Electronic supplementary information for Journal of Materials Chemistry

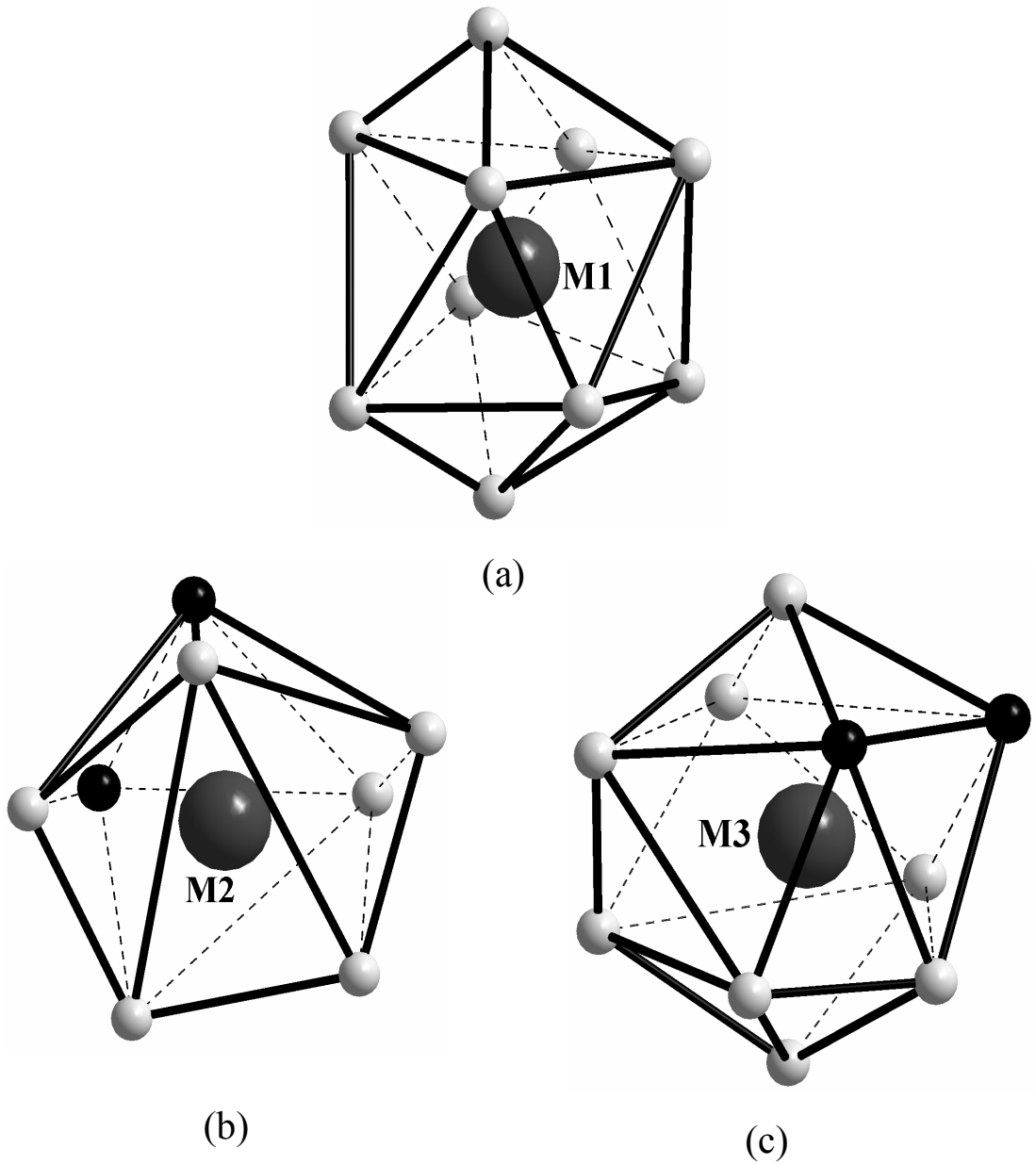
Hydrothermal Synthesis, Structure and Luminescent Properties of One-dimensional Lanthanide benzenedicarboxylates, $[M(NO_3)M_2(C_{12}H_8N_2)_2][(C_8H_4O_4)_4].H_2O$, (M=La, Pr), Possessing Infinite Ln – O – Ln linkages

A Thirumurugan[1] and Srinivasan Natarajan[2,*]

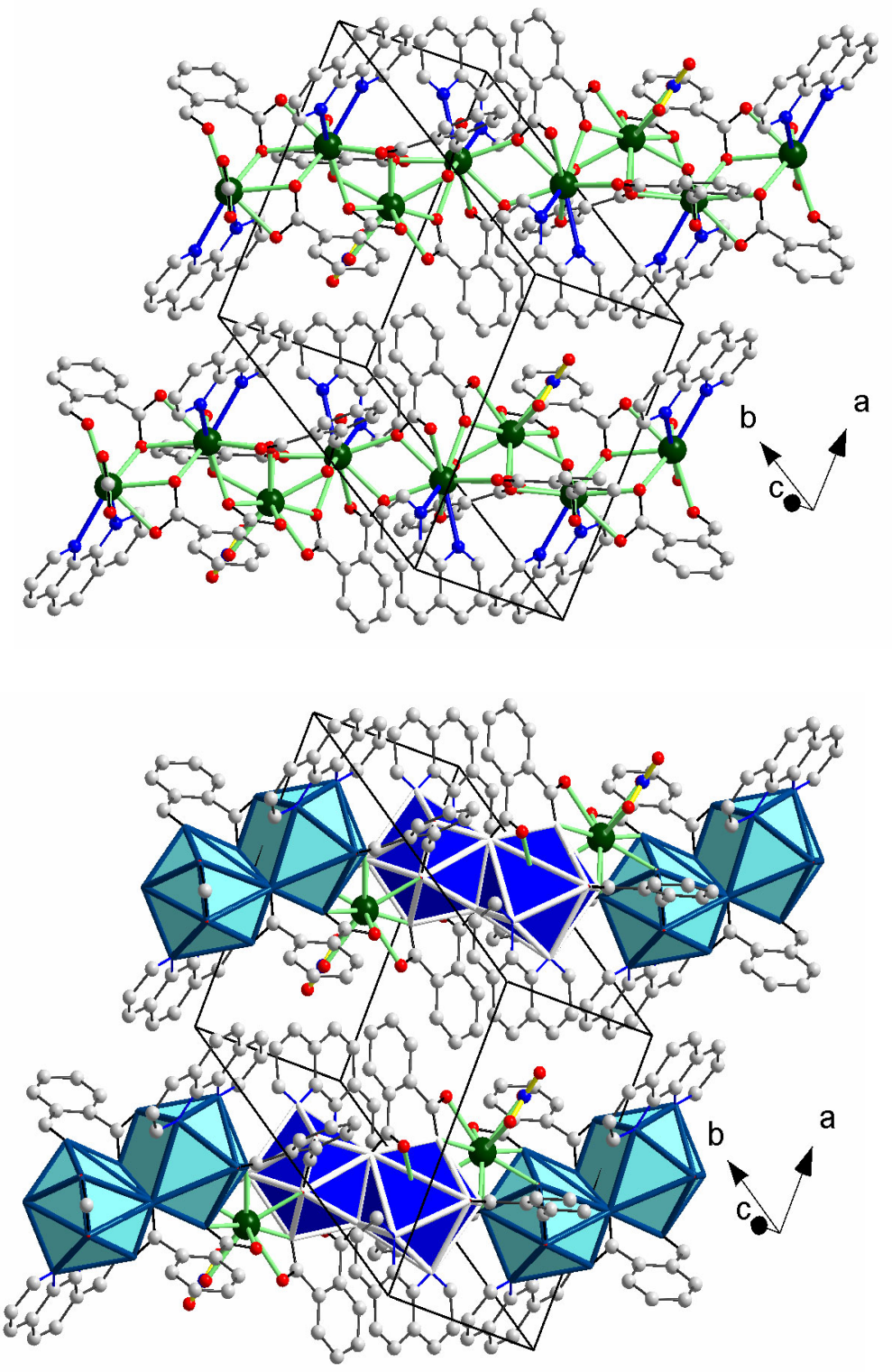
[1] Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur P.O., Bangalore 560064, India

[2] Framework Solids Laboratory, Solid State And Structural Chemistry Unit, Indian Institute of Science, Bangalore-560012, India

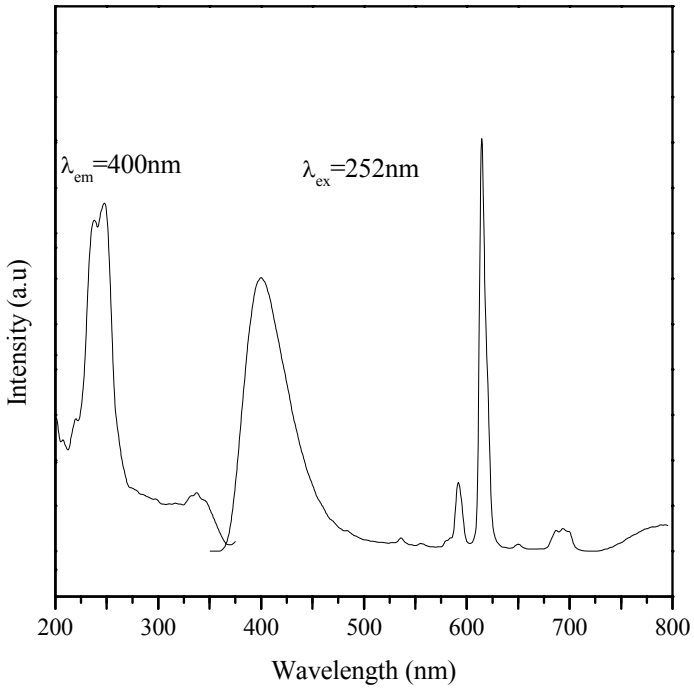
[*] E-mail: snatarajan@sscu.iisc.ernet.in



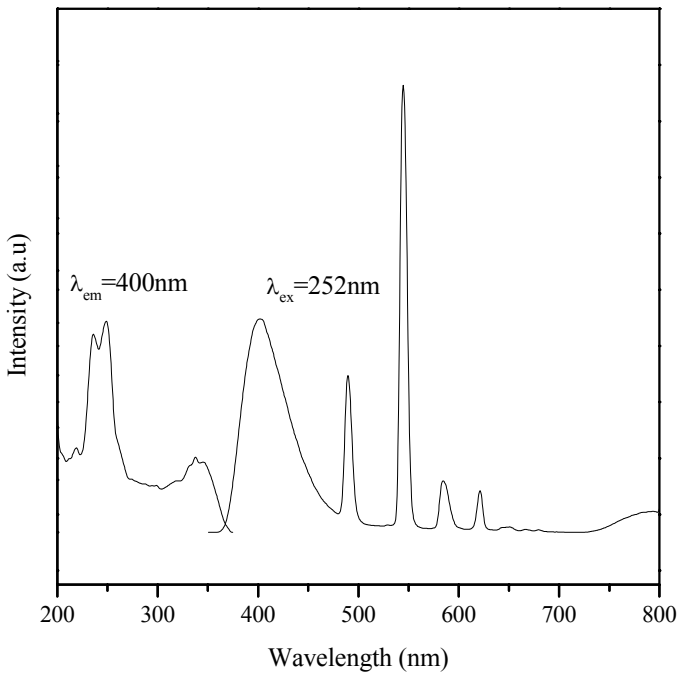
Coordination Environment around three crystallographically different metal sites. (a) and (c) distorted square anti-prism, (b) distorted dodecahedra.



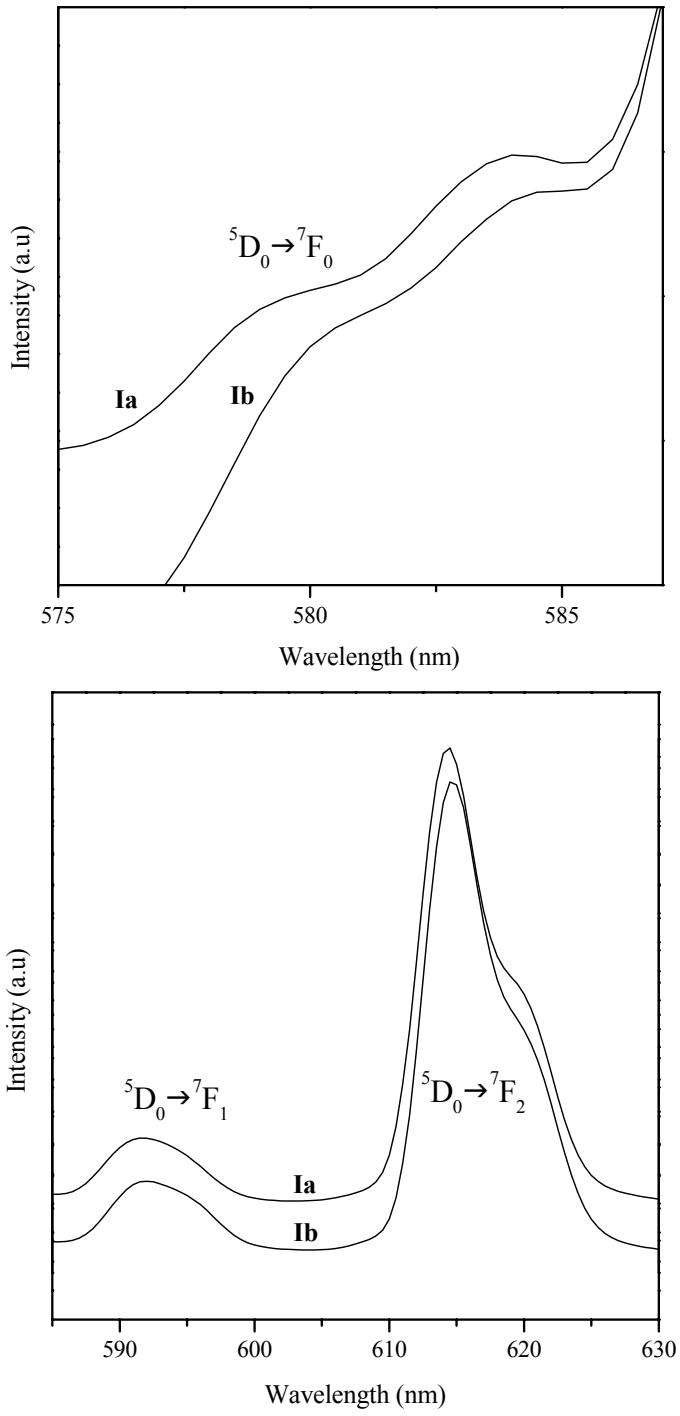
Crystal packing diagram in **I** and **II**



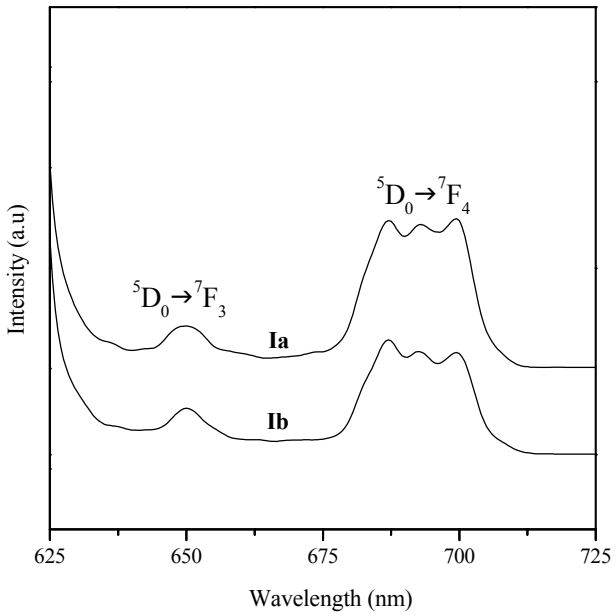
Room Temperature Photoluminescence spectra of Eu doped **I**



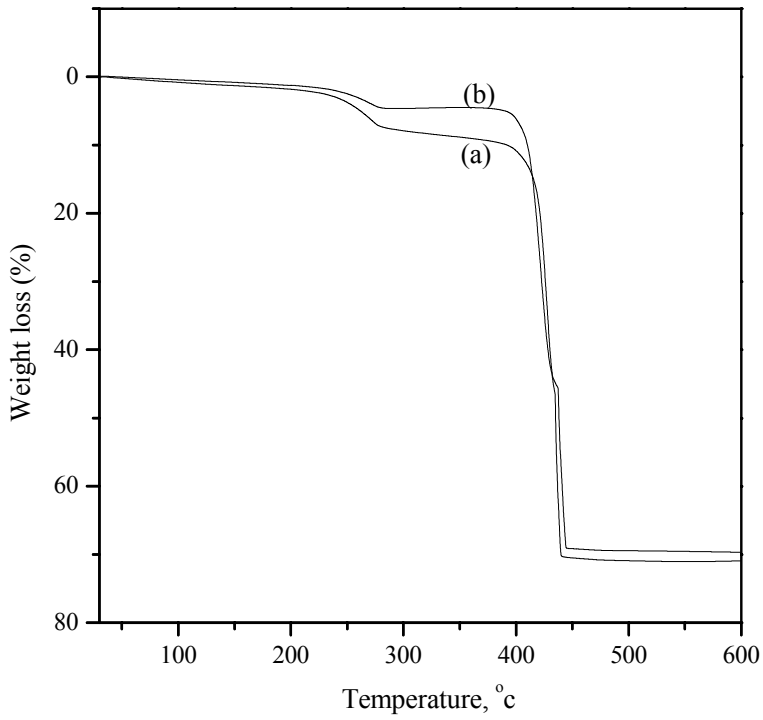
Room Temperature Photoluminescence spectra of Tb doped **I**



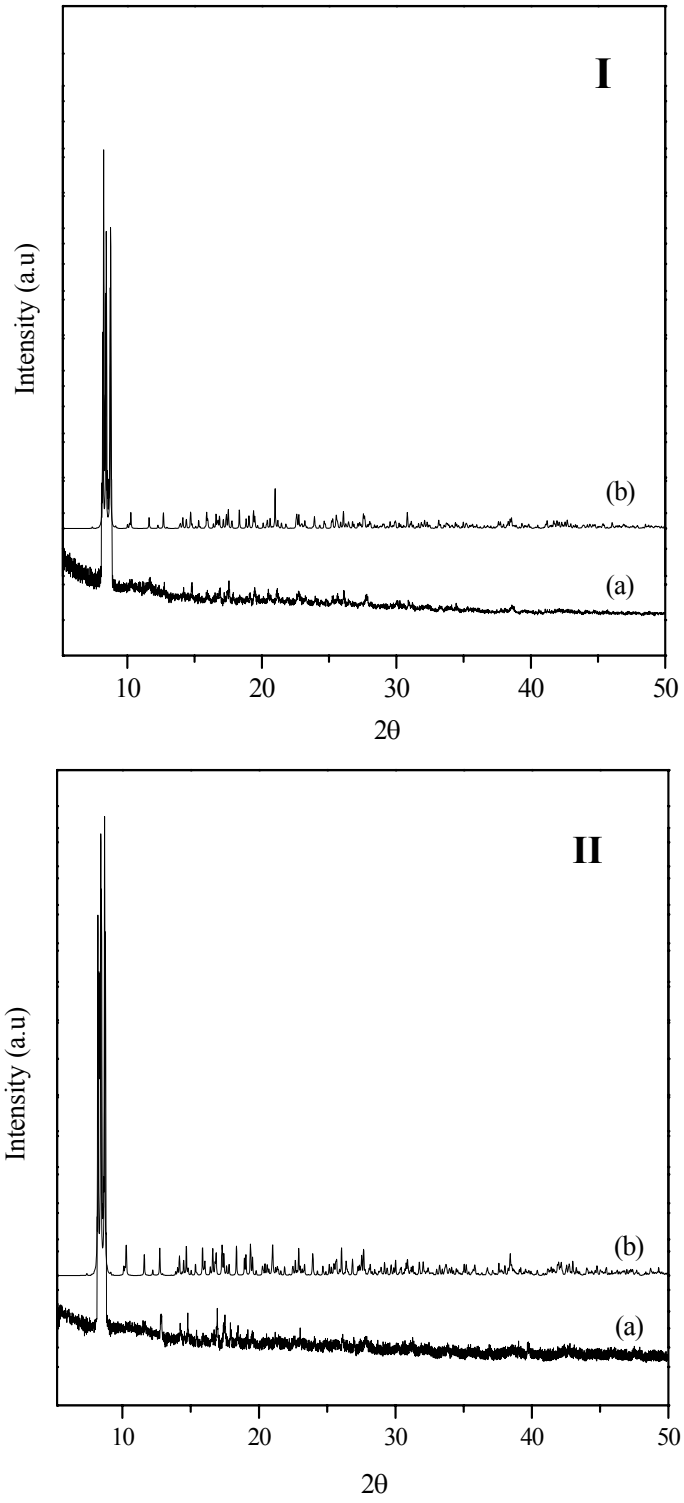
Room Temperature Photoluminescence spectra of Eu doped **I** (in selected region)



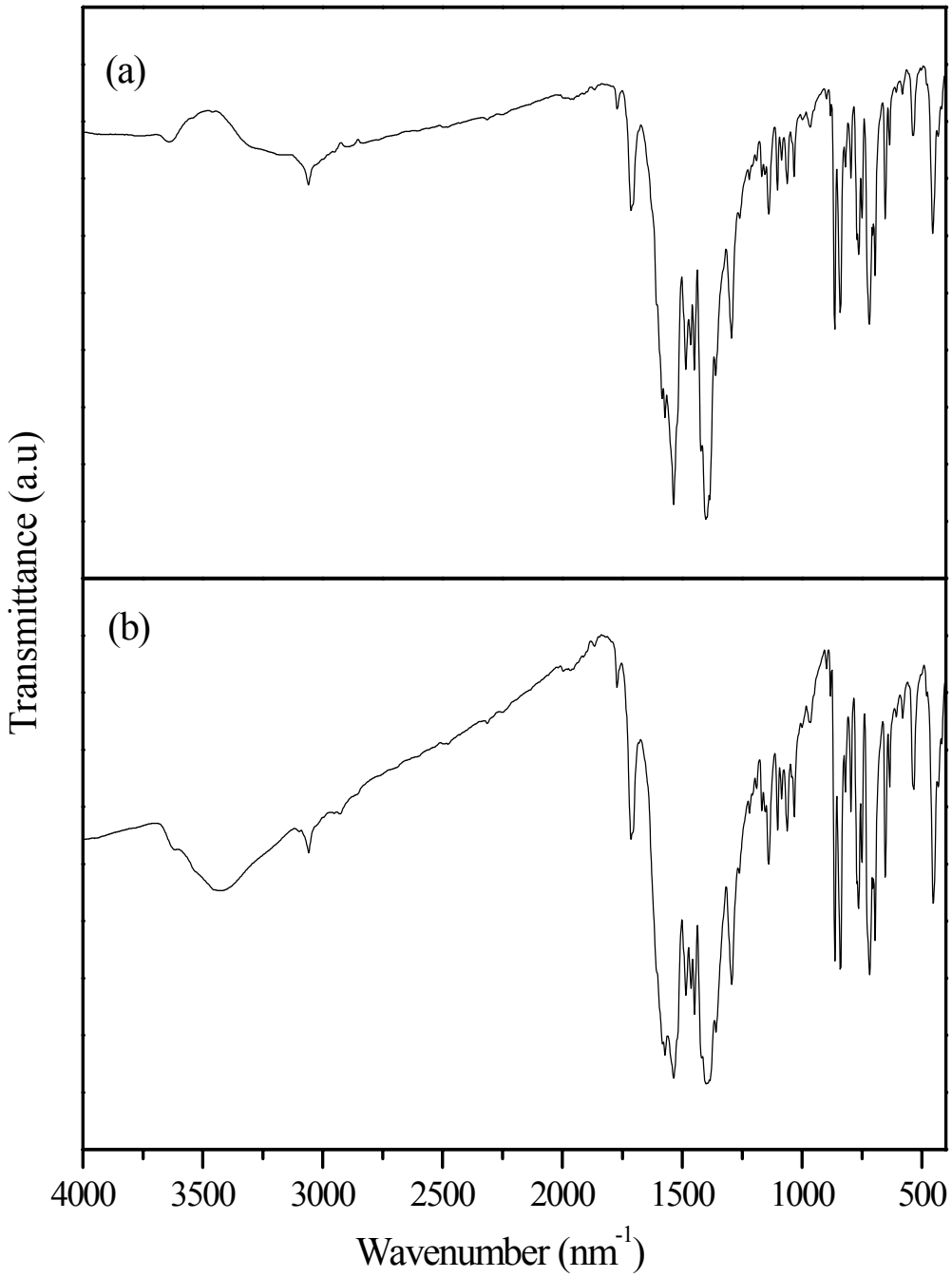
Room Temperature Photoluminescence spectra of Eu doped **I** (in selected region)



Thermogravimetric analysis for (a) **I** and (b) **II**



Experimental (a) and simulated (b) powder XRD pattern for **I** and **II**



Infra Red spectra for (a) **I** and (b) **II**

Table 1. Selected bond distances in $[M(NO_3)M_2(C_{12}H_8N_2)_2][(C_8H_4O_4)_4].H_2O$ (M = La, Pr).

Bond	Distance (Å)		Bond	Distance (Å)		Bond	Distance (Å)	
	La	Pr		La	Pr		La	Pr
M(1)-O(1)	2.693(3)	2.692(4)	M(2)-O(1)	2.544(3)	2.498(4)	M(3)-O(3)	2.598(3)	2.575(4)
M(1)-O(2)	2.550(4)	2.507(4)	M(2)-O(7)	2.657(3)	2.630(4)	M(3)-O(5)	2.586(3)	2.546(4)
M(1)-O(3)	2.639(3)	2.601(4)	M(2)-O(11)	2.532(4)	2.480(4)	M(3)-O(6)	2.655(3)	2.632(4)
M(1)-O(4)	2.554(4)	2.506(4)	M(2)-O(12)	2.555(4)	2.499(4)	M(3)-O(15)	2.591(4)	2.537(4)
M(1)-O(5)	2.586(3)	2.553(4)	M(2)-O(12)#1	2.498(4)	2.456(4)	M(3)-O(16)	2.562(4)	2.521(4)
M(1)-O(6)	2.547(4)	2.506(4)	M(2)-O(13)	2.571(4)	2.525(5)	M(3)-O(17)	2.699(4)	2.678(4)
M(1)-O(7)	2.581(3)	2.546(4)	M(2)-N(1)	2.703(5)	2.664(5)	M(3)-O(18)	2.729(4)	2.696(4)
M(1)-O(8)	2.567(4)	2.536(4)	M(2)-N(2)	2.747(5)	2.702(5)	M(3)-O(18)#2	2.535(3)	2.510(3)
M(1)-O(9)	2.609(4)	2.564(5)	O(12)-C (48)	1.293(6)	1.296(7)	M(3)-N(3)	2.708(4)	2.662(5)
M(1)-O(10)	2.631(4)	2.590(4)	O(14)-C (48)	1.230(7)	1.227(8)	M(3)-N(4)	2.707(4)	2.670(5)
O(1)-C (41)	1.289(6)	1.284(7)	O(7)-C (51)	1.292(6)	1.293(7)	O(6)-C (58)	1.290(6)	1.298(7)
O(2)-C (41)	1.246(6)	1.254(6)	O(11)-C (51)	1.250(6)	1.258(7)	O(17)-C (58)	1.248(6)	1.244(7)
O(3)-C (71)	1.286(6)	1.277(7)	O(4)-C (61)	1.271(6)	1.257(7)	O(5)-C (68)	1.281(6)	1.289(7)
O(8)-C (71)	1.270(6)	1.256(7)	O(13)-C (61)	1.246(6)	1.273(7)	O(16)-C (68)	1.251(6)	1.261(6)
O(4)-C (61)	1.271(6)	1.271(6)	N(1)-C (10)	1.323(8)	1.323(9)	O(15)-C (78)	1.247(6)	1.251(7)
O(9)-N(81)	1.271(6)	1.268(7)	N(1)-C (11)	1.372(8)	1.376(8)	O(18)-C (78)	1.295(6)	1.310(7)
O(10)-N(81)	1.259(7)	1.227(7)	N(2)-C (1)	1.325(8)	1.324(9)	N(3)-C (30)	1.330(7)	1.335(7)
N(81)-O(82)	1.228(6)		N(2)-C (12)	1.354(8)	1.366(8)	N(3)-C (31)	1.362(6)	1.372(7)
						N(4)-C (21)	1.324(7)	1.341(7)
						N(4)-C (32)	1.363(7)	1.358(7)

Symmetry transformations used to generated equivalent atoms: #1 -x,-y+1,-z+1 #2 -x+1,-y,-z

Table 2. Selected bond angles for $[M(NO_3)M_2(C_{12}H_8N_2)_2][(C_8H_4O_4)_4].H_2O$ (M = La, Pr).

Angle	Amplitude (°)		Angle	Amplitude (°)		Angle	Amplitude (°)	
	La	Pr		La	Pr		La	Pr
O(2)-M(1)-O(1)	49.56(11)	49.92(12)	O(1)-M(2)-O(7)	67.80(10)	67.44(12)	O(5)-M(3)-O(3)	66.32(10)	66.20(12)
O(3)-M(1)-O(1)	167.09(10)	167.15(12)	O(11)-M(2)-O(1)	81.60(12)	80.41(13)	O(3)-M(3)-O(6)	60.86(10)	60.55(12)
O(4)-M(1)-O(1)	62.94(11)	63.45(12)	O(1)-M(2)-O(12)	67.99(11)	68.85(13)	O(15)-M(3)-O(3)	151.69(12)	152.05(13)
O(5)-M(1)-O(1)	123.61(10)	124.03(11)	O(12)#1-M(2)-O(1)	124.68(12)	123.78(14)	O(16)-M(3)-O(3)	70.01(11)	70.41(13)
O(6)-M(1)-O(1)	128.25(11)	127.69(12)	O(1)-M(2)-O(13)	108.40(11)	108.50(13)	O(3)-M(3)-O(17)	108.56(11)	108.79(12)
O(7)-M(1)-O(1)	66.74(10)	65.81(12)	O(1)-M(2)-N(1)	147.61(14)	146.2(2)	O(3)-M(3)-O(18)	102.74(10)	102.30(12)
O(8)-M(1)-O(1)	120.24(11)	119.86(13)	O(1)-M(2)-N(2)	137.09(14)	135.9(2)	O(18)#2-M(3)-O(3)	66.29(10)	66.94(12)
O(9)-M(1)-O(1)	68.08(12)	67.41(13)	O(11)-M(2)-O(7)	50.45(11)	51.39(12)	O(3)-M(3)-N(3)	125.01(13)	124.94(14)
O(10)-M(1)-O(1)	102.01(12)	101.85(14)	O(12)-M(2)-O(7)	135.75(10)	136.29(12	O(3)-M(3)-N(4)	131.68(13)	131.7(2)
O(2)-M(1)-O(3)	117.55(11)	117.31(13)	O(12)#1-M(2)-O(7)	147.70(11)	147.95(13)	O(5)-M(3)-O(6)	67.69(11)	66.99(12)
O(2)-M(1)-O(4)	83.82(12)	82.69(14)	O(13)-M(2)-O(7)	78.14(11)	78.16(13)	O(5)-M(3)-O(15)	135.28(11)	134.70(12)
O(2)-M(1)-O(5)	139.71(13)	140.06(14)	O(7)-M(2)-N(1)	80.00(14)	79.1(2)	O(16)-M(3)-O(5)	50.80(11	51.88(12)
O(6)-M(1)-O(2)	150.29(12)	150.42(14)	O(7)-M(2)-N(2)	123.26(13)	123.1(2)	O(5)-M(3)-O(17)	77.61(12)	77.27(13)
O(2)-M(1)-O(7)	116.12(11)	115.62(12)	O(11)-M(2)-O(12)	123.50(12)	120.4(2)	O(5)-M(3)-O(18)	144.52(11)	143.96(12)
O(2)-M(1)-O(8)	78.01(12)	77.09(14)	O(12)#1-M(2)-O(11)	149.69(12)	150.82(14)	O(18)#2-M(3)-O(5)	126.74(11)	127.44(13)
O(2)-M(1)-O(9)	76.24(14)	76.2(2)	O(11)-M(2)-O(13)	119.97(13)	121.5(2)	O(5)-M(3)-N(3)	112.71(13)	113.54(14)
O(2)-M(1)-O(10)	72.84(14)	72.2(2)	O(11)-M(2)-N(1)	75.13(14)	75.2(2)	O(5)-M(3)-N(4)	68.55(12)	68.67(14)
O(4)-M(1)-O(3)	120.76(11)	120.37(13)	O(11)-M(2)-N(2)	79.74(13)	78.8(2)	O(15)-M(3)-O(6)	106.11(12)	106.34(14)
O(5)-M(1)-O(3)	65.71(10)	65.71(11)	O(12)#1-M(2)-O(12)	64.38(13)	63.9(2)	O(16)- M(3)-O(6)	112.24(11)	112.61(13)
O(6)-M(1)-O(3)	61.70(11)	61.85(13)	O(12)-M(2)-O(13)	114.51(13)	116.4(2)	O(6)- M(3)-O(17)	48.66(10)	49.17(12)
O(7)-M(1)-O(3)	125.98(10)	126.78(12)	O(12)-M(2)-N(1)	144.25(14)	144.5(2)	O(6)-M(3)-O(18)	77.49(10)	77.58(12)
O(8)-M(1)-O(3)	50.24(12)	51.01(13)	O(12)-M(2)-N(2)	91.28(14)	89.2(2)	O(18)#2-M(3)-O(6)	107.47(11)	107.82(11)
O(9)-M(1)-O(3)	110.55(12)	110.61(13)	O(12)#1-M(2)-O(13)	69.66(12)	69.81(14)	O(6)-M(3)-N(3)	174.03(12)	174.44(14)
O(10)-M(1)-O(3)	70.06(13)	69.63(14)	O(12)#1-M(2)-N(1)	84.80(14)	87.2(2)	O(6)-M(3)-N(4)	115.22(12)	114.85(14)
O(4)-M(1)-O(5)	64.64(11)	65.51(13)	O(12)#1-M(2)-N(2)	70.55(14)	72.3(2)	O(16)-M(3)-O(15)	136.00(12)	135.32(14)
O(6)-M(1)-O(4)	123.37(11)	124.60(13)	O(13)-M(2)-N(1)	66.38(14)	66.9(2)	O(15)-M(3)-O(17)	68.29(12)	67.80(13)
O(4)-M(1)-O(7)	70.49(11)	71.43(13)	O(13)-M(2)-N(2)	114.42(14)	115.6(2)	O(15)- M (3)-O(18)	48.95(11)	49.75(12)
O(4)-M(1)-O(8)	88.34(12)	86.58(14)	N(1)-M(2)-N(2)	60.1(2)	61.1(2)	O(18)#2-M(3)-O(15)	97.78(12)	97.68(13)
O(4)-M(1)-O(9)	128.51(12)	128.96(14)	O(14)-C(48)-O(12)	121.2(5)	121.7(6)	O(15)- M(3)-N(3)	69.21(14)	69.2(2)
O(4)-M(1)-O(10)	156.51(14)	154.4(2)	O(11)-C(51)-O(7)	121.1(5)	120.9(6)	O(15)- M(3)-N(4)	76.14(13)	75.6(2)
O(6)-M(1)-O(5)	69.30(11)	68.81(12)	O(13)-C(61)-O(4)	120.9(5)	121.1(6)	O(16)- M(3)-O(17)	125.21(12)	125.63(13)
O(7)-M(1)-O(5)	77.67(10)	77.70(12)	C(10)-N(1)-C(11)	118.1(6)	117.2(6)	O(16)- M(3)-O(18)	160.18(10)	159.52(11)
O(8)-M(1)-O(5)	76.73(12)	77.48(13)	C(1)-N(2)-C(12)	117.3(6)	117.1(6)	O(18)#2-M(3)-O(16)	90.73(11)	90.67(13)
O(5)-M(1)-O(9)	143.06(13)	142.82(14)				O(16)- M(3)-N(3)	70.85(14)	70.4(2)
O(5)-M(1)-O(10)	134.20(12)	133.96(14)				O(16)- M(3)-N(4)	68.66(13)	68.8(2)
O(6)-M(1)-O(7)	69.04(10)	69.70(12)				O(17)- M(3)-O(18)	74.38(11)	74.68(12)
O(6)-M(1)-O(8)	111.46(11)	112.38(13)				O(18)#2-M(3)-O(17)	140.87(12)	140.99(13)
O(6)-M(1)-O(9)	76.87(12)	77.10(14)				O(17)-M(3)-N(3)	125.37(13)	125.28(14)
O(6)-M(1)-O(10)	80.00(13)	80.95(14)				O(17)-M(3)-N(4)	77.12(13)	76.43(14)

O(8)-M (1)-O(7)	152.01(12)	152.01(13)	O(18)#2-M(3)-O(18)	69.61(13)	69.00(14)
O(7)-M a(1)-O(9)	76.73(12)	76.92(13)	N(4)-M(3)-O(18)	101.20(13)	101.08(14)
O(7)-M (1)-O(10)	122.19(14)	123.7(2)	N(5)-M(3)-O(18)	124.20(12)	124.49(14)
O(8)-M (1)-O(9)	131.23(13)	131.07(14)	O(18)#2-M(3)-N(3)	77.25(12)	76.44(13)
O(8)-M(1)-O(10)	84.30(14)	83.4(2)	O(18)#2-M(3)-N(4)	136.94(13)	137.02(14)
O(9)-M(1)-O(10)	48.71(14)	49.6(2)	N(4)-M(3)-N(3)	60.57(14)	61.3(2)
O(2)-C(41)-O(1)	120.5(5)	120.2(6)	O(17)-C(58)-O(6)	120.7(5)	120.7(6)
O(8)-C(71)-O(3)	119.8(5)	121.7(6)	O(16)-C(68)-O(5)	121.4(5)	119.7(5)
O(10)-N(81)-O(9)	117.4(5)	116.8(6)	O(15)-C(78)-O(18)	120.6(5)	118.9(6)
O(82)-N(81)-O(9)	119.9(6)	120.6(7)	C(30)-N(3)-C(31)	117.5(5)	116.3(5)
O(82)-N(81)-O(10)	122.8(6)	122.6(6)	C(21)-N(4)-C(32)	117.3(5)	117.3(5)

Symmetry transformations used to generated equivalent atoms: #1 -x,-y+1,-z+1 #2 -x+1,-y,-z

Table 3. Cell Parameters for **Ib** and **Id** (from single crystal XRD)

Structure parameter	**Ib**	**Id**
Crystal system	Triclinic	Triclinic
a./Å	12.8082(5)	12.7888(3)
b /Å	13.1203(4)	13.1131(4)
c /Å	17.5115(4)	17.5130(3)
α /°	89.0580(22)	88.957(16)
β /°	79.7230(23)	79.6730(15)
γ /°	65.8600(23)	65.8390(23)
V /Å^3	2636.07(6)	2631.28(3)
GOF	0.84	1.01