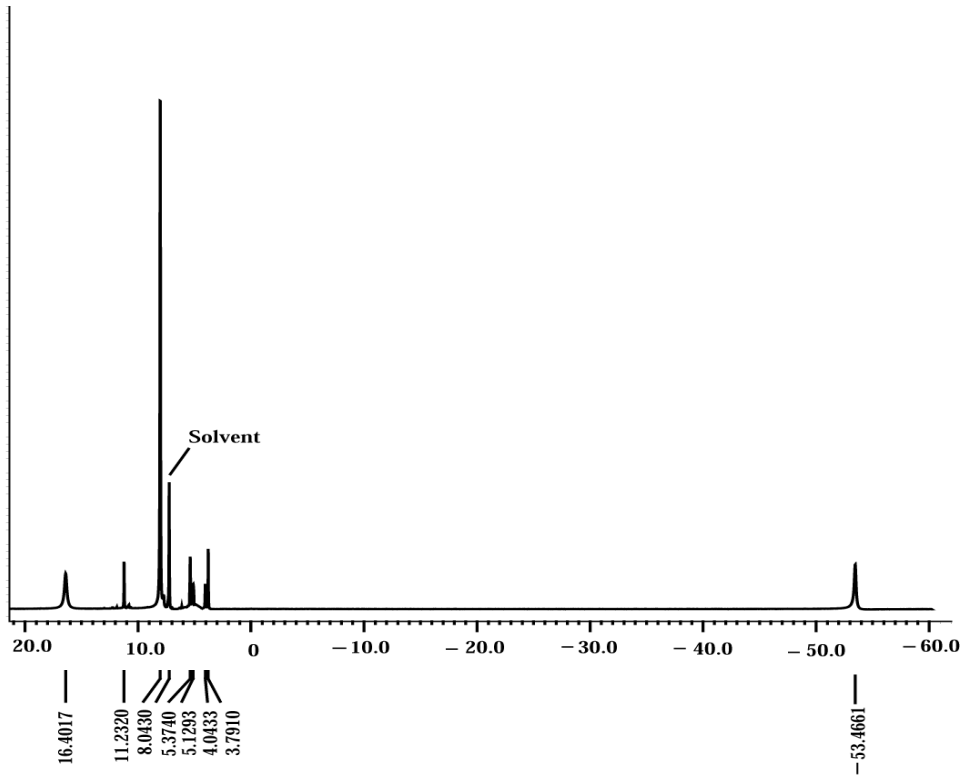


Fig. S17 ^{1}H NMR spectrum of **2** in $CDCl_3$ at 298 K

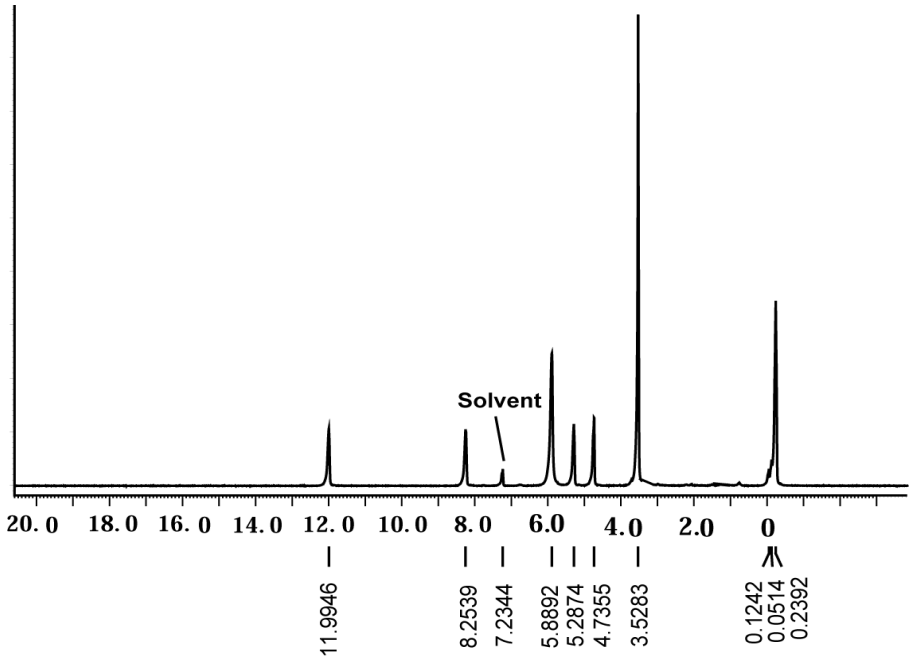


Fig. S18 ^{1}H NMR spectrum of **4** in $CDCl_3$ at 298 .

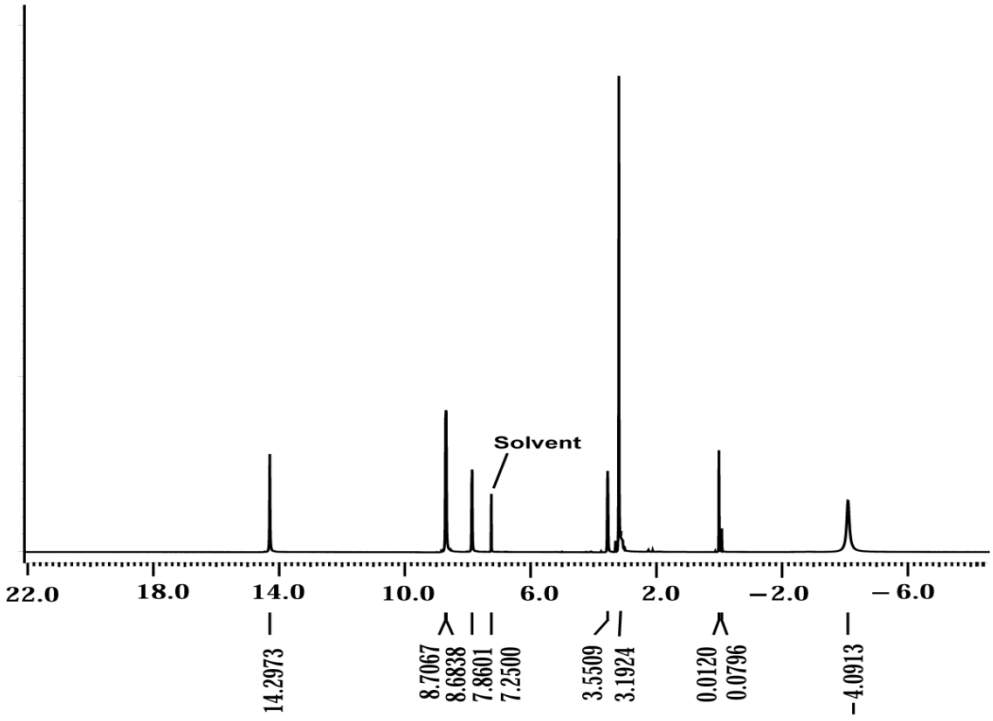


Fig. S19 ^{1}H NMR spectrum of **3** in $CDCl_3$ at 298 K.