Electronic Supplementary Material (ESI) for ChemComm.
This journal is © The Royal Society of Chemistry 2016

Multiple-Color Aggregation-Induced Emission (AIE) Molecules as Chemodosimeters for pH Sensing

Qi Feng,[a] Yuanyuan Li,[b] Lili Wang,[a] Chen Li,[a] Jingmin Wang,[a] Yuanyuan Liu,[a] Kai Li,*[a] and Hongwei Hou*[a]

[a] College of Chemistry and Molecular Engineering, Zhengzhou University, Zhengzhou 450001, P. R. China

[b] School of Chemistry and Chemical Engineering, Henan University of Technology, Zhengzhou 450001, P. R. China

Email: likai@zzu.edu.cn; houhongw@zzu.edu.cn

Contents

1. Experimental

1.1 Reagents

Unless otherwise noted, all materials used in this work were commercially available without any further purification. Salicylaldehyde, 4-methoxylsalicylaldehyde, 5-chlorosalicylaldehyde and 4-N,N-dimethylaminoaniline dihydrochloride were purchased from J&K Chemical Co., Beijing, China. All the other materials were purchased from Sinopharm Chemical Reagent Beijing Co., Beijing, China. Analytical grade absolute ethanol and doubly distilled deionized water were used throughout the experiment. Phosphate buffer solutions of 50 mM at various pH were prepared by mixing different ratios of phosphoric acid, sodium dihydrogen phosphate, disodium hydrogen phosphate and sodium hydroxide, and the pH values were detected by pH meter.

1.2 Apparatus

UV-Vis absorption spectra in solutions were obtained on HP-8543 UV-Vis spectrophotometer. Fluorescence spectra were determined on Hitachi F-4500 fluorescence spectrometer. Fluorescence lifetimes and quantum yields were obtained on Edinburgh FlS-980 fluorescence spectrometer. All pH measurements were carried on a Mettler Toledo FE20/EL20 pH meter. NMR spectra were recorded on a JOEL JNM-ECA300 spectrometer operated at 300 MHz. ESI-MS spectra were obtained on Agilent Technologies 6420 triple quadruopole LC/MS without using the LC part. Dynamic light scattering (DLS) experiments were conducted using a NanoPlus-3 dynamic light scattering particle size/zeta potential analyzer. Single crystal X-ray diffraction analyses carried out on a Rigaku Saturn 724 CCD diffractometer with Mo Kα radiation (λ = 0.71073 Å) at room temperature.

1.3 Determination of quantum yields in aqueous solution

Quantum yield of the solution measured by Edinburgh FlS-980 fluorescence spectrometer with an integrating sphere. Quantum yield measurement of **1-3** in aqueous solution are carried

47 by adding 30 μL of 0.05 mmol/L stock solution of **1-3** to 2.97 mL10 mmol/L PBS stock
48 solutions, after well mixed, the solutions were allowed to stand at 25 °C for 1 min before test.

2. General synthetic procedure

General synthetic procedure of compounds **1-3** is as follows. 1 mmol 4-N,N-dimethylaminoaniline dihydrochloride and 2 mmol NaOH were mixed in 20 mL absolute ethanol. The mixture was stirred and heated to 80 ^{o}C till all the reagents had dissolved. Then 1 mmol corresponding salicylaldehyde derivative was added. The mixture was stirred at room temperature for 3 h to form precipitate. The resulting precipitates were filtrated and washed with 20 mL of absolute ethanol three times. After being dried under reduced pressure, products were obtained in high yields (73−85%).

4-N,N-dimethylaminoaniline salicylaldehyde Schiff-base (**1**). ^{1}H NMR (DMSO-d_6) δ (ppm): 2.94 (s, 6H), 6.77 (d, 2H), 6.93 (d, 2H), 7.37 (d, 3H), 7.57 (m, 1H), 8.93 (s, 1H), 13.66 (s, 1H). ^{13}C NMR (DMSO-d_6) δ (ppm): 113.08 , 116.92 , 119.41 , 120.24 , 122.87 , 132.40 , 132.58 , 136.64 , 150.31 , 158.51, 160.62. ESI mass spectrometry: *m/z* 241.0 ([*M* + H]$^{+}$), M^{+} calculated 240.1.

4-N,N-dimethylaminoaniline-4-methoxylsalicylaldehyde Schiff-base (**2**). ^{1}H NMR (DMSO-d_6) δ (ppm): 2.93 (s, 6H), 3.79 (s, 3H), 6.45 (s, 1H), 6.50 (m, 1H), 6.77 (d, 2H), 7.31 (d, 2H), 7.46 (d, 1H), 8.82 (s, 1H), 14.16 (s, 1H). ^{13}C NMR (DMSO-d_6) δ (ppm): 55.91, 101.38 , 106.87 , 113.23 , 113.85 , 122.42 , 133.83 , 136.70 , 149.96 , 158.23 , 163.34 , 163.42. ESI mass spectrometry: *m/z* 271.0 ([*M* + H]$^{+}$), M^{+} calculated 270.1.

4-N,N-dimethylaminoaniline-5-chlorosalicylaldehyde Schiff-base (**3**). ^{1}H NMR (DMSO-d_6) δ (ppm): 2.96 (s, 6H), 6.79 (d, 2H), 6.97 (d, 1H), 7.36 (d, 3H), 7.67 (s, 1H), 8.93 (s, 1H), 13.66 (s, 1H). ^{13}C NMR (DMSO-d_6) δ (ppm): 113.04, 118.90, 121.55, 122.7, 123.06, 130.95, 131.97, 136.29, 150.56, 156.83, 159.30. ESI mass spectrometry: *m/z* 274.9 ([*M* + H]$^{+}$), M^{+} calculated 274.1.

3. Selected spectra and data referred in the paper

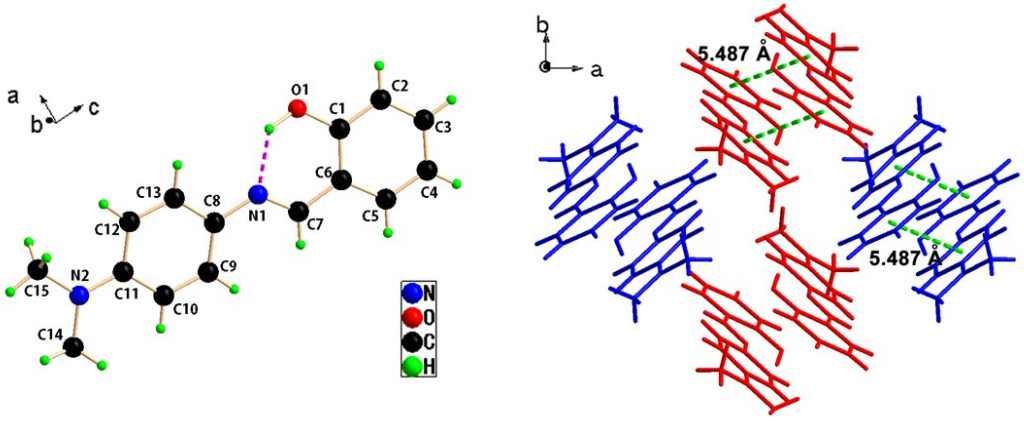


Figure S1. Crystal structure of compound **1**.

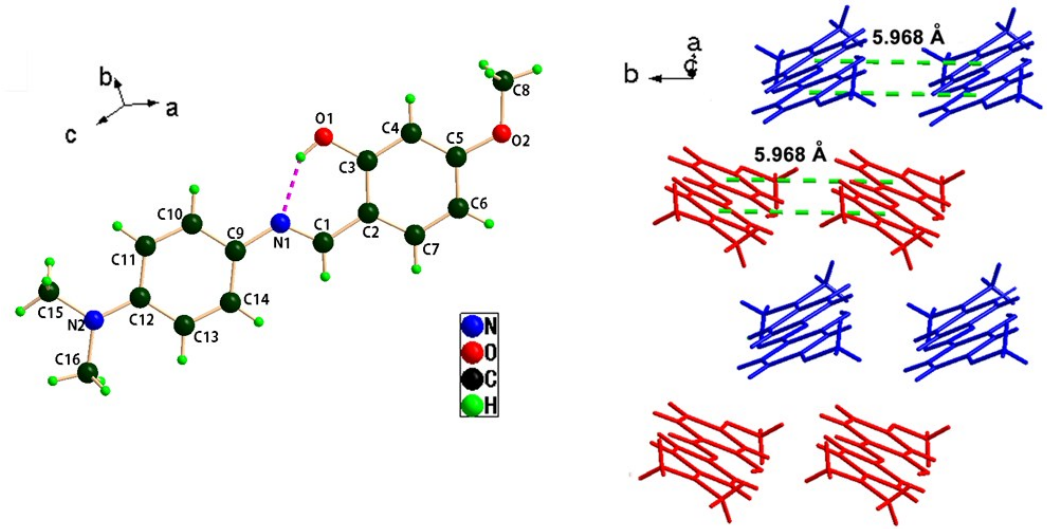


Figure S2. Crystal structure of compound **2**.

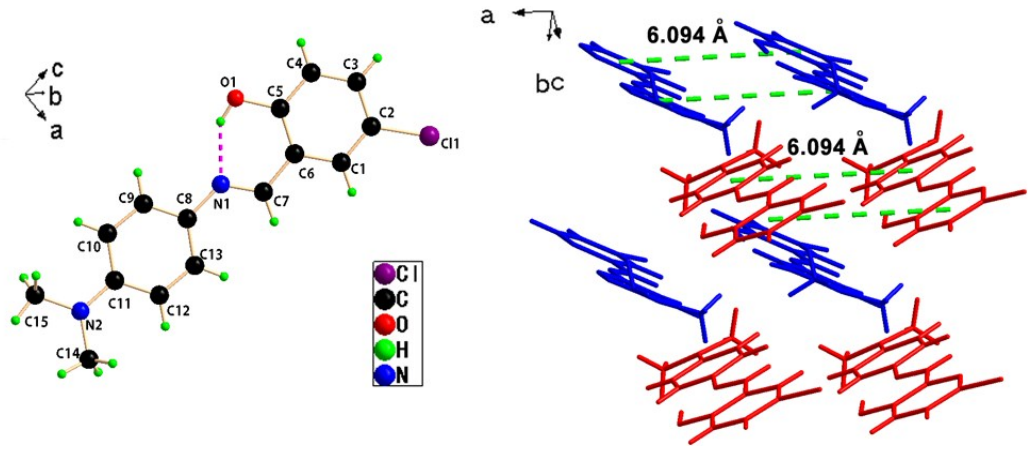


Figure S3. Crystal structure of compound **3**.

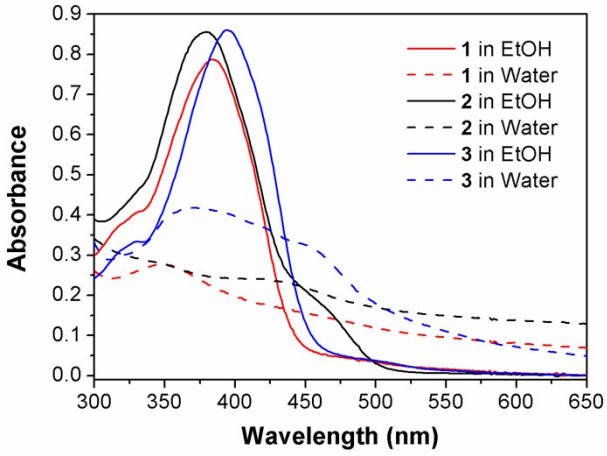


Figure S4. Absorption spectra of **1-3** in "solution" and "aggregate" states. Conditions: The concentrations of **1-3** are 50 μmol/L. "Water" in the legend represents 99% water/EtOH (*v*/*v*) at pH 7.0 buffered by 10 mmol/L PBS.

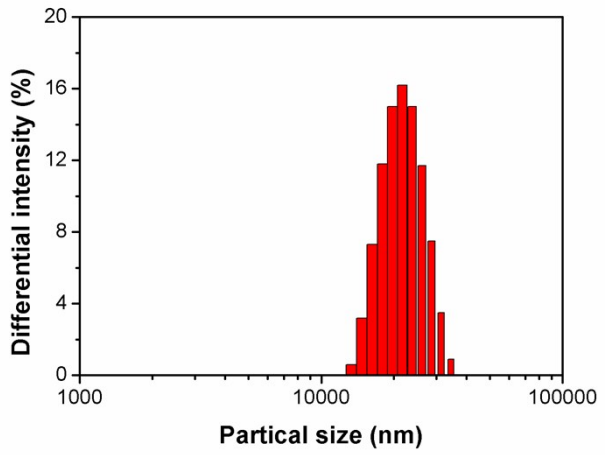


Figure S5. Dynamic lighte scattering results of **1** in aqueous solution of 99% water/EtOH (*v*/*v*) at pH 7.0 buffered by 10 mmol/L PBS. Condition: The concentration of **1** is 50 μmol/L.

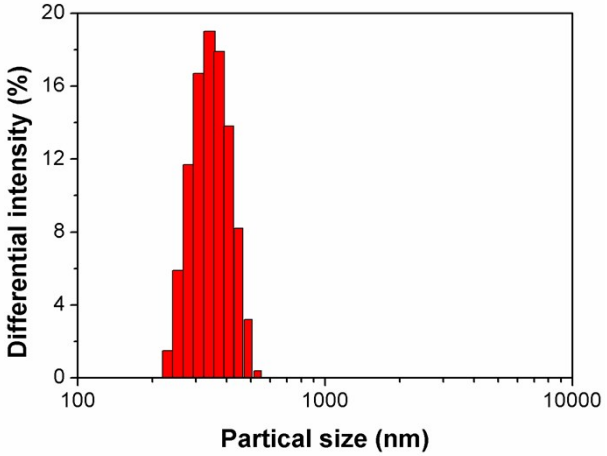


Figure S6. Dynamic lighte scattering results of **2** in aqueous solution of 99% water/EtOH (*v*/*v*) at pH 7.0 buffered by 10 mmol/L PBS. Condition: The concentration of **2** is 50 μmol/L.

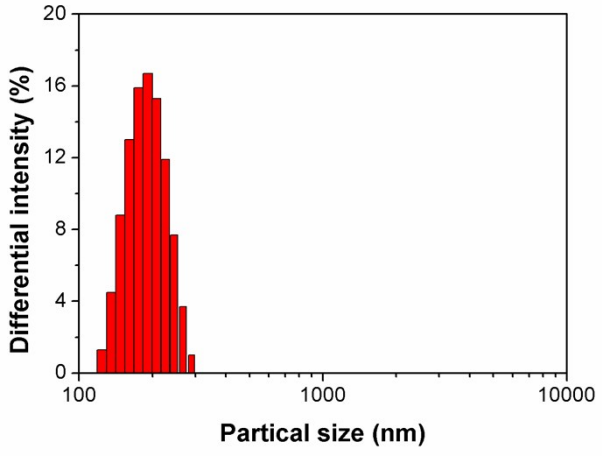


Figure S7. Dynamic lighte scattering results of **3** in aqueous solution of 99% water/EtOH (*v*/*v*) at pH 7.0 buffered by 10 mmol/L PBS. Condition: The concentration of **3** is 50 μmol/L.

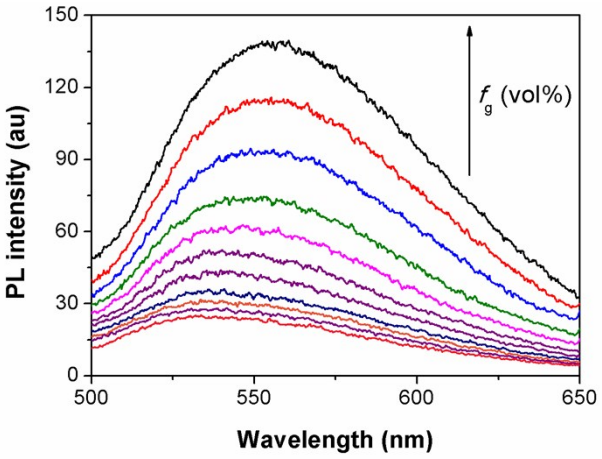


Figure S8. Fluorescence spectra of **1** in EtOH/glycerin mixtures with glycerin volume fraction (f_g) increased from 0% to 99%. Condition: The concentration of **1** is 50 μmol/L.

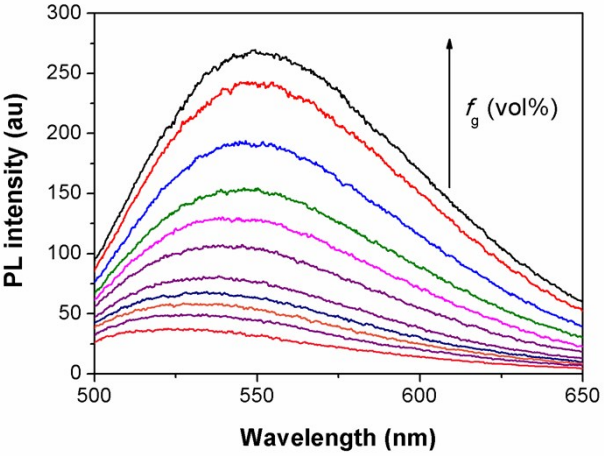


Figure S9. Fluorescence spectra of **2** in EtOH/glycerin mixtures with glycerin volume fraction (f_g) increased from 0% to 99%. Condition: The concentration of **2** is 50 μmol/L.

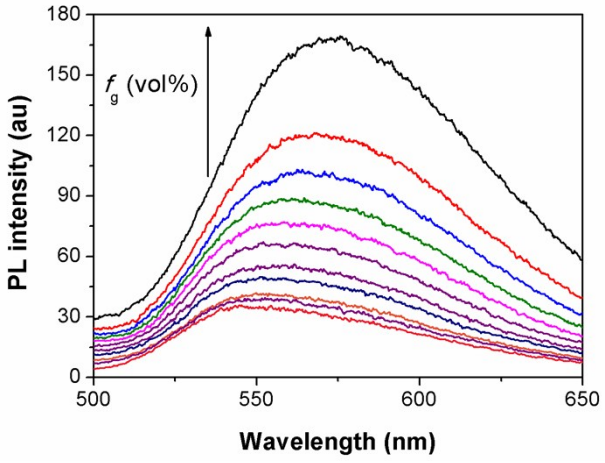


Figure S10. Fluorescence spectra of **3** in EtOH/glycerin mixtures with glycerin volume fraction (f_g) increased from 0% to 99%. Condition: The concentration of **3** is 50 μmol/L.

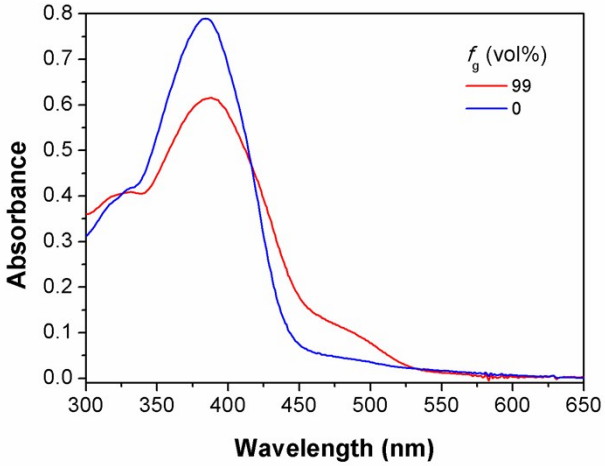


Figure S11. Absorption spectra of **1** in EtOH/glycerin mixtures with glycerin volume fraction (f_g) of 0% and 99%. Condition: The concentration of **1** is 50 μmol/L.

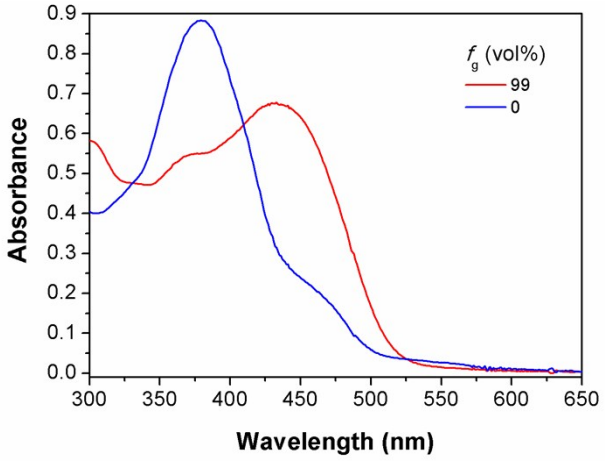


Figure S12. Absorption spectra of **2** in EtOH/glycerin mixtures with glycerin volume fraction (f_g) of 0% and 99%. Condition: The concentration of **2** is 50 μmol/L.

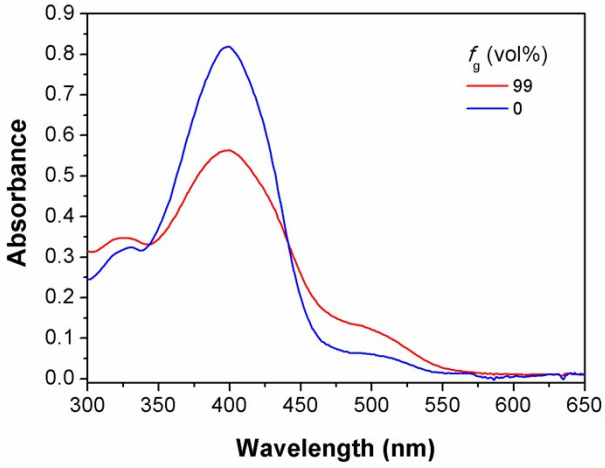


Figure S13. Absorption spectra of **3** in EtOH/glycerin mixtures with glycerin volume fraction (f_g) of 0% and 99%. Condition: The concentration of **3** is 50 μmol/L.

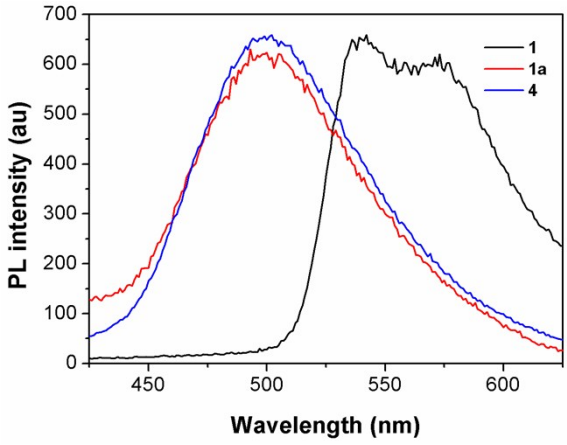


Figure S14. Black line: fluorescence spectra of **1**. Red line: fluorescence spectra of acid-treated **1**. Blue line: fluorescence spectra of **4**. Conditions: 99% water/EtOH (*v*/*v*) at pH 10.0 buffered by 10 mmol/L PBS. The concentrations of **1** and **4** are 50 μmol/L.

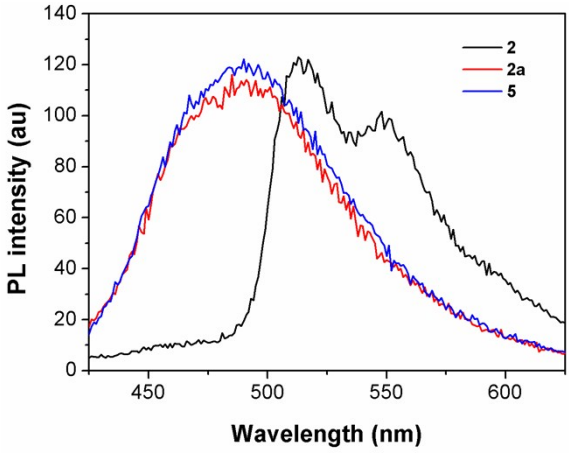


Figure S15. Black line: fluorescence spectra of **2**. Red line: fluorescence spectra of acid-treated **2**. Blue line: fluorescence spectra of **5**. Conditions: 99% water/EtOH (*v*/*v*) at pH 10.0 buffered by 10 mmol/L PBS. The concentrations of **2** and **5** are 50 μmol/L.

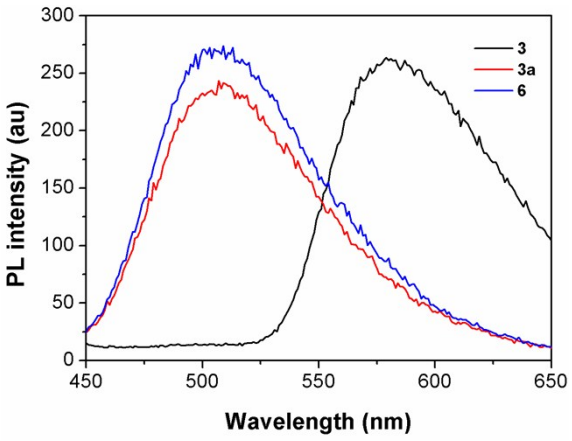


Figure S16. Black line: fluorescence spectra of **3**. Red line: fluorescence spectra of acid-treated **3**. Blue line: fluorescence spectra of **6**. Conditions: 99% water/EtOH (*v*/*v*) at pH 10.0 buffered by 10 mmol/L PBS. The concentrations of **3** and **6** are 50 μmol/L.

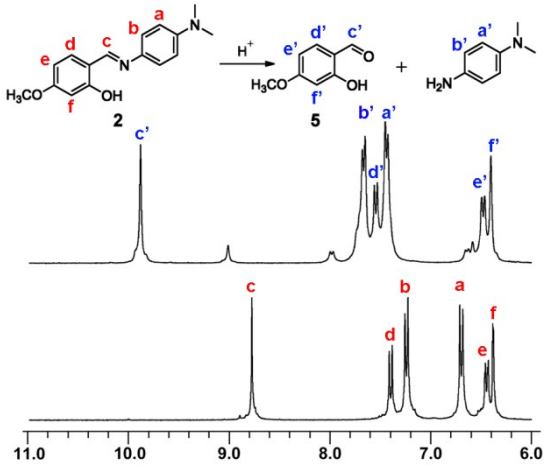


Figure S17. ^{1}H-NMR spectra of **2** in 500 μL DMSO-d_6 before and after the addition of 20 μL TFA/D_2O (1:9, *v*/*v*).

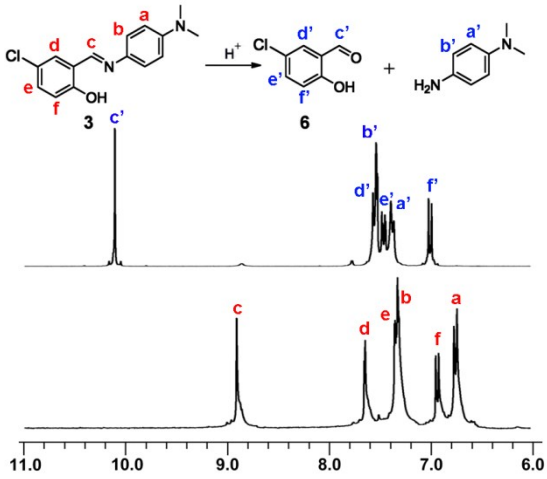


Figure S18. ^{1}H-NMR spectra of **3** in 500 μL DMSO-d_6 before and after the addition of 20 μL TFA/D_2O (1:9, *v*/*v*).

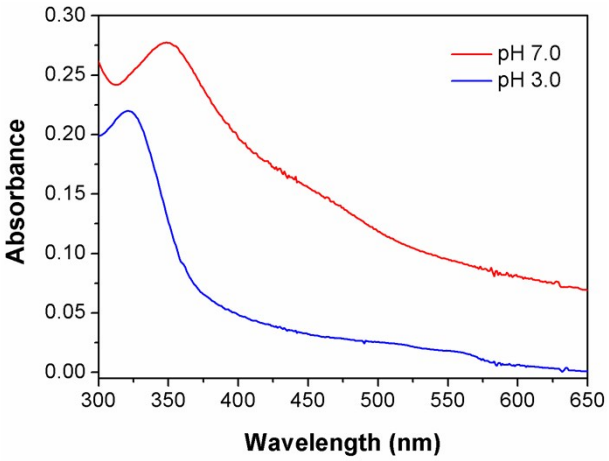


Figure S19. Absorption spectra of **1** in aqueous solution of 99% water/EtOH (*v*/*v*) at different pH buffered by 10 mmol/L PBS. Condition: The concentration of **1** is 50 μmol/L.

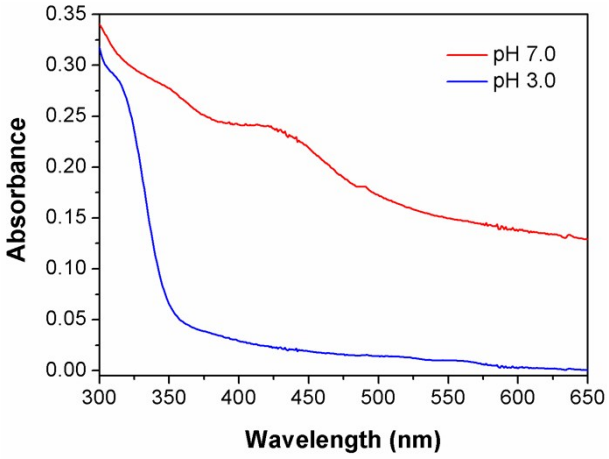


Figure S20. Absorption spectra of **2** in aqueous solution of 99% water/EtOH (*v*/*v*) at different pH buffered by 10 mmol/L PBS. Condition: The concentration of **2** is 50 μmol/L.

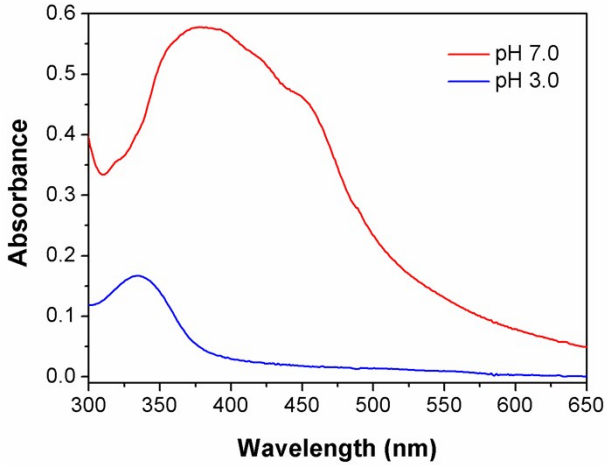
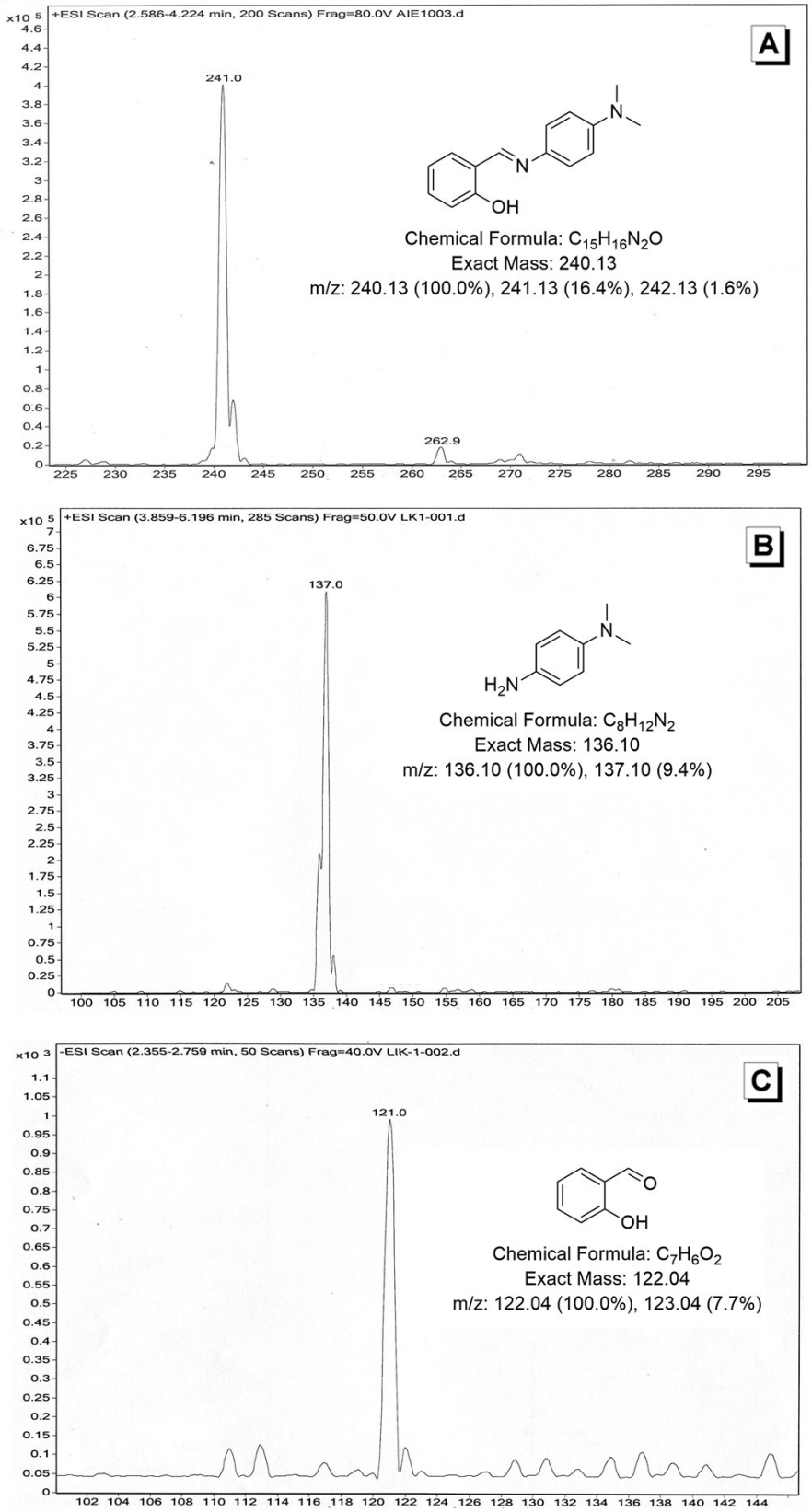


Figure S21. Absorption spectra of **3** in aqueous solution of 99% water/EtOH (*v*/*v*) at different pH buffered by 10 mmol/L PBS. Condition: The concentration of **3** is 50 μmol/L.



158

159 **Figure 22.** A) Positive ESI mass spectra of **1** in MeOH/H_2O (1:1, *v*/*v*). B) Positive ESI mass
160 spectra of **1** in MeOH/H_2O (1:1, *v*/*v*) after the addition of a drop of hydrochloric acid. C)
161 Negative ESI mass spectra of **1** in MeOH/H_2O (1:1, *v*/*v*) after the addition of a drop of
162 hydrochloric acid.

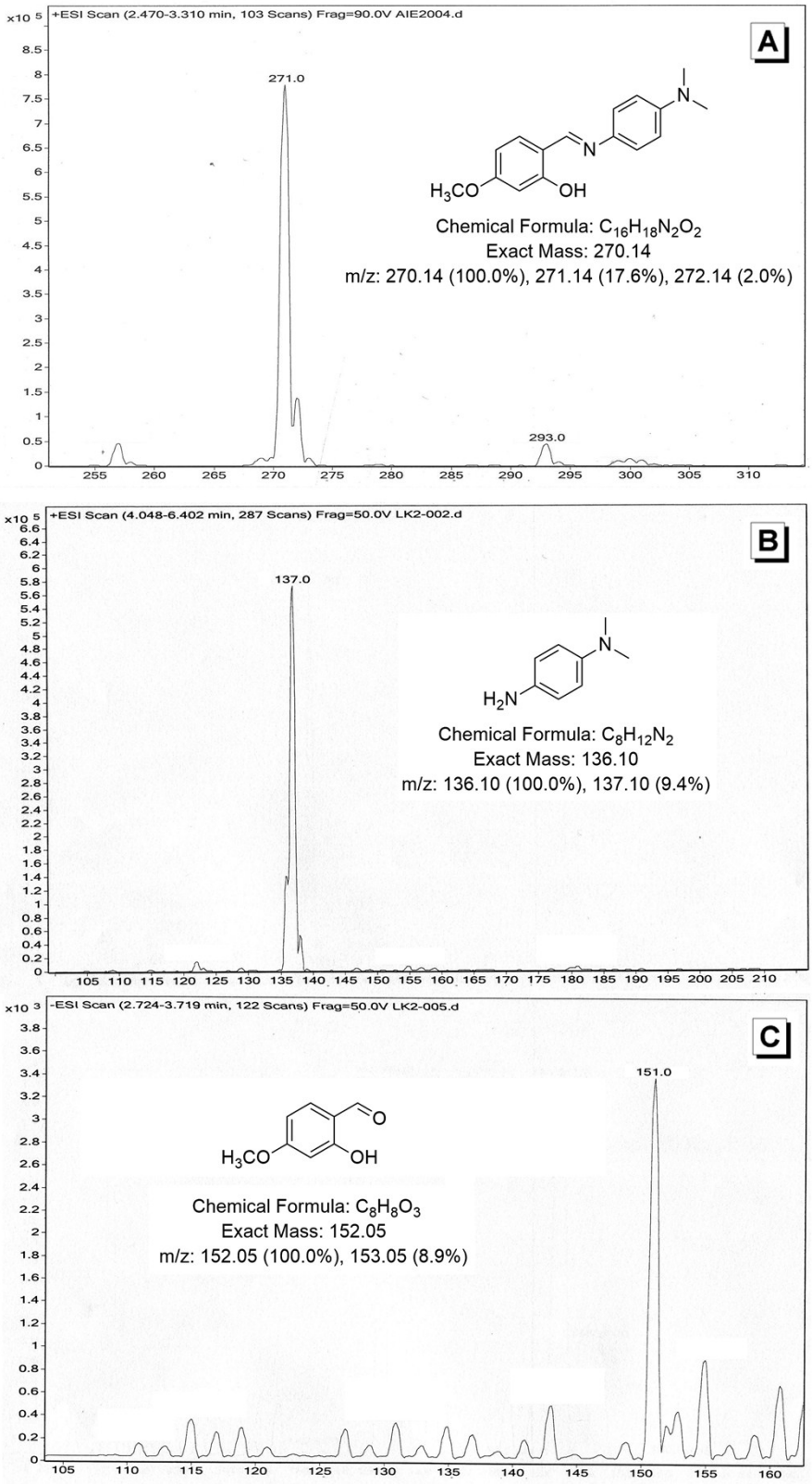
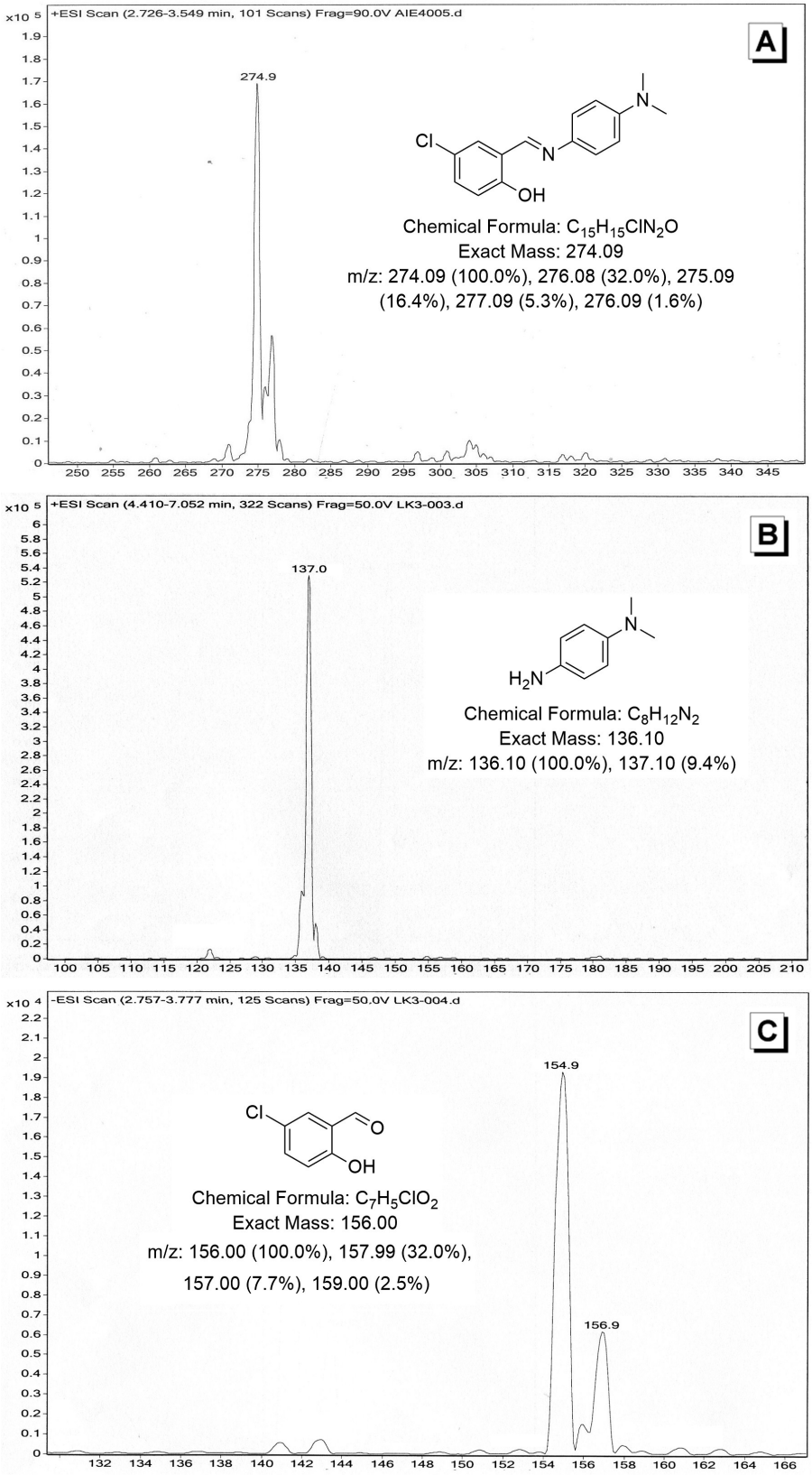


Figure 23. A) Positive ESI mass spectra of **2** in MeOH/H_2O (1:1, *v*/*v*). B) Positive ESI mass spectra of **2** in MeOH/H_2O (1:1, *v*/*v*) after the addition of a drop of hydrochloric acid. C) Negative ESI mass spectra of **2** in MeOH/H_2O (1:1, *v*/*v*) after the addition of a drop of hydrochloric acid.

169



170

171 **Figure 24.** A) Positive ESI mass spectra of **3** in MeOH/H_2O (1:1, *v*/*v*). B) Positive ESI mass
172 spectra of **3** in MeOH/H_2O (1:1, *v*/*v*) after the addition of a drop of hydrochloric acid. C)

Negative ESI mass spectra of **3** in MeOH/H_2O (1:1, *v*/*v*) after the addition of a drop of hydrochloric acid.

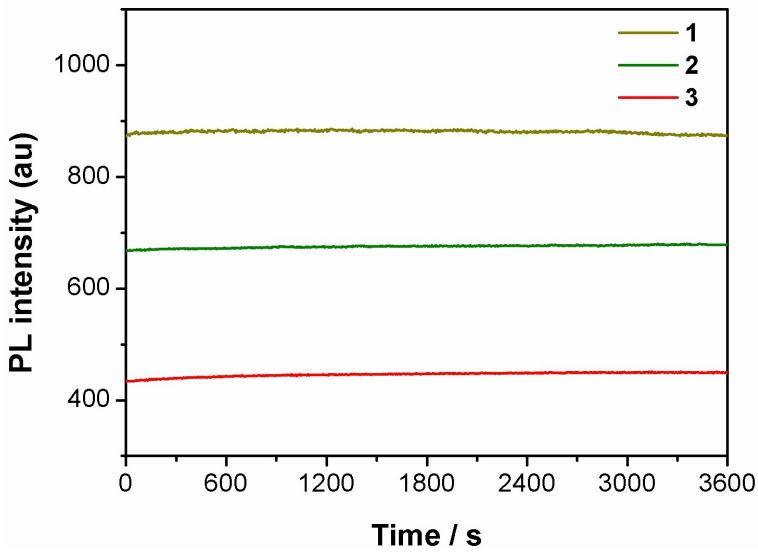


Figure 25. Time-dependent fluorescence spectra of **1-3** in aqueous solution of 99% water/EtOH (*v*/*v*) buffered by 10 mmol/L PBS at pH 7.0. The concentrations of **1-3** are 50 μmol/L.

Table S1. A comparison of fluorescence emission wavelengths of DAS and other AIE molecules.

Compounds	DAS	TPE	HPS	MPPS	2,3-dicyano-5,6-diphenylpyrazine	SAA	organoboron complexes
λ_{max} / nm	513-580	453[1]	495[2]	491[2,3]	413[4]	513-570[5]	448-661[6-8]

Table S2. Fluorescence dynamics parameters of **1-3**.[a]

	τ (ns	Φ (%	k_r (s^{-1})	k_{nr} (s^{-1})

	)	)		
1	2.54	14.9	5.87×10	3.35×10
			7	8
2	0.93	7.4	7.96×10	9.96×10
			7	8
3	2.27	8.0	3.52×10	4.05×10
			7	8

[a] These parameters are determined in 99% water/EtOH (*v*/*v*) buffered by 10 mmol/L PBS at pH 7.0. The concentrations of **1-3** are 50 μmol/L.

4. Crystallographic data and structure refinement for 1-3

Compound	**1**	**2**	**3**
Empirical formula	$C_{15}H_{16}N_2O$	$C_{16}H_{18}N_2O_2$	$C_{15}H_{15}ClN_2O$
Formula weight	240.3	270.32	274.74
Temperature	293(2)	293(2)	293(2)
Wavelength	0.71073	0.71073	0.71073
Crystal system	orthorhombic	Monoclinic	orthorhombic
Space group	Pbca	P2(1)/n	P2(1)2(1)2(1)
a/Å	11.278(2)	14.9189(13)	6.0936(12)
b/Å	8.2043(16)	5.9680(5)	8.4244(17)
c/Å	27.475(6)	20.9971(18)	26.374(5)
α/deg	90	90	90
β/deg	90	130.968(3)	90
γ/deg	90	90	90
Volume	2542.2(9)	1411.6(2)	1353.9(5)
Z	8	4	4
Density (calculated)	1.256	1.272	1.348
F(000)	1024	576	576
Reflections collected	11128	6735	5769
Independent reflections	2169 R(int) = 0.0652	2472 [R(int) =0.0363]	2524 [R(int) = 0.0571]
Data / restraints /	2169/0/169	2472/0/181	2524/0/175

parameters			
Goodness-of-fit	1.179	1.052	1.11
Final R indices [I>2sigma(I)]	R1=0.0940, wR2 = 0.1812	R1 = 0.0492, wR2 = 0.1095	R1 = 0.0888, wR2 = 0.1309
R indices (all data)	R1= 0.1461, wR2 = 0.2099	R1 = 0.0929, wR2 = 0.1304	R1 = 0.1296, wR2 = 0.1505

190

5. Reference

(1) Shi, J.; Chang, N.; Li, C.; Mei, J.; Deng, C.; Luo, X.; Liu, Z.; Bo, Z.; Dong, Y. Q.; Tang, B. Z. *Chem. Commun.* **2012**, *48*, 10675.

(2) Chen, J.; Law, C. C.; Lam, J. W.; Dong, Y.; Lo, S. M.; Williams, I. D.; Zhu, D.; Tang, B. Z. *Chem. Mater.* **2003**, *15*, 1535.

(3) Luo, J.; Xie, Z.; Lam, J. W.; Cheng, L.; Chen, H.; Qiu, C.; Kwok, H. S.; Zhan, X.; Liu, Y.; Zhu, D. *Chem. Commun.* **2001**, 1740.

(4) Qin, A.; Lam, J. W. Y.; Mahtab, F.; Jim, C. K. W.; Tang, L.; Sun, J.; Sung, H. H. Y.; Williams, I. D.; Tang, B. Z. *Appl. Phys. Lett.* **2009**, *94*, 253308.

(5) Tang, W.; Xiang, Y.; Tong, A. *J. Org. Chem.* **2009**, *74*, 2163.

(6) Ryousuke, Y.; Amane, H.; Kazuo, T.; Yoshiki, C. *Chem. - Eur. J.* **2014**, *20*, 8320.

(7) Xiaoqing, W.; Yanping, W.; Qingsong, L.; Zhenyu, L.; Hui, Y.; Chonglei, J.; Jicheng, D.; Zhipeng, L. *Chem. Commun.* **2014**, *51*, 784.

(8) Yoshii, R.; Suenaga, K.; Tanaka, K.; Chujo, Y. *Chem. - Eur. J.* **2015**, *21*, 7231.