

Electronic Supplementary Information (ESI)

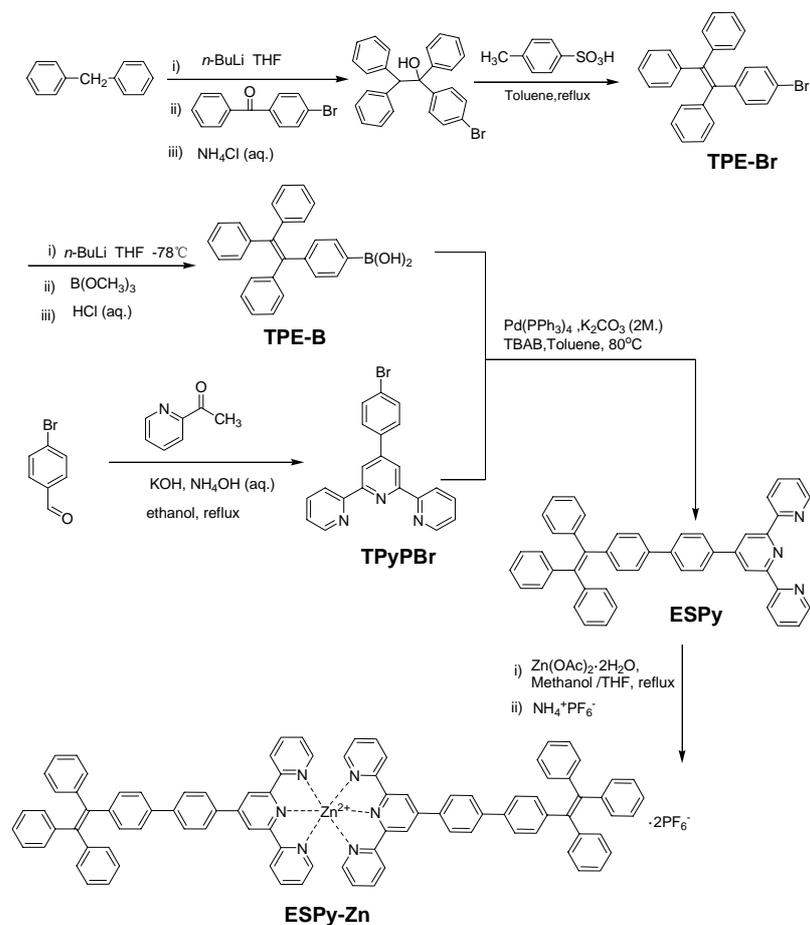
A New Ligand and Its Complex with Multi-Stimuli-Responsive and Aggregation-Induced Emission Effects

**Bingjia Xu, Zhenguo Chi,* Xiqi Zhang, Haiyin Li, Chengjian Chen, Siwei Liu, Yi
Zhang, and Jiarui Xu***

*PCFM Lab, DSAPM Lab and KLGHEI of Environment and Energy Chemistry, FCM
Institute, State Key Laboratory of Optoelectronic Materials and Technologies, School of
Chemistry and Chemical Engineering, Sun Yat-sen University, Guangzhou 510275,
China. Fax: +86 20 84112222; Tel: +86 20 84111081; E-mail:
chizhg@mail.sysu.edu.cn (Zhenguo Chi); xjr@mail.sysu.edu.cn(Jiarui Xu)*

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1. Experimental Section



Scheme S1. Synthetic routes to the ligand and its complex.

Materials and Measurements: 4-Bromobenzophenone, diphenylmethane, 4-bromobenzaldehyde, 2-acetylpyridine, n -butyllithium in hexane (2.2 M), tetrakis (triphenylphosphine) palladium(0), trimethylborate, p -toluenesulphonic acid and tetrabutyl ammonium bromide (TBAB) were purchased from Alfa Aesar and used as received. All other reagents and solvents were purchased as analytical grade from Guangzhou Dongzheng Company (China) and used without further purification. Tetrahydrofuran (THF) was distilled from sodium/benzophenone. Ultra-pure water

was used in the experiments. TPE-B¹ and TPyPBr² were synthesized according to the literature methods.

Proton and carbon-13 nuclear magnetic resonance spectra (¹H NMR and ¹³C NMR) were measured on a Mercury-Plus 300 spectrometer (DMSO and CDCl₃ as solvents, and tetramethylsilane TMS as the internal standard). Mass spectra (MS) were measured on a Thermo DSQ and LCQ DECA XP MS spectrometer. Elemental analyses (EA) were performed with an Elementar Vario EL elemental analyzer. FT-IR spectra were obtained on a Nicolet NEXUS 670 spectrometer (KBr pellet). UV-visible absorption spectra (UV) were determined on a Hitachi U-3900 spectrophotometer. Fluorescence spectra (PL) were measured on a Shimadzu RF-5301PC spectrometer with a slit width of 1.5 nm for excitation and 3 nm for emission. Thermal behaviors were determined by differential scanning calorimetry (DSC) at heating and cooling rate of 10 °C/min under N₂ atmosphere using a NETZSCH thermal analyzer (DSC 204F1). Thermogravimetric analyses (TGA) were performed with a thermal analyzer (TA thermal analyzer, Q50) under N₂ atmosphere with a heating rate of 20 °C/min. Time-resolved emission decay behaviors were measured on an Edinburgh Instruments Ltd spectrometer (FLSP920) and the data were processed according to the literature method.³ Wide-angle X-ray diffraction (WAXD) measurements were performed by using a Bruker X-ray diffractometer (D8 ADVANCE, Germany) with an X-ray source of Cu Kα (λ= 0.15406 nm) at 40 kV and 40 mA, at a scan rate of 4° (2θ)/ 1 min.

A 2 cm ×5 cm filter paper is dipped into the 10^{-3} M solution (ESPy in THF and ESPy-Zn in acetone) for 5 s, and then it is air dried for 5 min.

Synthesis of ESPy: TPE-B (2.00 g, 5.32 mmol) and TPyPBr (1.72 g; 4.44 mmol) were dissolved in toluene (30 mL), and then 2 M aqueous K_2CO_3 solution (3.0 mL) and TBAB (0.1 g) were added. The mixture was stirred for 40 min under an argon atmosphere at room temperature. Then the $Pd(PPh_3)_4$ catalyst was added and the reaction mixture was stirred at 80 °C for 16 h. After cooling to room temperature, the product was concentrated and purified by neutral alumina column chromatography with dichloromethane/*n*-hexane (v/v=1/2) as eluent. The obtained solid was dissolved in 10 ml dichloromethane and a great deal of methanol was added to get the precipitation. Then the mixture was filtered and a white powder of ESPy was obtained in 82% yield (3.01 g). 1H NMR (300 MHz, DMSO) δ (ppm): 8.77 (s, 4H); 8.66 (d, 2H); 8.00 (q, 4H); 7.84 (d, 2H); 7.54 (m, 4H); 7.24-6.96 (m, 17H). ^{13}C NMR (75MHz, $CDCl_3$) δ (ppm): 155.90, 155.58, 149.46, 148.83, 148.75, 143.45, 143.39, 142.91, 140.99, 140.94, 140.15, 137.70, 136.75, 136.68, 131.64, 131.59, 131.10, 127.38, 127.02, 126.26, 125.93, 123.59, 121.20, 121.13, 118.45, 118.37. FT-IR (KBr) ν (cm^{-1}): 3052, 1600, 1580, 1500, 1438, 820, 757, 700. EI-MS, m/z : $[M]^+$ 639, calcd for $C_{47}H_{33}N_3$ 639. Anal. calcd for $C_{47}H_{33}N_3$: C 88.23, H 5.20, N 6.57; found: C 88.35, H 5.26, N 6.61.

Synthesis of ESPy-Zn: A solution of ESPy (0.40 g, 0.63 mmol) in anhydrous THF (10 mL) was stirred at room temperature. Then a solution of $Zn(OAc)_2 \cdot 2H_2O$ (0.069 g, 0.31 mmol) in anhydrous methanol (30 ml) was added and the mixture was heated to

reflux over night. A water solution of ammonium hexafluorophosphate was added and stirred for 1 h precipitating the corresponding zinc hexafluorophosphate salt. The reaction mixture was filtered, washed extensively with water and ether obtaining a light green powder. Yield: 75% (0.38 g). ^1H NMR (300 MHz, DMSO) δ (ppm): 9.43 (s, 2H); 9.18 (d, 2H); 8.53 (d, 2H); 8.28 (t, 2H); 8.04 (d, 2H); 7.95 (d, 2H); 7.73 (d, 2H); 7.48 (t, 2H); 7.22-6.98 (m, 17H). ^{13}C NMR (75MHz, DMSO) δ (ppm): 154.43; 149.55; 147.79; 143.40; 143.21; 143.18; 141.92; 141.35; 141.14; 140.08; 136.57; 134.28; 131.56; 130.79; 130.71; 128.83; 128.09; 128.02; 127.92; 127.77; 127.27; 126.87; 126.76; 126.31; 123.70; 120.85. FT-IR (KBr) ν (cm^{-1}): 3052, 1600, 1570, 1435, 840, 759, 702. ESI-MS, m/z : $[\text{M}-2\text{PF}_6]^{2+}$ 672, calcd for $[\text{C}_{94}\text{H}_{66}\text{N}_6\text{Zn}]^{2+}$ 672. Anal. calcd for $\text{C}_{47}\text{H}_{33}\text{N}_3$: C 69.06, H 4.07, N 5.14, P 3.79, F 13.94, Zn 4.00; found: C 69.17, H 4.15, N 5.11.

Reference

1. W. Yuan, P. Lu, S. Chen, J. W. Y. Lam, Z. M. Wang, Y. Liu, H. S. Kwok, Y. Ma, B. Tang, *Adv. Mater.* 2010, **22**, 2159.
2. X. Piao, Y. Zou, J. Wu, C. Li, T. Yi, *Org. Lett.* 2009, **11**, 3818.
3. A. Qin, C. K. Jim, Y. Tang, J. W. Y. Lam, J. Liu, F. Mahtab, P. Gao, B. Tang, *Phys. Chem. B* 2008, **112**, 9281.

2. Table S1 and S2

Table S1. Changes of PL wavelengths of ESPy and ESPy-Zn

ESPy	Procedure	a _{as}	G _{a1}	F _{a1}	A _{a1}	G _{a2}	F _{a2}	A _{a2}
	PL (nm)	453	491	456	453	491	454	453
ESPy-Zn	Procedure	b _{as}	G _{b1}	F _{b1}	A _{b1}	G _{b2}	F _{b2}	A _{b2}
	PL (nm)	474	555	476	501 ^a	556	476	500 ^a

a_{as} and b_{as} represent as-synthesized sample; G₁, ground sample; F₁, fumed sample (ground sample in methanol vapor for five minutes); A₁, annealed sample (The ground sample was annealed at 160 °C for five minutes and cooled down to room temperature.); G₂, re-ground sample; F₂, re-fumed sample; A₂, re-annealed sample.^a
 The ground sample was annealed at 300 °C for 1 h and cooled down to room temperature.

Table S2. Fluorescence decay parameters of the compounds before and after grinding.

		τ ₁ (ns) ^{a)}	A ₁ ^{b)}	τ ₂ (ns) ^{a)}	A ₂ ^{b)}	τ ₃ (ns) ^{a)}	A ₃ ^{b)}	<τ> (ns) ^{c)}
ESPy	a _{as}	0.75	0.49	1.99	0.48	7.68	0.03	1.55
	G _{a1}	1.37	0.43	2.61	0.55	5.78	0.02	2.14
ESPy-Zn	b _{as}	1.56	0.25	6.77	0.53	26.14	0.22	9.73
	G _{b1}	0.43	0.23	4.86	0.49	27.13	0.27	9.81

^{a)} Fluorescence lifetime; ^{b)} fractional contribution; ^{c)} weighted mean lifetime

3. Figs. S1-S13

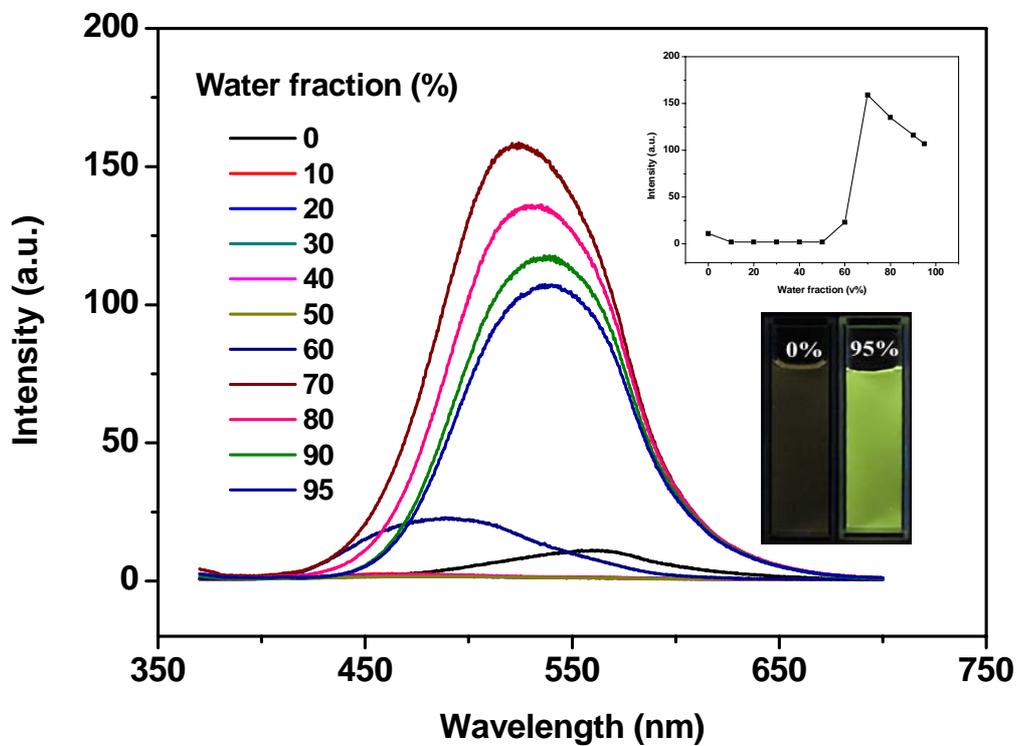


Fig. S1. PL spectra of the dilute solution of ESPy-Zn in water/acetone mixtures with different water fractions (concentration: 10 μM ; excitation wavelength: 365 nm). The inset depicts changes in PL peak intensity (up) and emission images of the compound in pure solvent and 95% water fraction mixtures under 365 nm UV illumination (10 μM) (down).

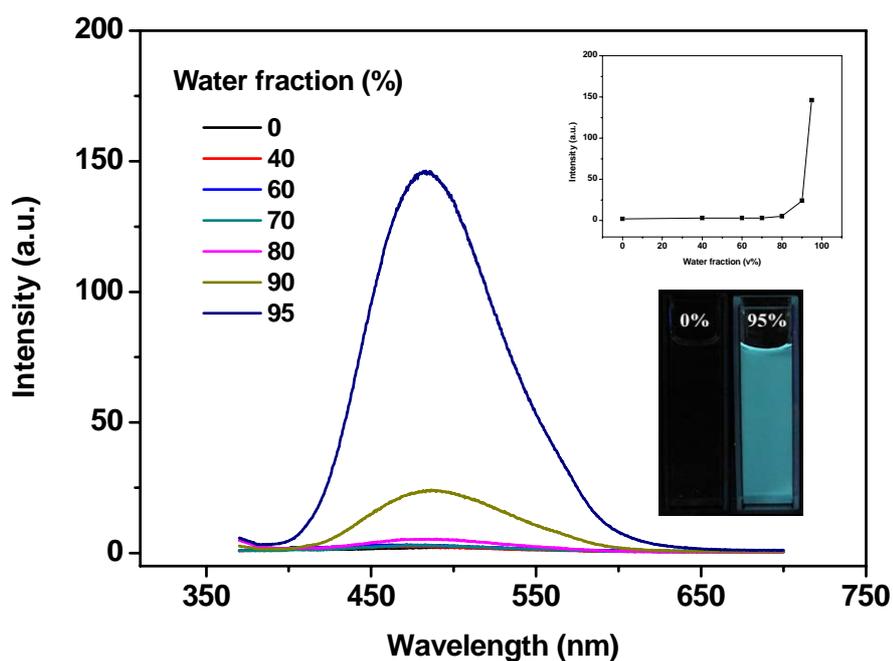


Fig.S2. PL spectra of the dilute solutions of ESPy in water/THF mixtures with different water fractions (concentration: 10 μM ; excitation wavelength: 365 nm). The inset depicts changes in PL peak intensity (up) and emission images of the compound in pure solvent and 95% water fraction mixtures under 365 nm UV illumination (10 μM) (down).

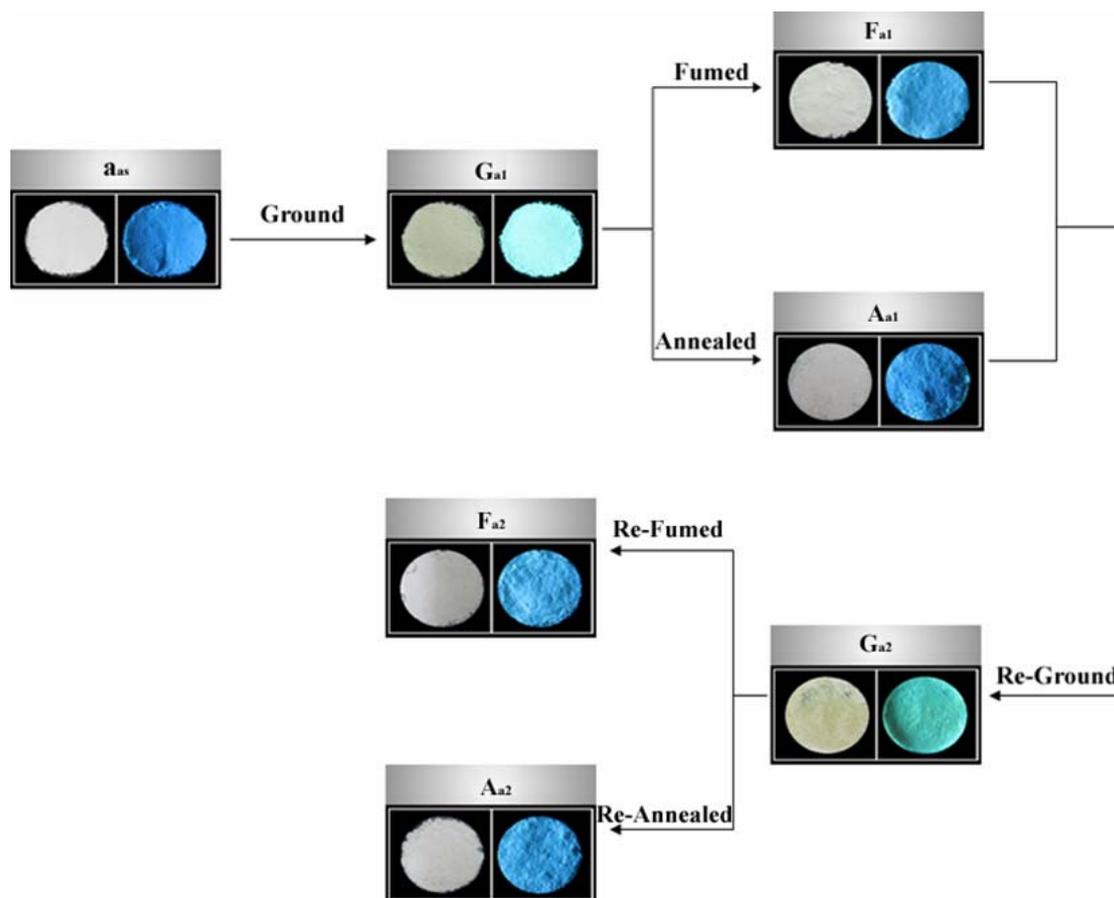


Fig. S3. ESPy taken at room temperature under ambient light (left) and UV light (right). Samples: a_{as}, as-synthesized sample; G_{a1}, ground sample; F_{a1}, fumed sample (ground sample in methanol vapor for five minutes); A_{a1}, annealed sample (The ground sample was annealed at 160 °C for five minutes and cooled down at room temperature.); G_{a2}, re-ground sample; F_{a2}, re-fumed sample; A_{a2}, re-annealed sample.

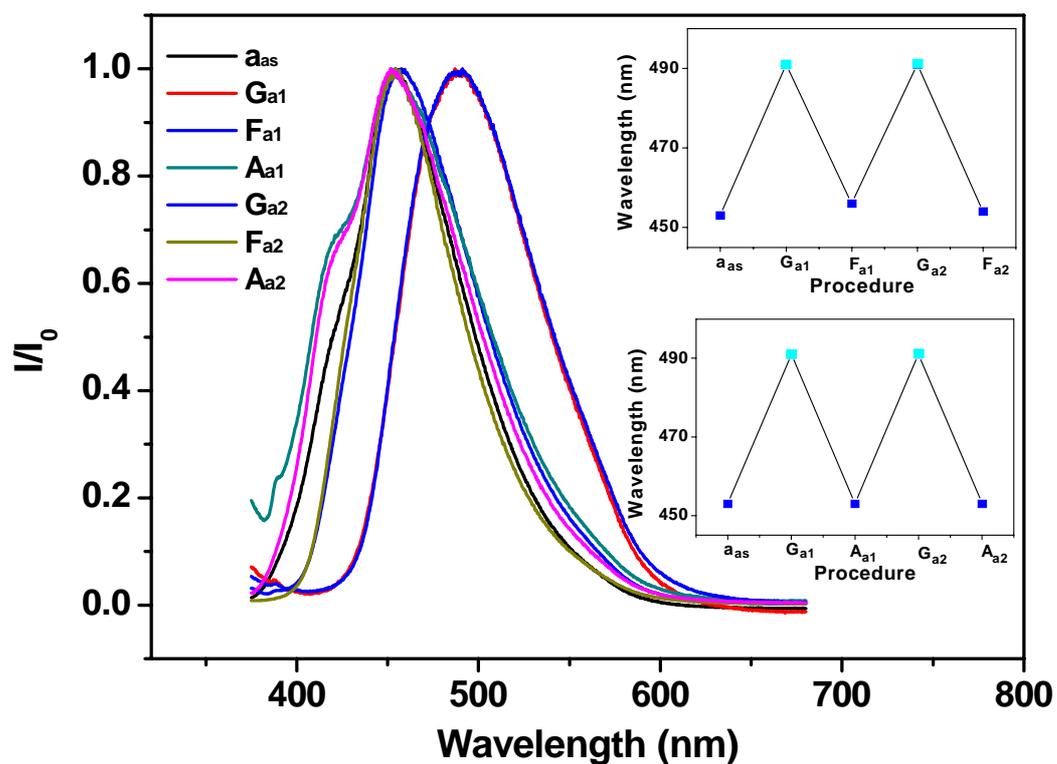


Fig. S4. PL spectra of ESPy: a_{as} , as-synthesized sample; G_{a1} , ground sample; F_{a1} , fumed sample (ground sample in methanol vapor for five minutes); A_{a1} , annealed sample (The ground sample was annealed at 160 °C for five minutes and cooled down at room temperature.); G_{a2} , re-ground sample; F_{a2} , re-fumed sample; A_{a2} , re-annealed sample. Inset: reversibility of the PL wavelengths of ESPy: by grinding and fuming treatments (up); and by grinding and annealing treatments (down).

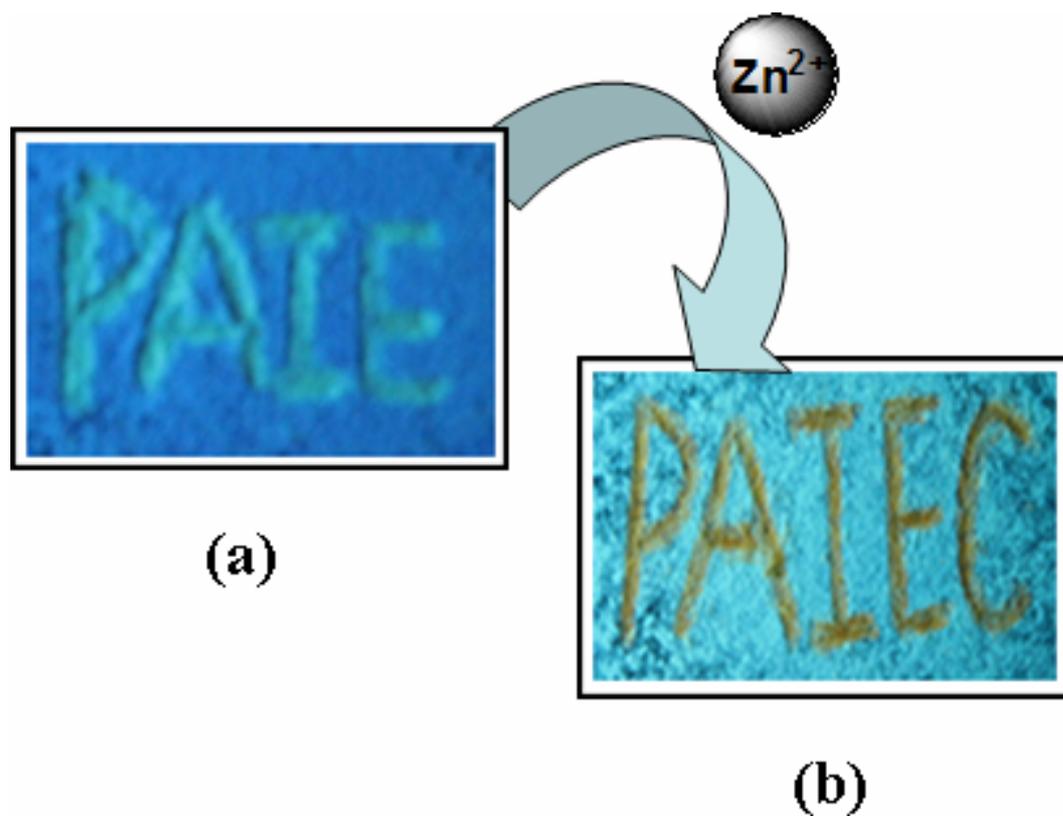


Fig.S5. The images taken at room temperature under 365 nm UV lamp: The as-synthesized powder of ESPy (a) and ESPy-Zn (b) were outspread on filter papers and written “PAIE” and “PAIEC” with a metal spatula, respectively.

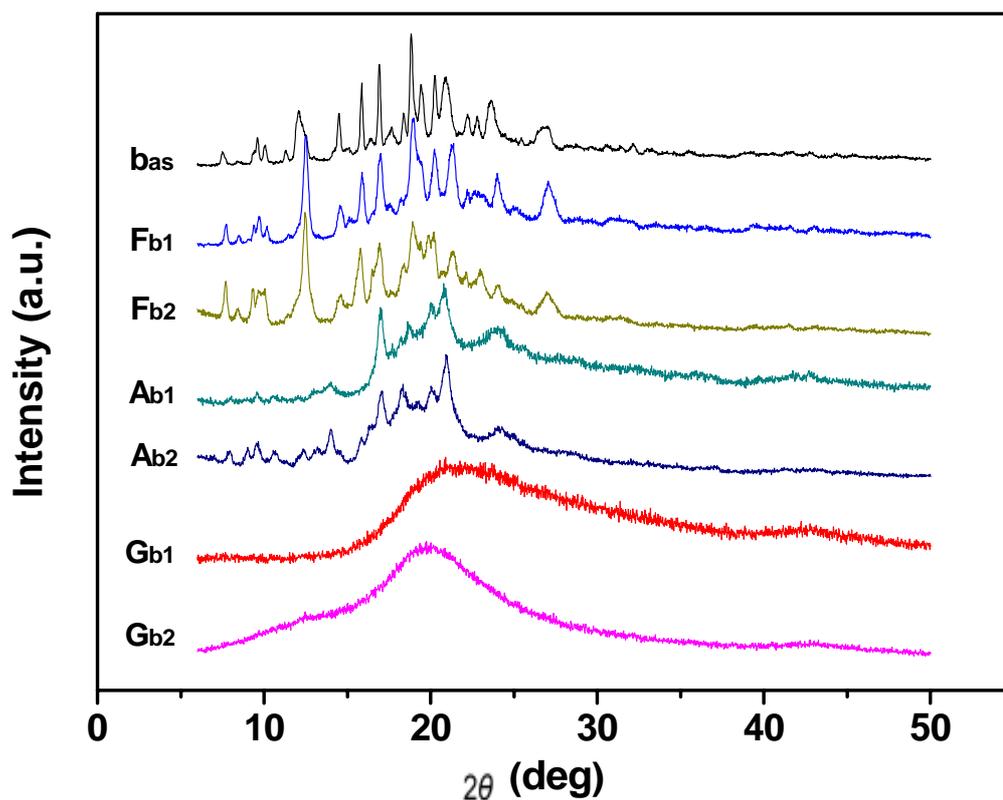


Fig. S6. PXRD patterns of ESPy-Zn at different morphology: **b_{as}**, as-synthesized sample; **G_{b1}**, ground sample; **F_{b1}**, fumed sample (ground sample in methanol vapor for five minutes); **A_{b1}**, annealed sample (The ground sample was annealed at 300 °C for 1 hour and cooled down at room temperature.); **G_{b2}**, re-ground sample; **F_{b2}**, re-fumed sample; **A_{b2}**, re-annealed sample.

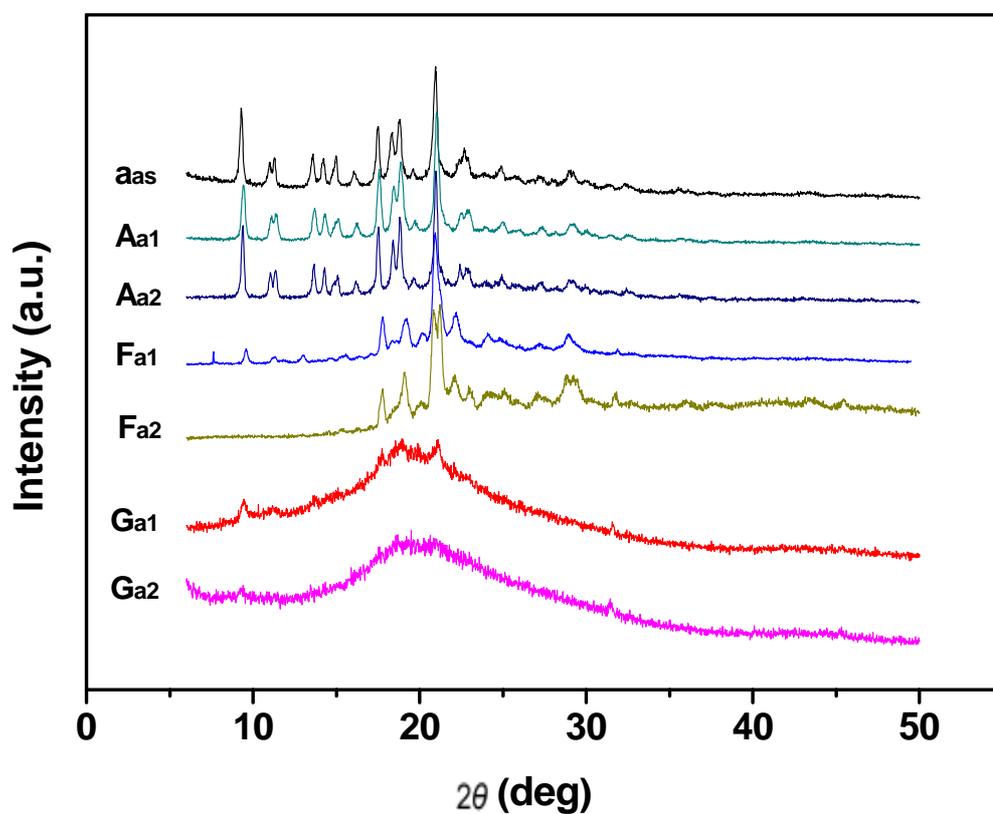


Fig. S7. PXRD patterns of ESPy at different morphology: a_{as}, as-synthesized sample; G_{a1}, ground sample; F_{a1}, fumed sample (ground sample in methanol vapor for five minutes); A_{a1}, annealed sample (The ground sample was annealed at 160°C for five minutes and cooled down at room temperature.); G_{a2}, re-ground sample; F_{a2}, re-fumed sample; A_{a2}, re-annealed sample.

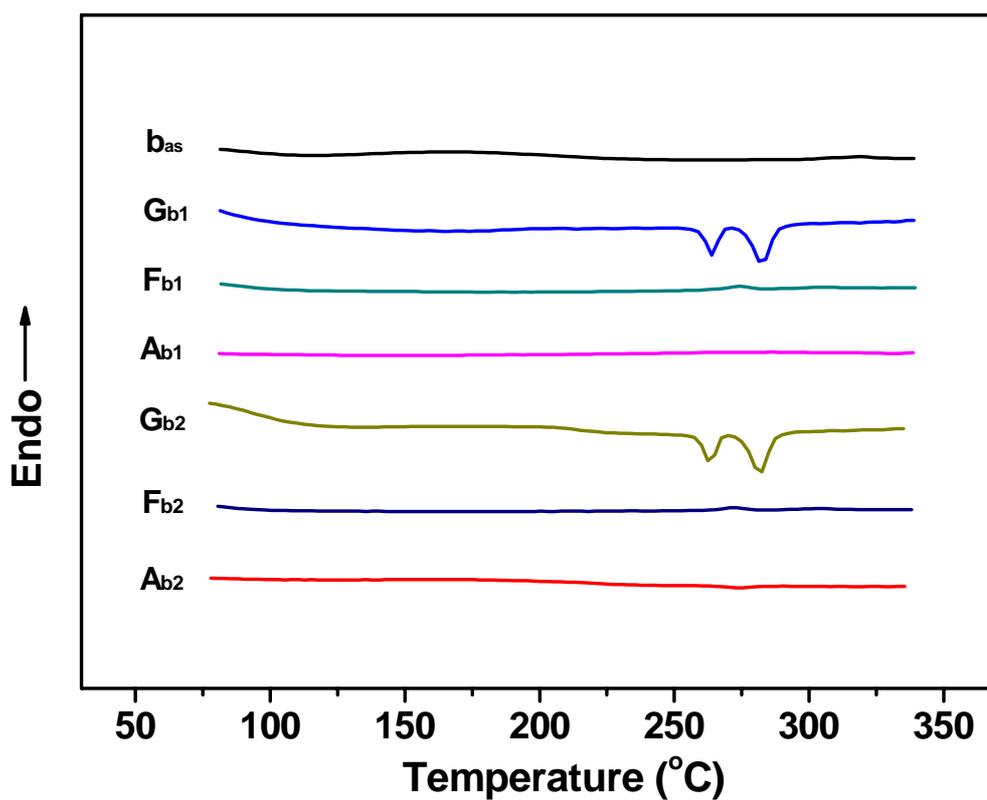


Fig. S8. DSC of ESPy-Zn : **b_{as}**, as-synthesized sample; **G_{b1}**, ground sample; **F_{b1}**, fumed sample (ground sample in methanol vapor for five minutes); **A_{b1}**, annealed sample (The ground sample was annealed at 300 °C for 1 hour and cooled down at room temperature.); **G_{b2}**, re-ground sample; **F_{b2}**, re-fumed sample; **A_{b2}**, re-annealed sample. (First heating runs).

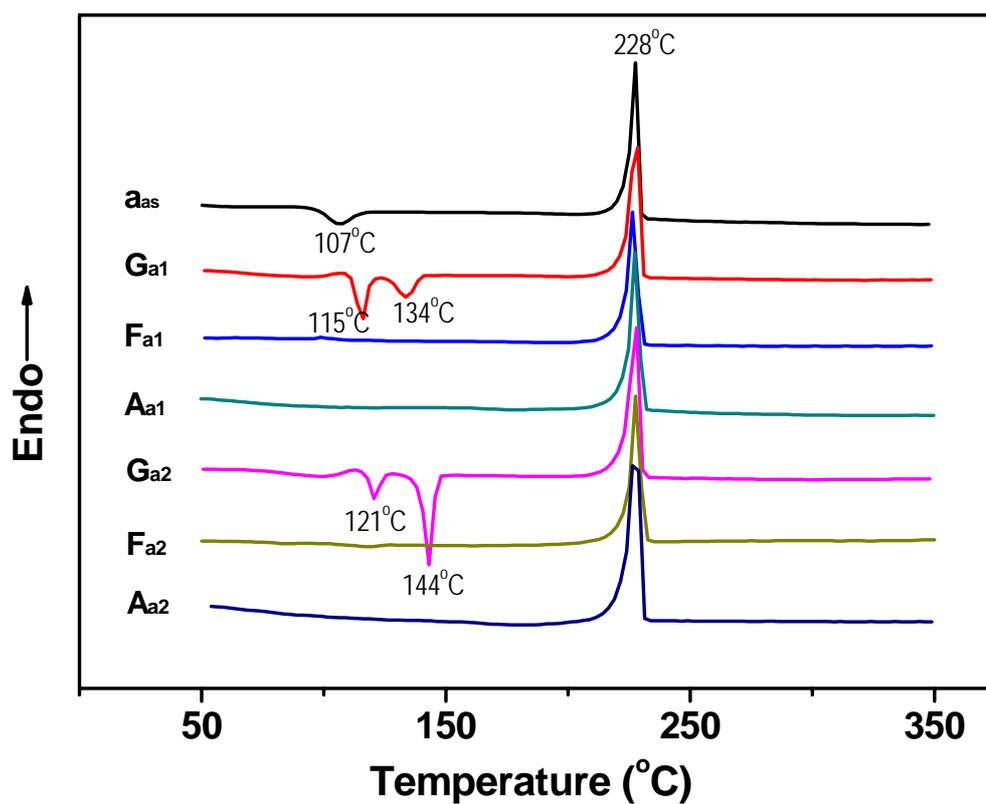


Fig. S9. DSC of ESPy : (a_{as}) as-synthesized sample; G_{a1} , ground sample; F_{a1} , fumed sample (ground sample in methanol vapor for five minutes); A_{a1} , annealed sample (The ground sample was annealed at 160°C for five minutes and cooled down at room temperature.); G_{a2} , re-ground sample; F_{a2} , re-fumed sample; A_{a2} , re-annealed sample. (First heating runs)

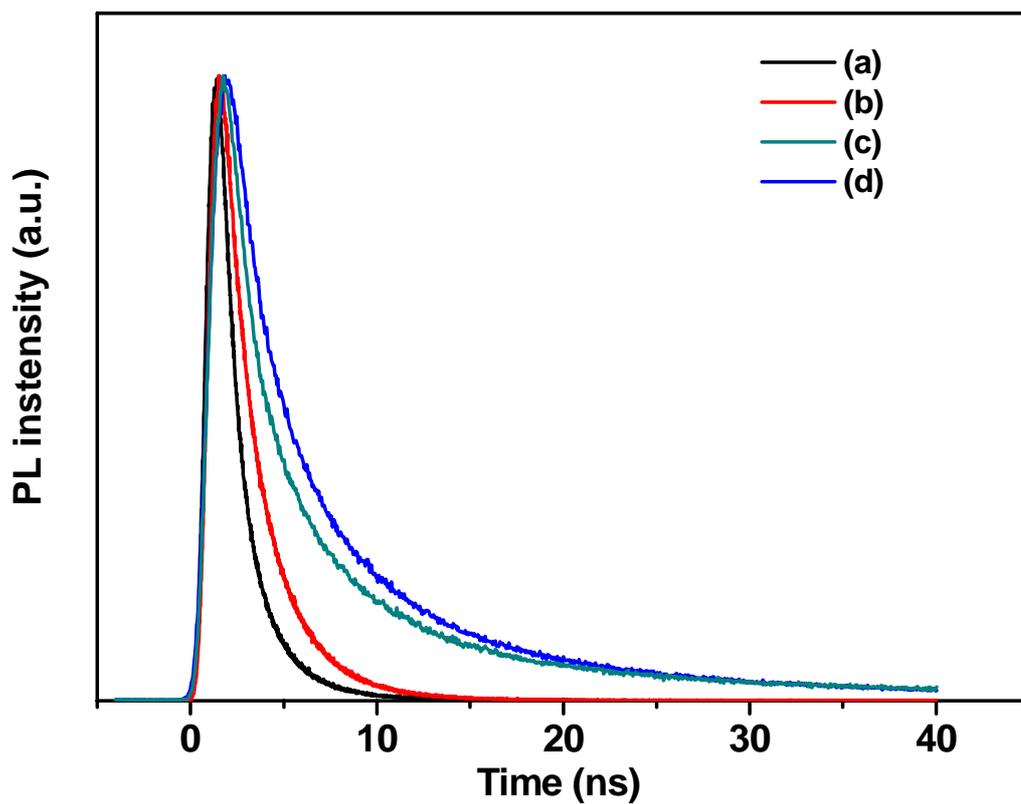


Fig. S10. Time-resolved emission decay curves of the samples: (a) as-synthesized sample of ESPy; (b) ground sample of ESPy; (c) as-synthesized sample of ESPy-Zn; (d) ground sample of ESPy-Zn.

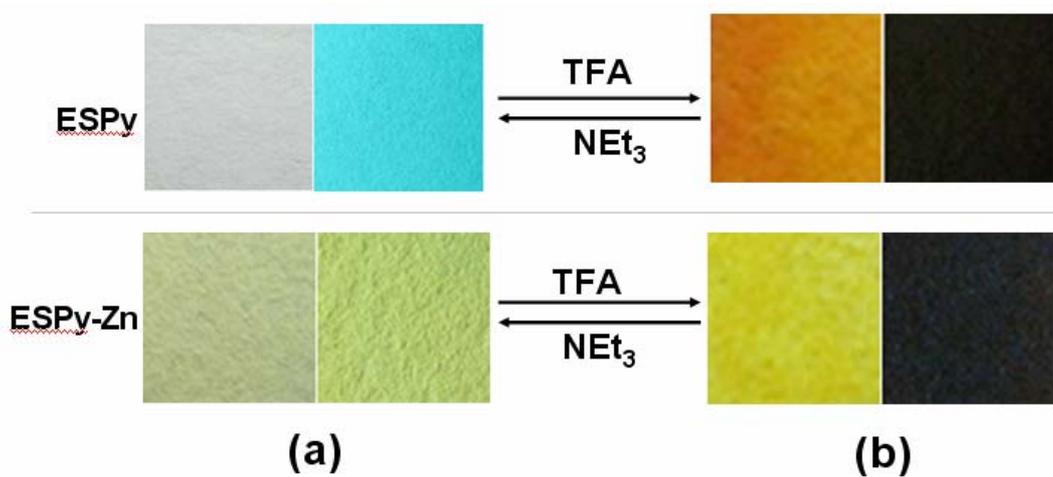


Fig. S11. ESPy and ESPy-Zn taken at room temperature under ambient light (left) and UV light (right). Samples: (a) as-synthesized sample or NEt₃ vapor fumed sample; (b) TFA vapor fumed sample.

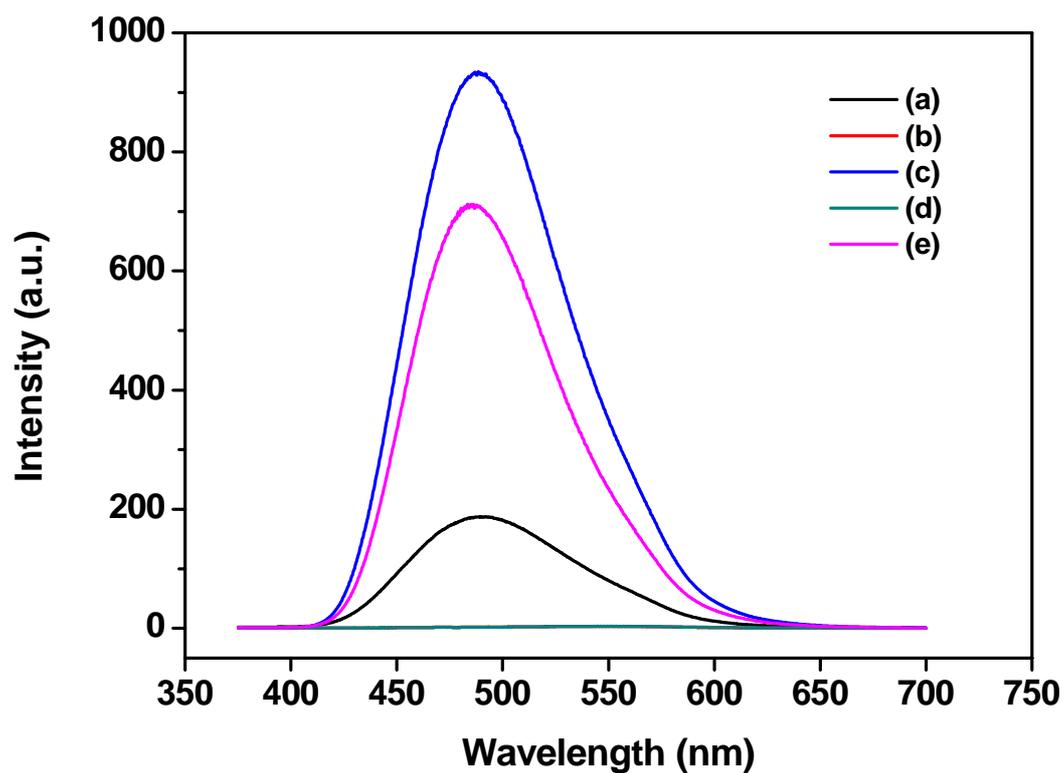


Fig. S12. PL spectra of ESPy : (a) as-synthesized sample [filter paper wetted by the solution of ESPy (in THF) and then dried]; (b) fumed with TFA (filter paper thin film in TFA vapor for 10 s) ; (c) fumed with NEt_3 (filter paper thin film in NEt_3 vapor for 10 s); (d) re-fumed with TFA; (e) re-fumed with NEt_3 .

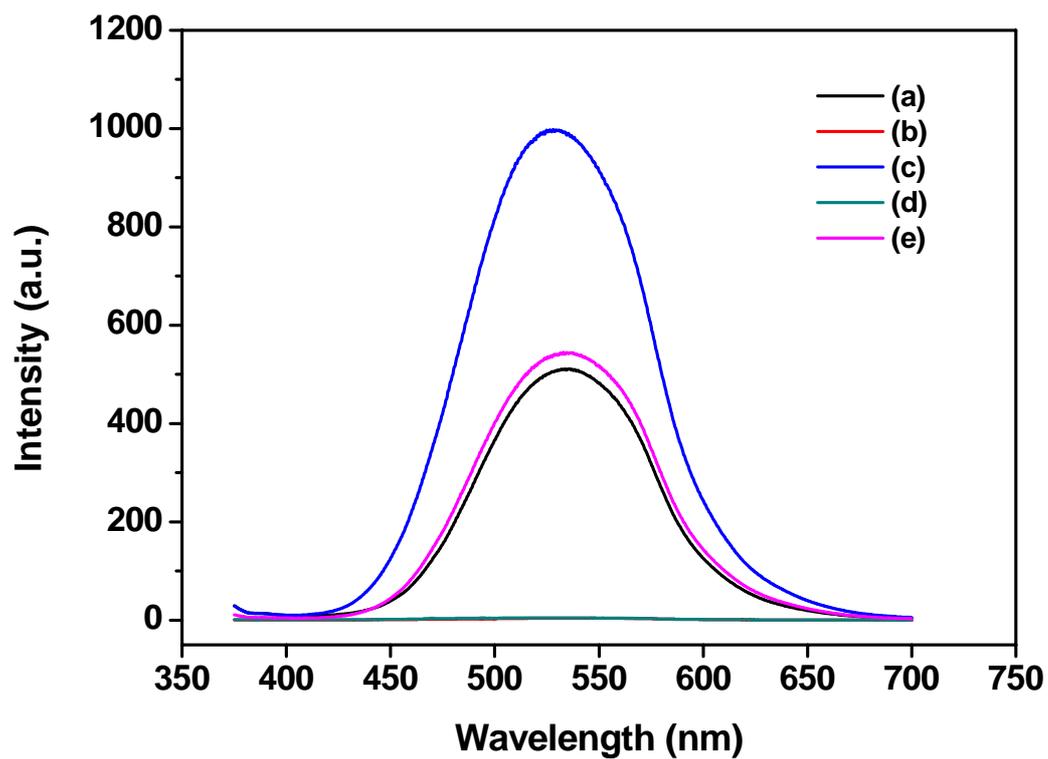
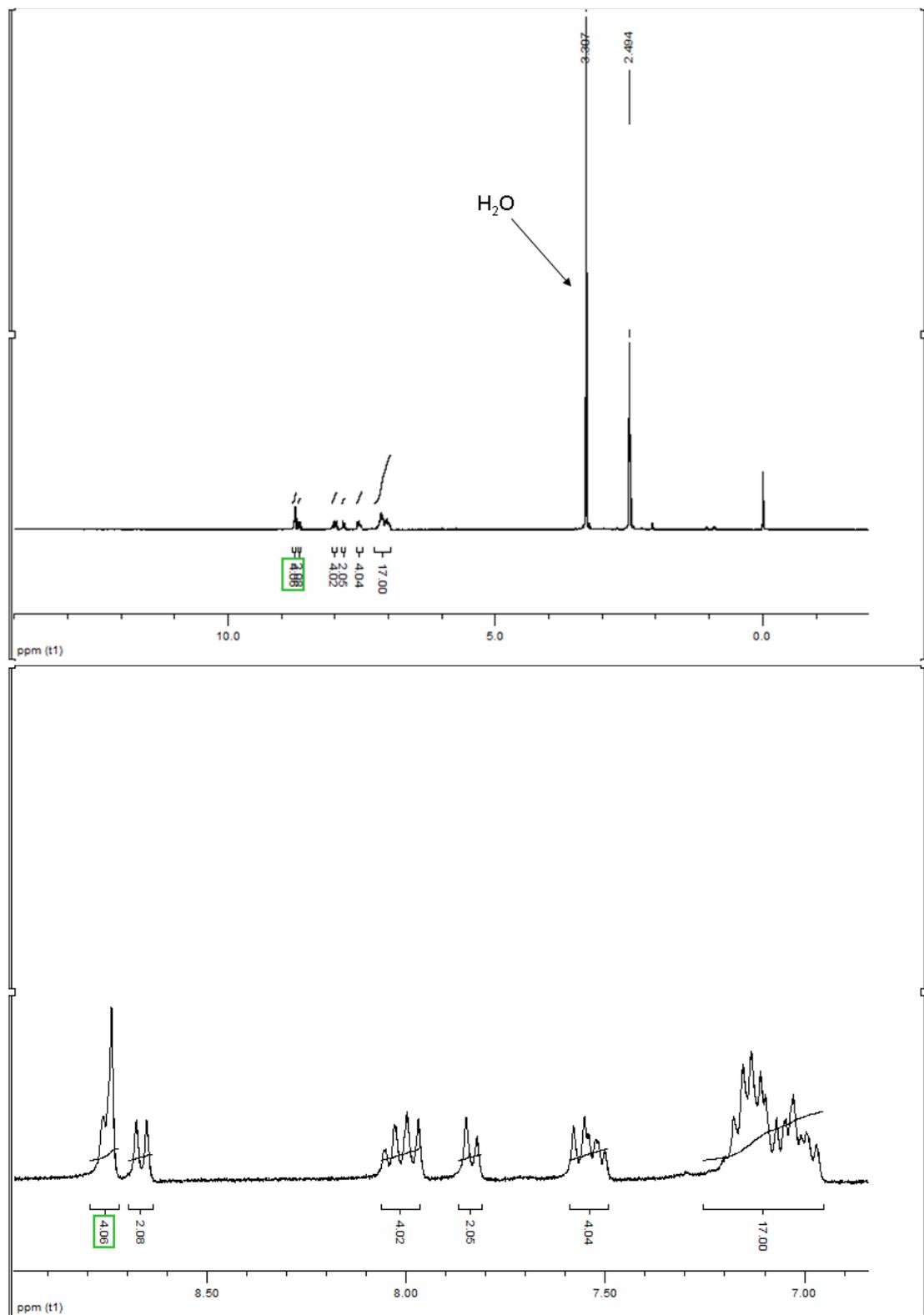


Fig. S13. PL spectra of ESPy-Zn : (a) as-synthesized sample [filter paper wetted by the solution of ESPy-Zn (in acetone) and then dried]; (b) fumed with TFA (filter paper thin film in TFA vapor for 10 s) ; (c) fumed with NEt_3 (filter paper thin film in NEt_3 vapor for 10 s); (d) re-fumed with TFA; (e) re-fumed with NEt_3 .

4. NMR and MS spectra

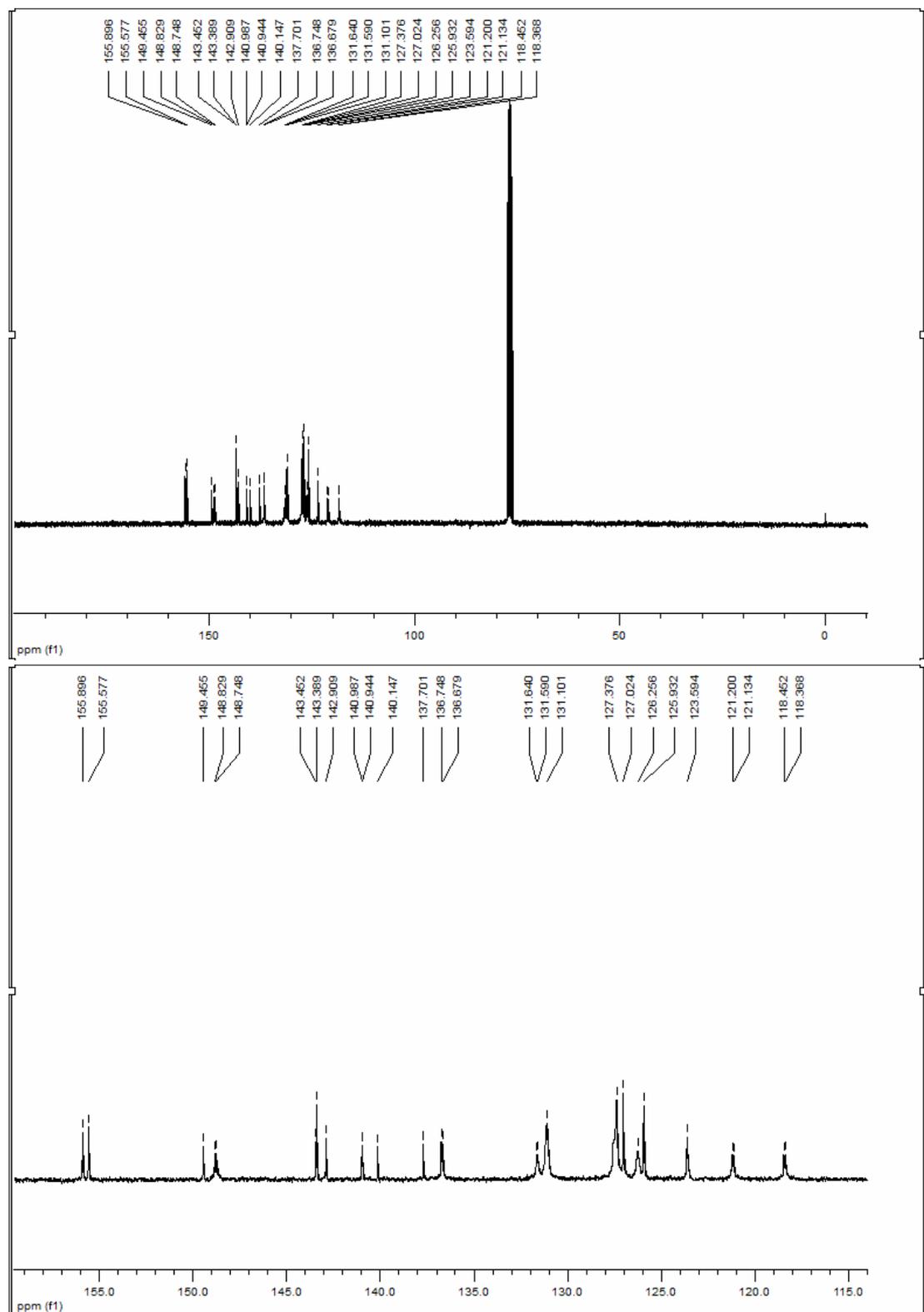
(1) ESPy

$^1\text{H-NMR}$



^1H NMR (300 MHz, DMSO) δ (ppm): 8.77 (s, 4H); 8.66 (d, 2H); 8.00 (q, 4H); 7.84 (d, 2H); 7.54 (m, 4H); 7.24-6.96 (m, 17H).

^{13}C NMR



^{13}C NMR (75MHz, CDCl_3) δ (ppm): 155.90, 155.58, 149.46, 148.83, 148.75, 143.45, 143.39, 142.91, 140.99, 140.94, 140.15, 137.70, 136.75, 136.68, 131.64, 131.59, 131.10, 127.38, 127.02, 126.26, 125.93, 123.59, 121.20, 121.13, 118.45, 118.37.

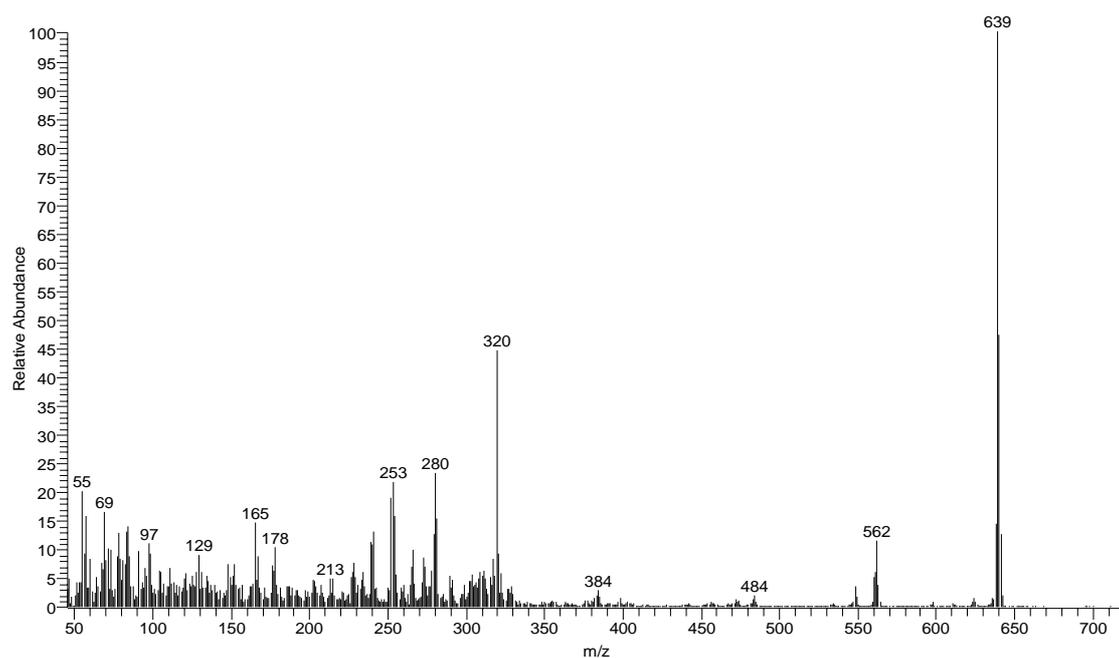
MS

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12/20/2010 10:11:27 AM

EsPy

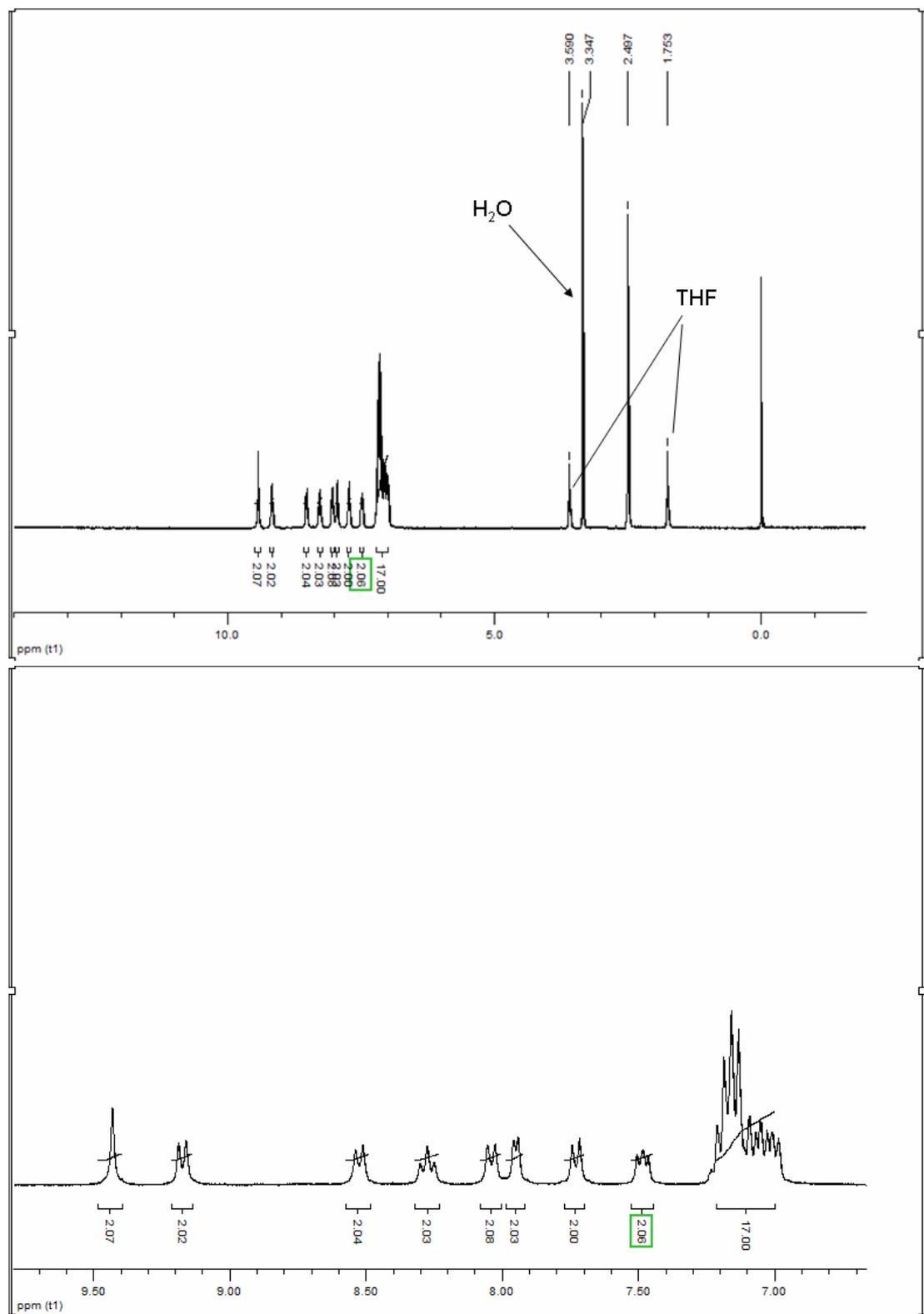
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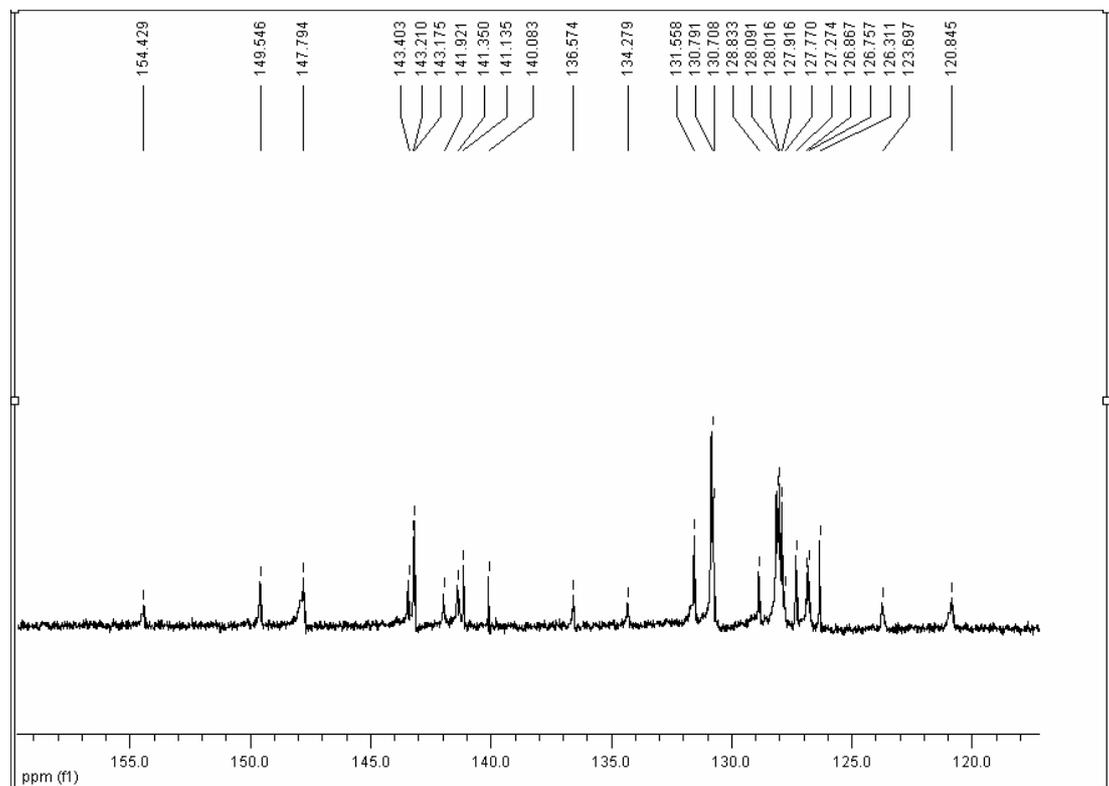
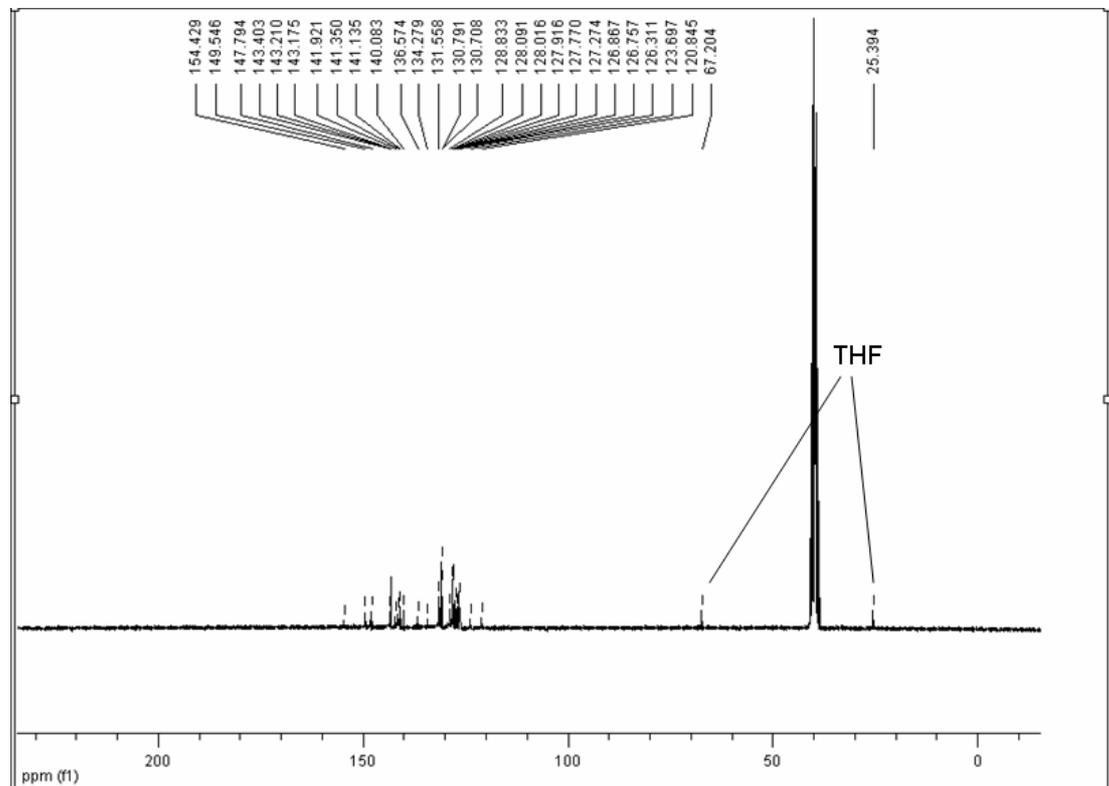
(2) ESPy-Zn

¹H-NMR



^1H NMR (300 MHz, DMSO) $\delta(\text{ppm})$: ^1H NMR (300 MHz, CDCl_3) $\delta(\text{ppm})$: 9.43 (s, 2H); 9.18 (d, 2H); 8.53 (d, 2H); 8.28 (t, 2H); 8.04 (d, 2H); 7.95 (d, 2H); 7.73 (d, 2H); 7.48 (t, 2H); 7.22-6.98 (m, 17H).

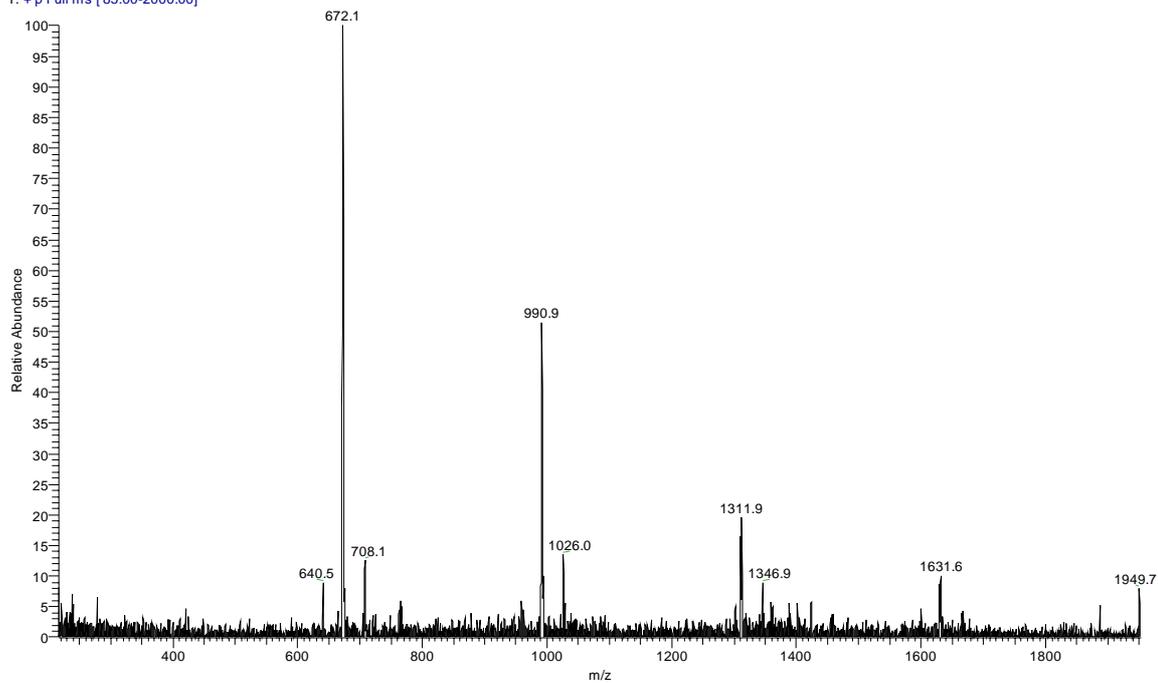
^{13}C NMR



^{13}C NMR (75 Hz, DMSO) δ (ppm): 154.43; 149.55; 147.79; 143.40; 143.21; 143.18;
141.92; 141.35; 141.14; 140.08; 136.57; 134.28; 131.56; 130.79; 130.71; 128.83;
128.09; 128.02; 127.92; 127.77; 127.27; 126.87; 126.76; 126.31; 123.70; 120.85.

MS

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MS (ESI-MS), m/z: $[\text{M}-2\text{PF}_6]^{2+}$ 672, calcd for $[\text{C}_{94}\text{H}_{66}\text{N}_6\text{Zn}]^{2+}$ 672.