

The $(\text{Zn}_{0.95}\text{Mn}_{0.05}\text{S})_2\cdot\text{L}$ (L = hexylamine, and octylamine) Inorganic/Organic Hybrid Luminescence Films By Spin-Coating Method

Shuo Wei,^{*a} Jing Peng,^a Meng Wang,^a Yunxiao Fan,^a Xinxin Li^b and Jun Lu^c

^a College of Chemistry, Beijing Normal University 19 Xijiekou Outerside Street, Beijing, 100875, China, vshuo@bnu.edu.cn

^b Analytical Center, Beijing Normal University, 19 Xijiekou Outerside Street, Beijing, 100875, China;

^c State key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, 15 Beisanhuan East Road, Beijing, 100029, China.

1. Experimental Section

1.1 Materials

Zinc acetate (ZnAc_2 , AR) and sublimed sulfur (S, AR) are purchased from Beijing Yili Fine Chemicals Co., Ltd. Manganese acetate (MnAc_2 , AR) is brought in Tianjin Kermel Chemical Reagent Development Center. *n*-hexylamine (ha, 99%, Alfa Aesar). *n*-octylamine (oa, CP) and dodecylamine (dda, CP) are produced by Sinopharm Chemical Reagent Beijing co., Ltd. All chemicals were used as received without further purification.

1.2 Synthesis

Synthesis of $[(\text{Zn}_{0.95}\text{Mn}_{0.05}\text{S})_2\cdot(\text{ha})]$. Zinc acetate(0.439g, 2mmol), manganese acetate(0.025g, 0.1mmol), sulfur(0.064g, 2mmol) and hexamine(ha, 20 mL) were mixed and sealed in a 23mL Teflon liner autoclave and heated at 150 °C for 7 days. After being cooled naturely, the white product was filtrated and washed with deionized water and 90% ethanol, followed by vacuum drying at 60°C. The white powder of $[(\text{Zn}_{0.95}\text{Mn}_{0.05}\text{S})_2\cdot(\text{ha})]$ was obtained.

Synthesis of $[(\text{Zn}_{1-x}\text{Mn}_x\text{S})_2\cdot(\text{oa})]$. Zinc acetate(0.439g, 2mmol), sulfur(0.064g, 2mmol), manganese acetate(0.025g, 0.1mmol) and octylamine(oa, 20 mL) were

mixed and sealed in a 23mL Teflon liner autoclave and heated at 150 °C for 7 days. After being cooled naturally, the white product was filtrated and washed with deionized water and 90% ethanol, followed by vacuum drying at 60°C. The white powder of $[(Zn_{0.95}Mn_{0.05}S)_2 \cdot (oa)]$ was obtained.

1.3 Fabrication of the hybrid thin films.

The quartz substrate was treated by a routine chemical cleaning procedure including ultrasonication in a detergent (das spuelmittel aqueous solution, $H_2SO_4:30\%H_2O_2(3:1,v/v)$ for 40 minutes, and then dried after washing by deionized water. Afterwards, the quartz substrate was hydrophobic treated by refluxing in 3% (3-amino propyl) triethoxy silane toluene solution using a Soxhlet extractor for 6 h and dried. The hybrid suspension for spin-coating was prepared by ultrasonically dispersing the $(Zn_{0.95}Mn_{0.05}S)_2 \cdot ha$ or $(Zn_{0.95}Mn_{0.05}S)_2 \cdot oa$ in ethyl acetate for over 5 hours. The hybrid thin films were fabricated by using a KW-4A spin coater. After dripping three drops of the ultrasonized hybrid suspension on the substrate, the substrate was rotated at lower speed of 1.5 kr/min for 6s and then higher speed of 4.0 kr/min for 15s to form one layer of the thin film. The multilayer thin films were fabricated by tautologically spin-coating the quartz substrate without affecting the layer underneath. Different series of hybrid thin films were fabricated with the layer number of 5, 10, 15, 20, 25, 40, 50, 60, 70 layers.

2. Characterization

The powder and thin films XRD patterns were recorded on a X' Pert PRO MPD X-ray diffractometer (PANaytical) with Cu-K α radiation ($\lambda=1.541844 \text{ \AA}$), operated at 40 kV and 40 mA. The data were collected at room temperature with a step size of 0.0330° and a scan step time of 59.98 s/step. FE-SEM images were taken with a Hitachi S-4800 cold field-emission scanning electron microscope operated at 10 kV. Elemental analysis of C, H, and N were carried out by the combustion method using a German Elementar Vario elemental analyzer. The Mn²⁺ contents of the doping hybrid

samples were determined by using an induced coupling plasma -atomic emission spectroscopy(ICP-AES) using an iCAP 6300 spectrometer (Thermo Fisher Scientific Corp). The thermal gravimetric analysis (TGA) was carried out in the range from 30 °C to 800°C with a Mettler Toledo TGA/DSC 1 STAR[®] thermal analyzer, with a heating rate of 10 °C/min, and a N₂ flow of 20 mL/min.

The ultraviolet and visible (UV–Vis) absorption spectra were recorded on a Shimadzu UV-365 spectrometer. The photoluminescence spectra were recorded at were collected on a Shimadzu RF-5301PC fluorescence spectrophotometer and Fluorolog-Tau-3 luminescence spectrometer (ISA Co., Ltd., USA) luminescence spectrometer with a Xe lamp as the excitation light source at room temperature. Fluorescent lifetime measurements were recorded with an Edinburgh Instruments FL 900 fluorimeter. The percentage contribution of each lifetime component to the total decay was calculated with the Edinburgh F900 instruments software. The Fluorescence Imaging of series of thin films were photographed by Fusion FX5 gel imaging system from France Vilber Lourmat company. The Electron spin resonance (ESR) spectra was recorded on a Bruker 300E ESR spectrometer (300k, 9.80GHz). Microwave power employed was 10.02mW, sweep width ranged from 3000 to 4000 G. Modulation frequency and modulation amplitude were 100kHz and 0.974G, respectively.

The weight percentages of C, H, N of the the pure hybrid compounds without Mn²⁺ doping were listed in Table S1. The metal contents analysis of the Mn²⁺ doping hybrid samples were listed in Table S2. It was easy to figure out that the results of C, H, and N were consistent with the calculated values in the range of experimental error ($\pm 0.5\%$). were used to determine the Mn contents of (Zn_{1-x}Mn_xS)₂·L. For the nominal composiotn of Zn²⁺:Mn²⁺ = 20:1 ($x = 0.0476$), the ICP-AES determined x was 0.0406 for (Zn_{1-x}Mn_xS)₂·(ha), and 0.0557 for (Zn_{1-x}Mn_xS)₂·(oa). Consequently, the solvothermal Mn²⁺ doping reactions for the hybrids can be regarded as quantitative.

Table S1. Analysis Results of C, H, and N contents of $(\text{ZnS})_2\cdot\text{L}$

	C, H, N (wt%)	
	$(\text{ZnS})_2(\text{ha})$	$(\text{ZnS})_2(\text{oa})$
Calcd	24.33, 5.11, 4.73	29.64, 5.91, 4.32
Found	25.38, 5.09, 4.63	31.41, 5.52, 4.24

Table S2. Analysis Results of Mn^{2+} contents of $(\text{Zn}_{1-x}\text{Mn}_x\text{S})_2\cdot\text{L}$

	Mn content (x, at%)	
	$(\text{Zn}_{1-x}\text{Mn}_x\text{S})_2(\text{ha})$	$(\text{Zn}_{1-x}\text{Mn}_x\text{S})_2(\text{oa})$
Calcd	0.0476	0.0476
Found	0.0406	0.0557

3 The TGA curve of the hybrid samples

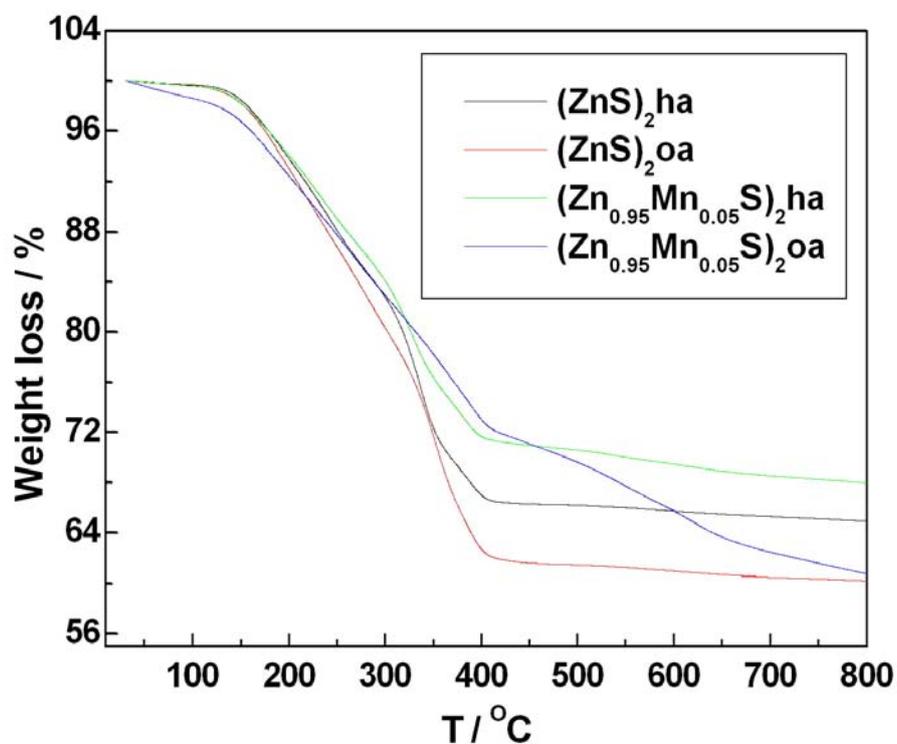


Figure S1 The TGA curve of the hybrid powders.

4. The Tyndall effect of the hybrid suspension

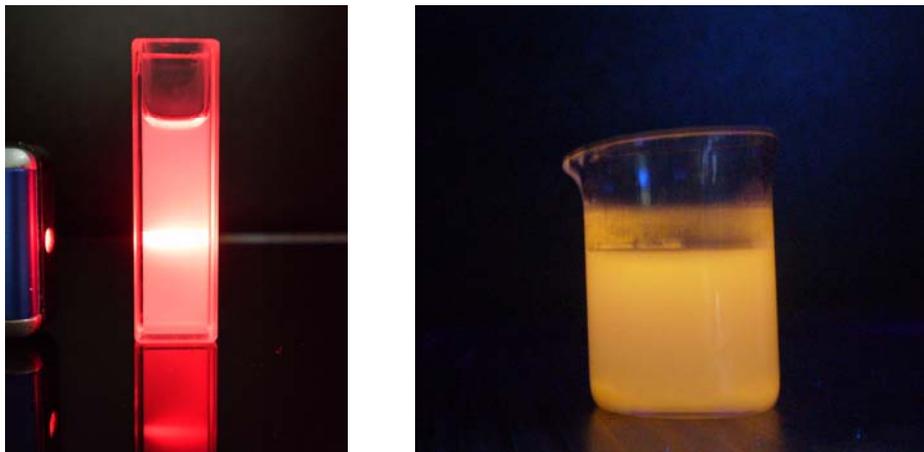


Figure S2 The Tyndal Effects (left image) and the photograph illuminated by UV light(right image) of the Mn^{2+} doping hybrid suspension.

5. The UV-visible absorption spectra for $(\text{ZnS})_2\cdot(\text{ha})$ and $(\text{ZnS})_2\cdot(\text{oa})$ hybrid powders

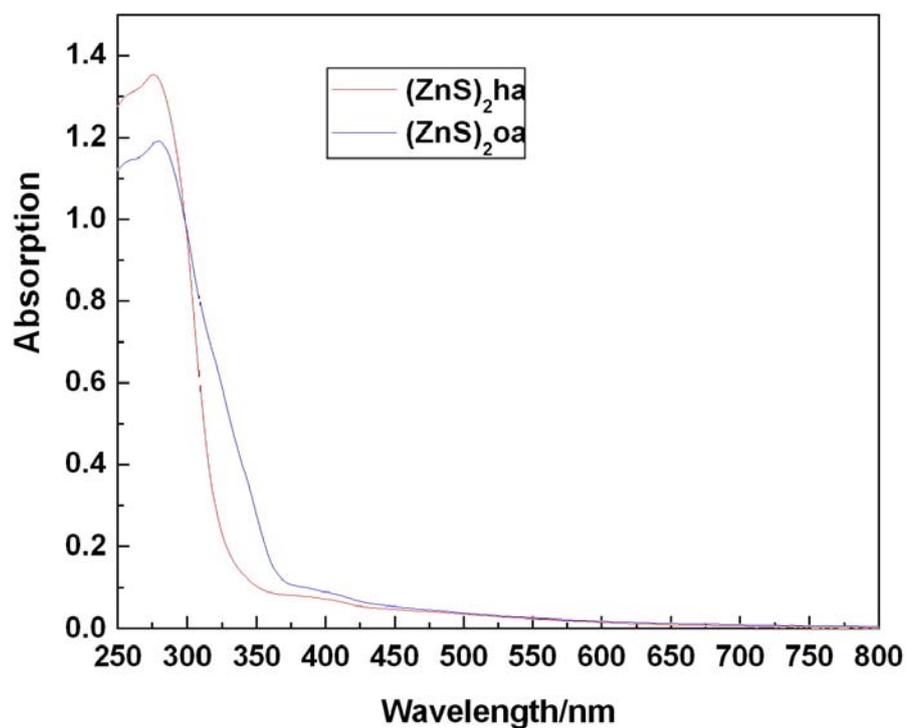


Figure S3 The UV-Visible absorption spectra of the $(\text{ZnS})_2\cdot\text{ha}$ and $(\text{ZnS})_2\cdot\text{oa}$ hybrid powders.

6. The ESR spectra of the Mn-doping hybrid powders.

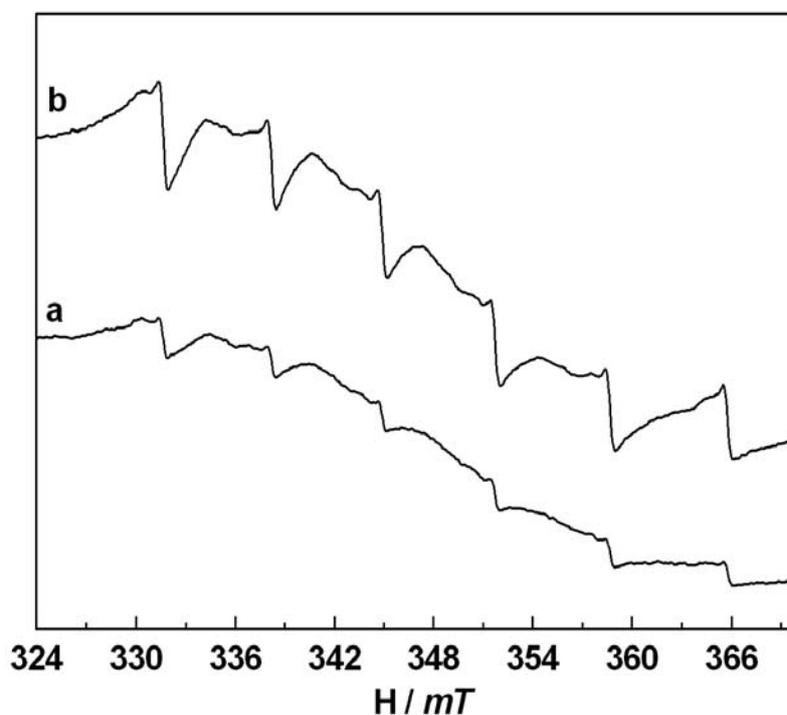


Figure S4 The ESR spectra of the $(\text{Zn}_{0.95}\text{Mn}_{0.05}\text{S})_2\cdot\text{ha}$ (a) and $(\text{Zn}_{0.95}\text{Mn}_{0.05}\text{S})_2\cdot\text{oa}$ (b) hybrid powders.

7. The fluorescence lifetime analysis of the as-prepared hybrid thin films

Table S3. The fluorescence lifetimes of the resulting hybrids*.

Samples	$\tau_1(\text{ms})$	$A_1(\%)$	$\tau_2(\text{ms})$	$A_2(\%)$	$\langle\tau\rangle(\text{ms})$	χ^2
$(\text{Zn}_{0.95}\text{Mn}_{0.05}\text{S})_2\cdot\text{ha}$ powders	0.6878	49.23	2.869	50.77	1.795	1.267
$[(\text{Zn}_{0.95}\text{Mn}_{0.05}\text{S})_2\cdot\text{ha}]_5$	0.5390	32.17	2.544	67.83	1.899	1.223
$[(\text{Zn}_{0.95}\text{Mn}_{0.05}\text{S})_2\cdot\text{ha}]_{15}$	0.5429	31.26	2.805	68.74	2.098	1.277
$[(\text{Zn}_{0.95}\text{Mn}_{0.05}\text{S})_2\cdot\text{ha}]_{25}$	0.5662	30.32	2.773	69.68	2.104	1.539
$(\text{Zn}_{0.95}\text{Mn}_{0.05}\text{S})_2\cdot\text{oa}$ powders	0.9601	32.82	3.223	67.18	2.480	1.482
$[(\text{Zn}_{0.95}\text{Mn}_{0.05}\text{S})_2\cdot\text{oa}]_5$	0.7174	28.60	2.892	71.40	2.270	1.275

$[(\text{Zn}_{0.95}\text{Mn}_{0.05}\text{S})_2\cdot\text{oa}]_{15}$	0.6933	29.65	2.832	70.35	2.198	1.241
$[(\text{Zn}_{0.95}\text{Mn}_{0.05}\text{S})_2\cdot\text{oa}]_{25}$	0.6141	25.98	2.635	74.02	2.110	1.377

* τ_1 and τ_2 correspond to two lifetimes; A_i stands for the percentage of τ_i . The goodness of fit is indicated by the value of χ^2 . In the double-exponential case, $\langle\tau\rangle = A_1\tau_1 + A_2\tau_2$; $A_1 + A_2 = 1$.

8. The UV-visible absorption and photoluminescence spectra for $[(\text{Zn}_{0.95}\text{Mn}_{0.05}\text{S})_2\cdot(\text{oa})]$ hybrid films

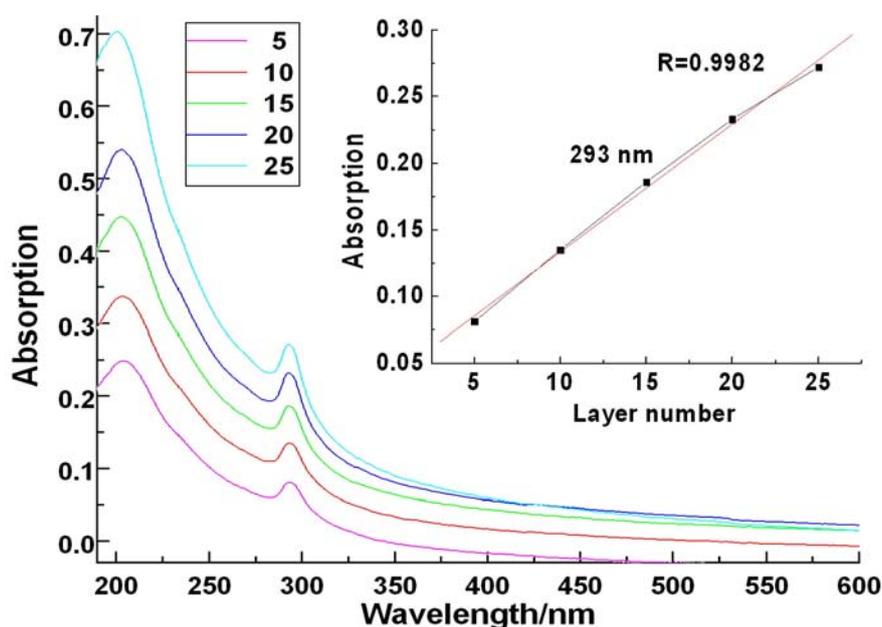


Figure S5 The UV-vis absorption spectra for the $[(\text{Zn}_{0.95}\text{Mn}_{0.05}\text{S})_2\cdot\text{oa}]_n$ hybrid film with different n (5–25). The inset is the plot of the absorbance at 293 nm versus the spin-coated cycle numbers.

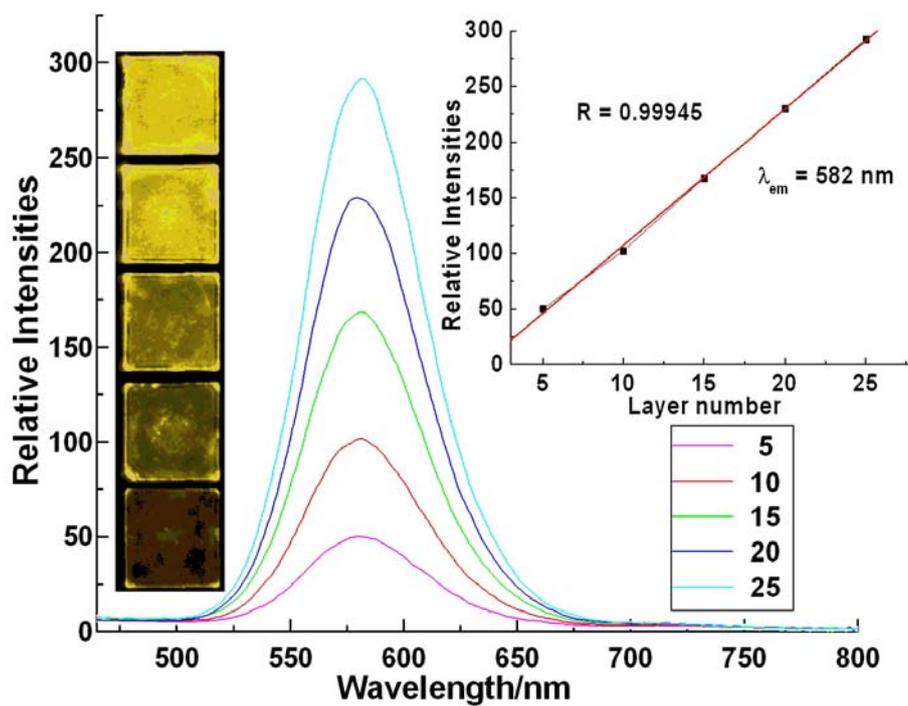


Figure S6 The PL emission spectra of $[(\text{Zn}_{0.95}\text{Mn}_{0.05}\text{S})_2 \cdot \text{oa}]_n$ thin films ($\lambda_{\text{ex}} = 293 \text{ nm}$) with the deposition cycle number n varying from 5 to 25. The right inset is a plot of film relative intensities at 582 nm versus n and the left inset was the photographs for the thin film illuminated with UV light.