Mg(II)-Induced Second-Harmonic Generation Based on Bis-monodentate Coordination Mode of Thiobarbiturate

Yun Gong, Zhi Hao, Jing Hua Li, Tao Wu and Jian Hua Lin*

Department of Applied Chemistry, College of Chemistry and Chemical Engineering, Chongqing University, Chongqing 400030, P. R. China. Fax (Tel.): +86-023-65102316

E-mail: jhlin@cqu.edu.cn or jhlin@pku.edu.cn

Table S1 Selected bond lengths (Å) and angles (º) for complexes **1-3**

Complex 1			
Mg(1)-O(2)	2.044(6)	Mg(1)-O(1)	2.111(4)
Mg(1)-O(2)#1	2.044(6)	C(2)-C(3)	1.398(7)
S(1)=C(1)	1.629(8)	O(1)=C(2)	1.275(7)
C(1)-N(1)	1.364(6)	N(1)-C(2)	1.373(7)
O(1)#2-Mg(1)-O(1)#1	173.0(2)	O(2)#1-Mg(1)-O(1)	86.51(12)
C(1)-N(1)-C(2)	126.5(5)	N(1)-C(2)-C(3)	117.7(5)
N(1)-C(1)-S(1)	123.7(3)	O(1)-C(2)-N(1)	117.2(4)
Complex 2			
Ni(1)-O(2)	2.0098	Ni(1)-O(1)	2.109(4)
Ni(1)-O(1)#1	2.109(4)	C(3)-C(2)	1.390(7)
S(1)=C(1)	1.643(9)	O(1)=C(2)	1.255(8)
C(1)-N(1)	1.355(7)	C(2)-N(1)	1.405(8)
O(1)#1-Ni(1)-O(1)#2	173.2(4)	O(2)#1-Ni(1)-O(1)	86.6(3)
C(1)-N(1)-C(2)	125.6(5)	N(1)-C(2)-C(3)	117.0(5)
N(1)-C(1)-S(1)	122.8(4)	O(1)-C(2)-N(1)	116.3(5)

Complex 3			
Co(1)-O(3)	2.030(2)	Co(1)-O(2)	2.130(2)
Co(1)-S(1)#3	2.6577(10)	S(1)=C(4)	1.686(4)
O(1)=C(1)	1.272(4)	O(2)=C(3)	1.274(4)
N(1)-C(1)	1.379(5)	N(1)-C(4)	1.351(5)
N(2)-C(4)	1.337(4)	N(2)-C(3)	1.390(5)
C(2)-C(3)	1.378(5)	C(2)-C(1)	1.396(5)
O(3)-Co(1)-O(2)	89.96(11)	O(3)-Co(1)-O(2)#4	90.04(11)
O(2)-Co(1)-O(2)#4	180.00(1)	S(1)#3-Co(1)-S(1)#5	180.0
O(2)-Co(1)-S(1)#5	88.03(7)	O(2)#4-Co(1)-S(1)#5	91.97(7)
N(2)-C(4)-S(1)	122.4(3)	O(1)-C(1)-N(1)	117.3(3)

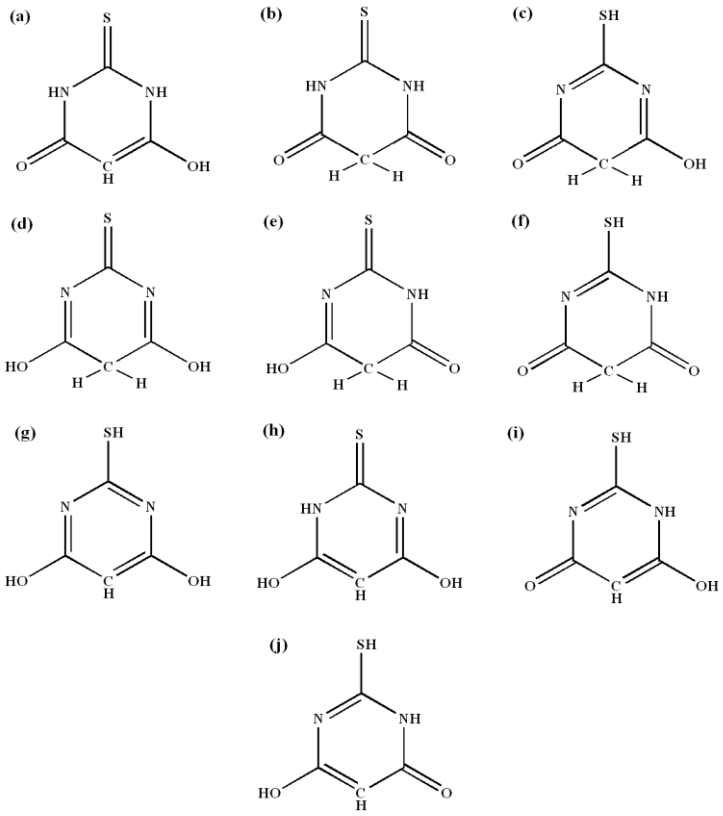
Symmetry transformations used to generate equivalent atoms:

#1 y,-x+1,-z	#2 -y+1,x,-z	#3 x,y,z+1
#4 -x+1,-y+1,-z+1	#5 -x+1,-y+1,-z	

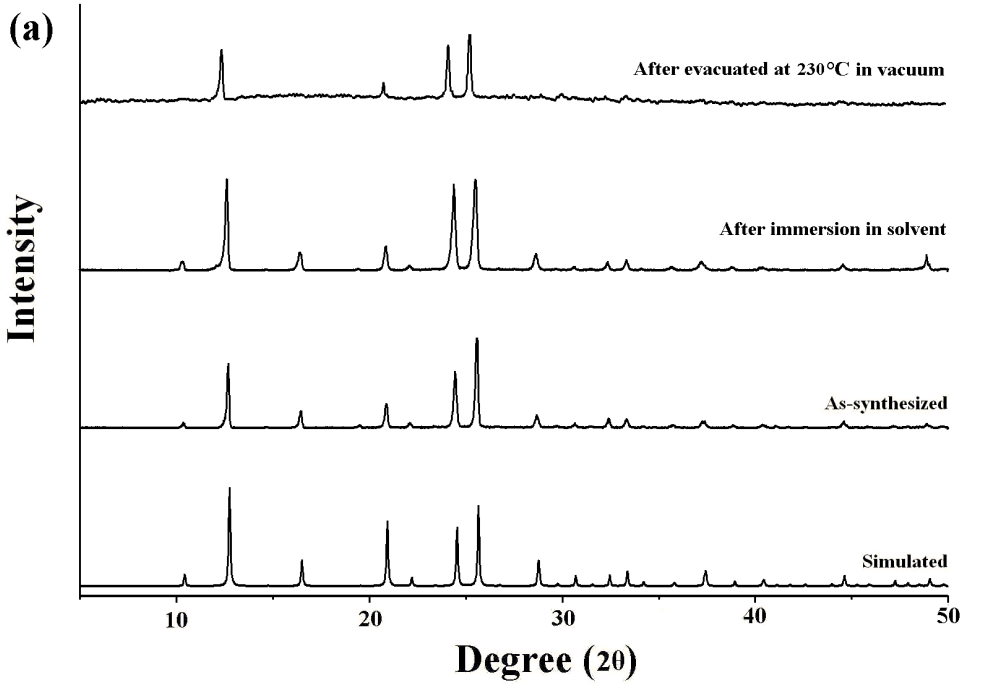
Table S2 Selected bond lengths (Å) for the different isomers of **H_3L** in previous work [1]

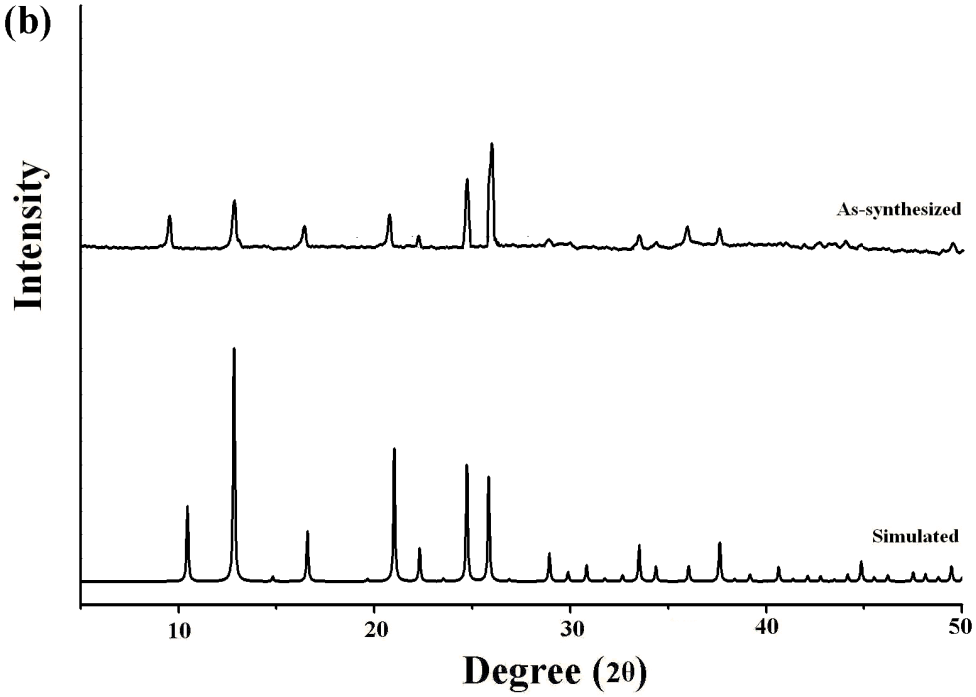
II form			
S=C	*1.674(3)*	*C=O*	*1.246(4)*
C-OH	*1.308(4)*	*C-NH*	*1.342(5)-1.396(4)*
C-CH	*1.357(5)-1.397(5)*		
III form			
S=C	1.6394(2)	C=O	1.211(2)-1.216(2)
C-NH	1.365(2)- 1.378(2)	C-CH_2	1.488(3) -1.498(3)
IV form			
S=C	1.657(4)-1.677(4)	C=O	1.215(4)-1.248(5)
C-NH	1.335(4) -1.405(5)	C-OH	1.323(4)
C-CH_2	1.491(5) - 1.493(5)	C-CH	1.348(5) -1.408(5)
V form			

S=C	1.632(5) -1.665(5)	C=O	1.197(6)-1.224(6)
C-NH	1.347(6) -1.392(6)	C-CH_2	1.479(7) - 1.531(9)
VI form			
S=C	1.638(2) -1.656(2)	C=O	1.204(2) -1.217(2)
C-NH	1.356(3) - 1.390(3)	C-CH_2	1.487(3) - 1.494(3)
Hydrate			
S=C	1.658(2)	C=O	1.243(2)
C-OH	1.313(2)	C-NH	1.347(3)-1.378(3)
C-CH	1.345(3) -1.409(3)		



Scheme S1 Different tautomeric forms of **H_3L**





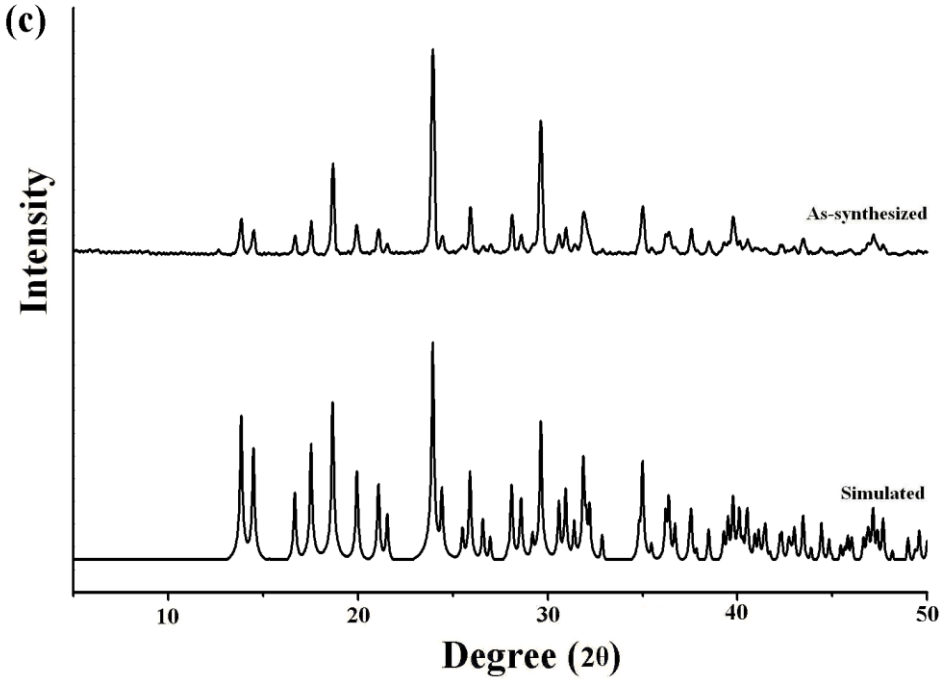


Fig.S1 The PXRD patterns of complexes **1** (**a**), **2** (**b**) and **3** (**c**).

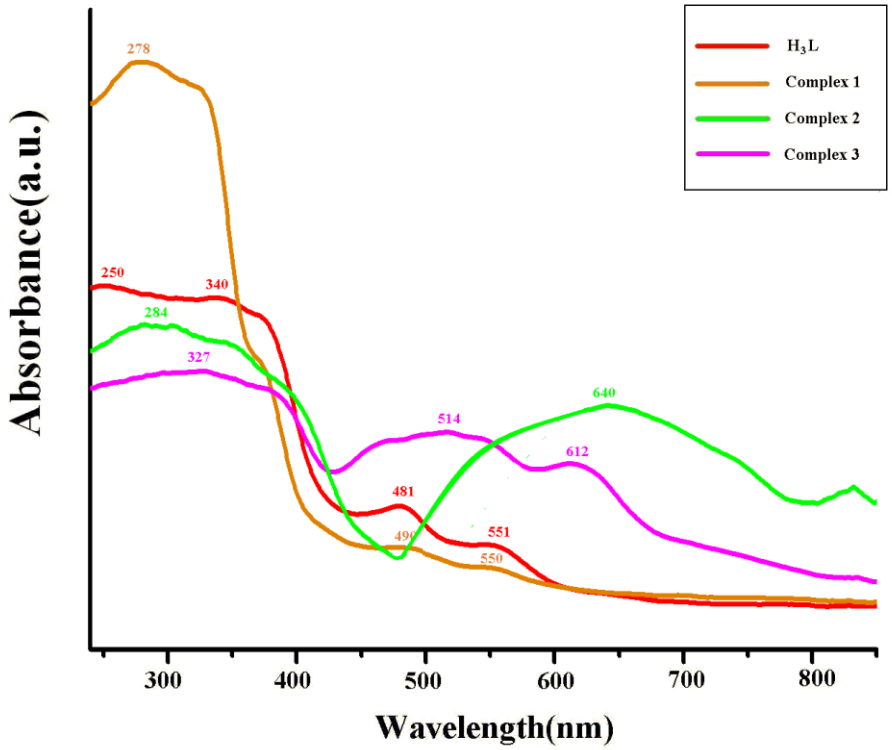


Fig. S2 UV-Vis absorption spectra at room temperature for **H_3L** and complexes **1-3**.

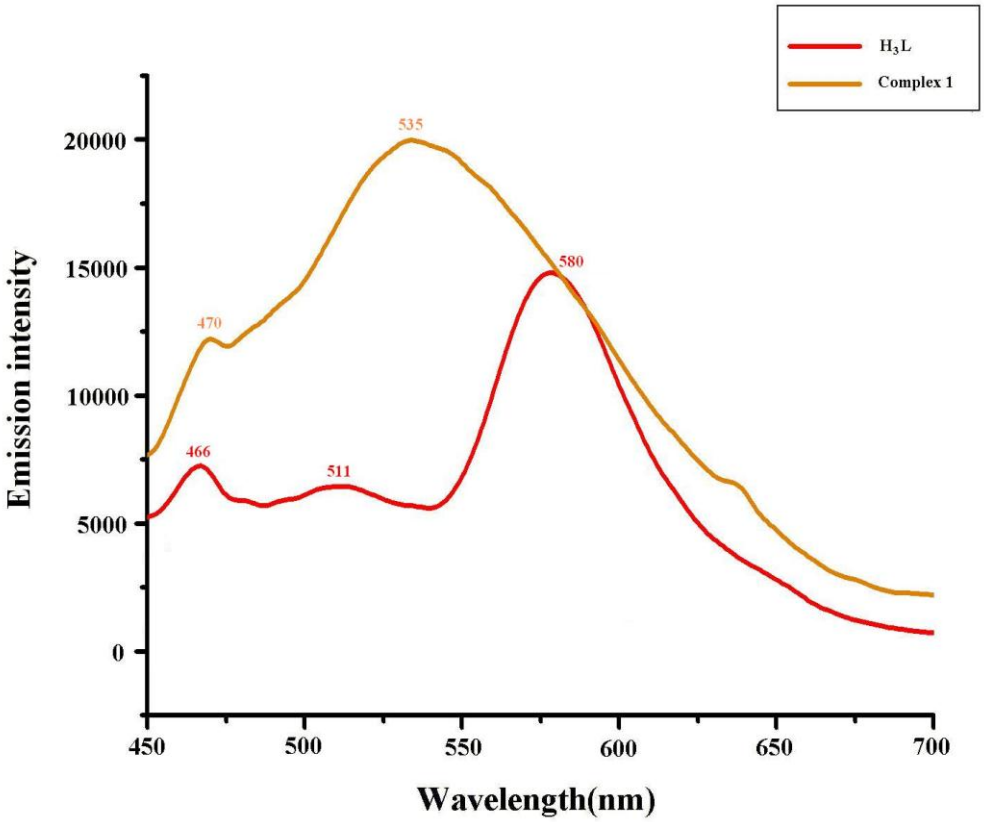


Fig. S3 Solid-state emission spectra at room temperature for the free **H_3L** and complex **1**.

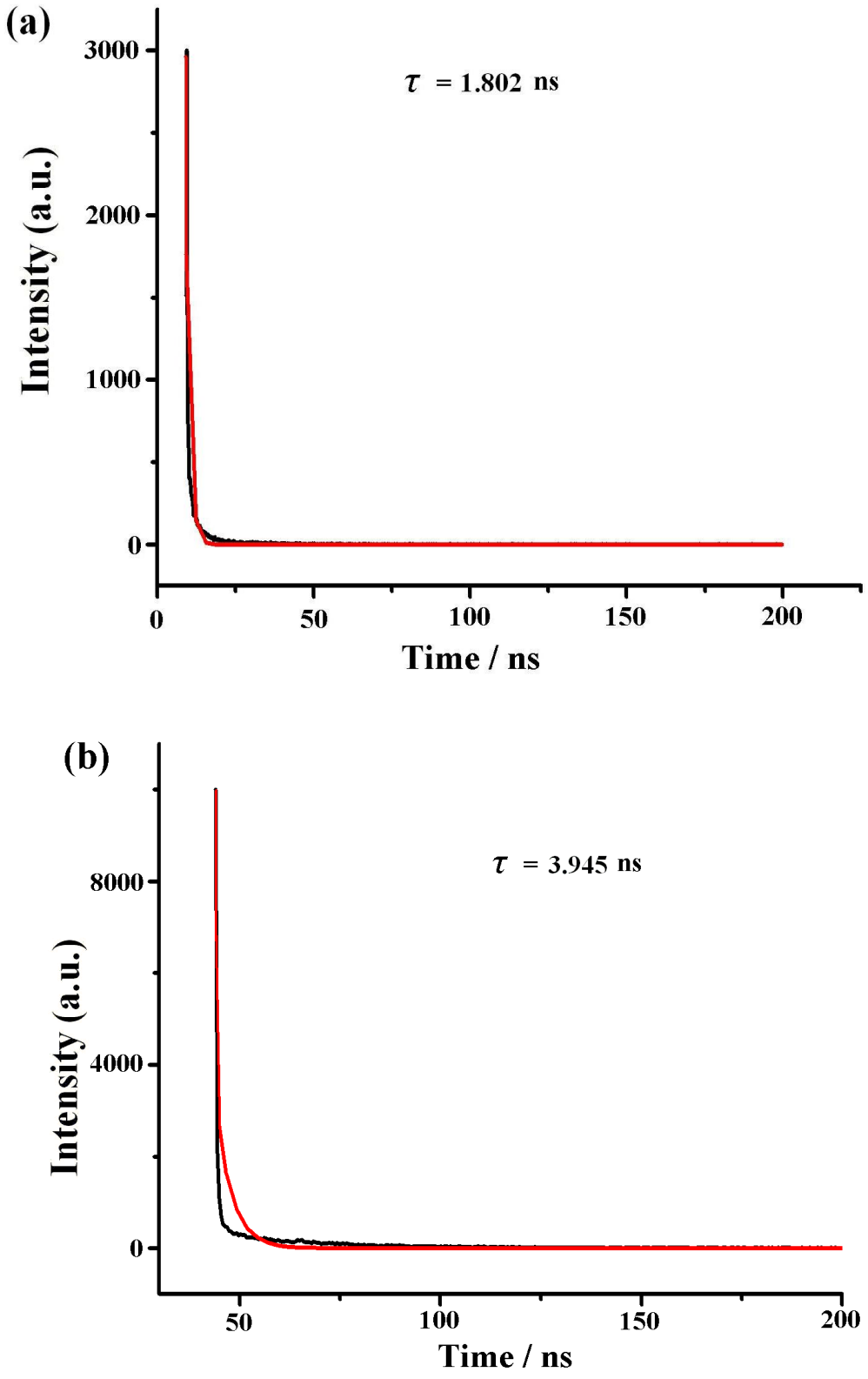
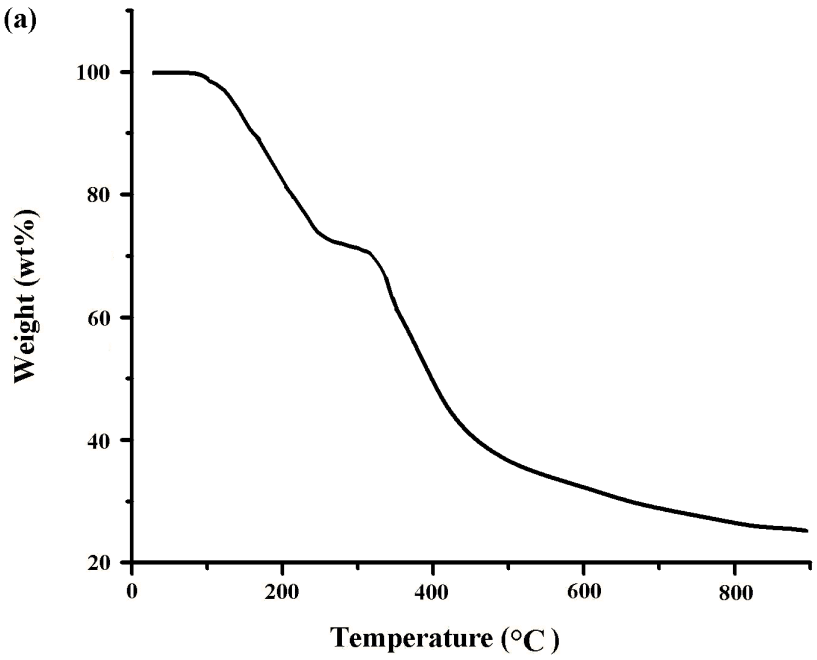


Fig. S4. Typical luminescence decay profile observed in the solid state at room

temperature (black lines) and the corresponding monoexponential fits (red lines) for **H_3L** (**a**) and complex **1** (**b**).

The equation $I_t = A \times \exp(-t/\tau)$ was utilized for fitting the fluorescence decay curves, which gave the best parameters as $A = 2.654\times10^{14}$ and $\tau = 1.802$ ns with an overall χ^2 of 0.9863 for **H_3L**, $A = 2.218\times10^{8}$ and $\tau = 3.945$ ns with an overall χ^2 of 0.4375 for complex **1**.



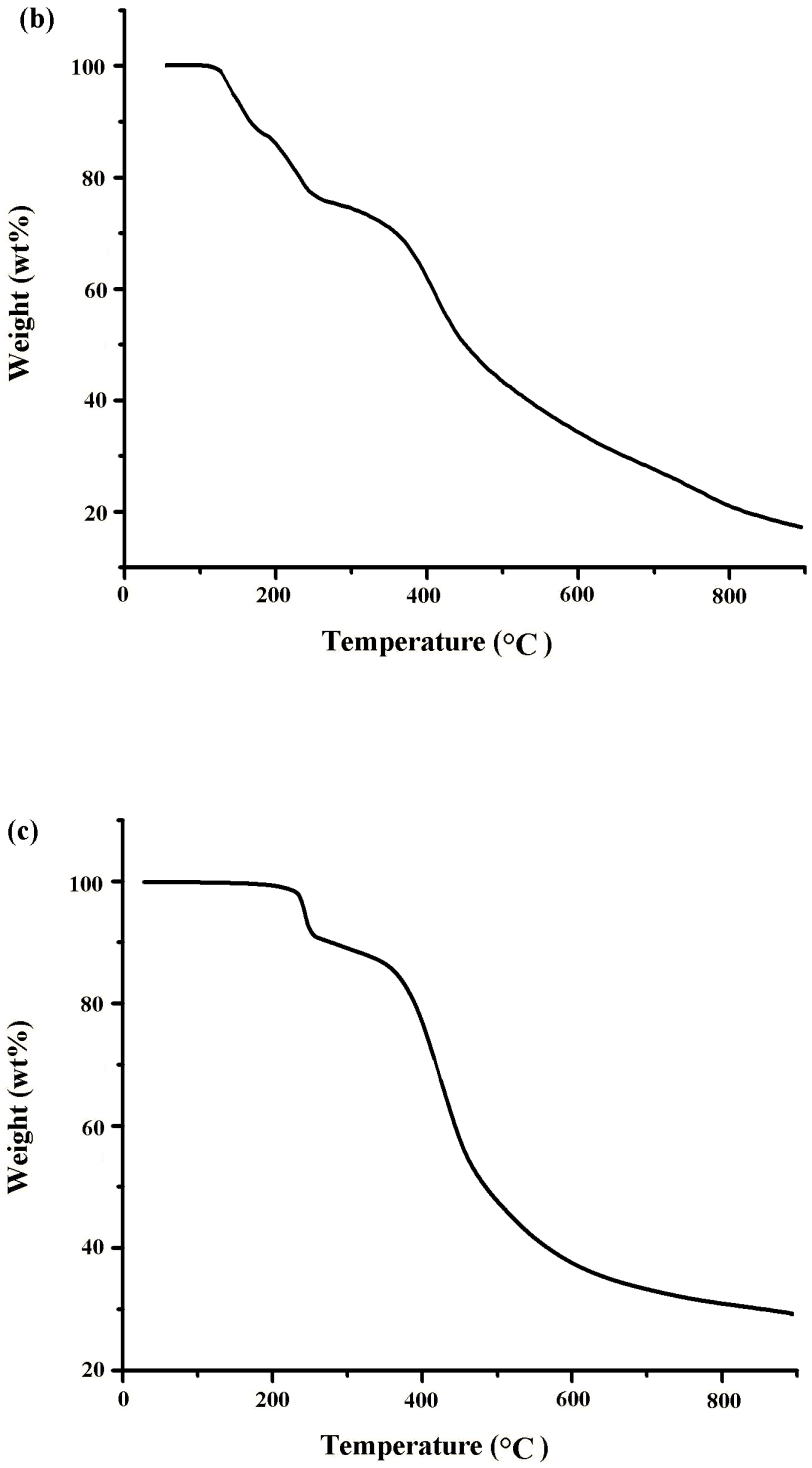


Fig.S5 TG curves of complexes **1** (**a**), **2** (**b**) and **3** (**c**).

References:

1 (a) M. R. Chierotti, L. Ferrero, N. Garino, R. Gobetto, L. Pellegrino, D. Braga, F. Grepioni and L. Maini, *Chem. Eur. J.*, 2010, **16**, 4347; (b) N. Zencirci, T. Gelbrich, D. C. Apperley, R. K. Harris, V. Kahlenberg, U. J. Griesser, *Cryst. Growth Des.*, 2010, **10**, 302.