

Supporting Information

A New Red Fluorophore with Aggregation Enhanced Emission by an Unexpected “One-step” Protocol

Rui Wang,^a Meili Hou,^a Zhigang Xu,^a Luxi Tan,^c Cheng Zhong^{*b} and Linna Zhu^{*a}

^a *Chongqing Key Laboratory for Advanced Materials and Technologies of Clean Energy, Faculty of Materials & Energy, Southwest University, Chongqing 400715, P.R. China.*

^b *Department of Chemistry, Hubei Key Lab on Organic and Polymeric Optoelectronic Materials, Wuhan University, Wuhan 430072, P.R. China.*

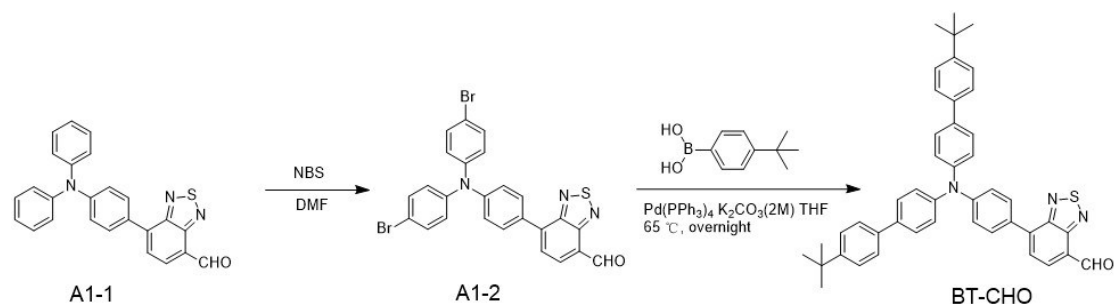
^c *School of Chemistry and Chemical Engineering, Chongqing University, Chongqing 401331, P.R. China.*

Corresponding author e-mail: lnzhu@swu.edu.cn; zhongcheng@whu.edu.cn.

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Synthesis of compound BT-CHO



Scheme S1. The synthetic route for BT-CHO.

Synthesis of compound A1-1

Compound **A1-1** were synthesized according to previously reported method.^[1]

Synthesis of compound A1-2

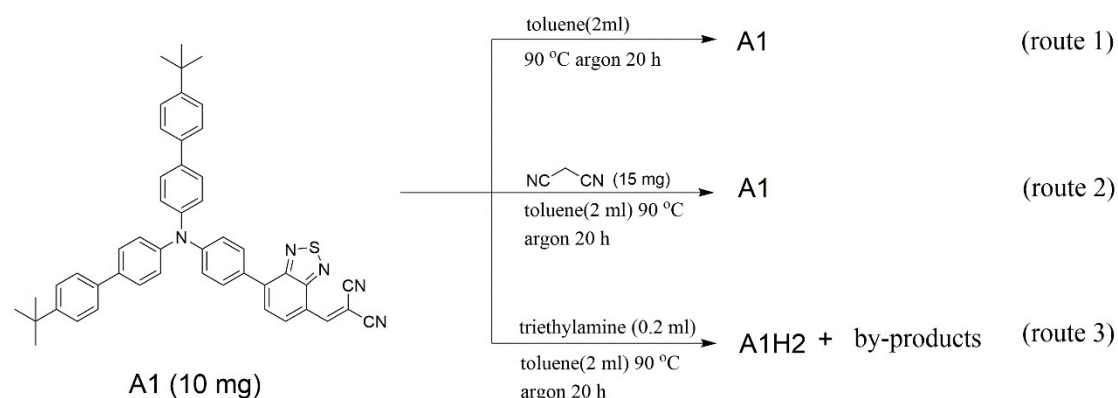
A 100 mL of Schlenk flask containing A1-1 (700 mg, 1.02 mmol) was added DMF (15 mL). NBS (670 mg, 3.76 mmol dissolved in 15 mL of DMF) was dropped slowly and the solution was stirred at room temperature for overnight. After the reaction was complete, the reaction mixture was poured into water and then extracted with CH₂Cl₂. The organic extract was dried over anhydrous Na₂SO₄ and was further purified by column chromatography using a dichloromethane/hexanes (2:3) mixture as the eluent. Compound **A1-2** was isolated as a bright red powder in 99% yield. ¹H NMR (600 MHz, CDCl₃) δ 10.77 (s, 1H), 8.29 (d, *J* = 7.8 Hz, 1H), 7.95 (d, *J* = 9.0 Hz, 2H), 7.85 (d, *J* = 7.2 Hz, 1H), 7.42 (d, *J* = 12.0 Hz, 4H), 7.19 (d, *J* = 6.0 Hz, 2H), 7.05 (d, *J* = 8.4 Hz, 4H). ¹³C NMR (150 MHz, CDCl₃) δ 188.80, 153.99, 153.83, 148.33, 145.87, 139.55, 132.69, 132.44, 130.75, 130.54, 126.49, 126.11, 125.98, 122.80, 116.80.

Synthesis of compound BT-CHO

Compound **A1-2** (800 mg, 1.42 mmol), (4-(tert-butyl)phenyl)boronic acid (755 mg, 4.24 mmol), Pd(PPh₃)₄ (97 mg, 0.084 mmol) were loaded into 100 ml Schlenk flask. A mixture of aqueous solution of K₂CO₃ (7.04 ml, 2 M) and THF (35 ml) were added to flask and stirred at reflux (65 °C) for overnight under argon atmosphere. After the reaction was complete, the reaction mixture was poured into water and then extracted with CH₂Cl₂, and evaporated under reduced pressure. The remaining crude product was purified by column chromatography using a dichloromethane/hexanes (2:3) mixture as the eluent. Compound **BT-CHO** was isolated as a red powder in 84% yield. ¹H NMR (600 MHz, CDCl₃) δ 10.77 (s, 1H), 8.28 (d, *J* = 7.8 Hz, 1H), 7.98

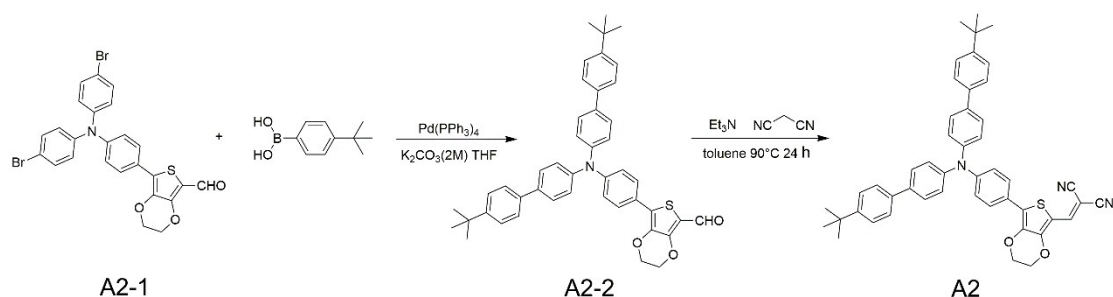
(d, $J = 8.4$ Hz, 2H), 7.86 (d, $J = 7.8$ Hz, 1H), 7.55 (t, $J = 7.8$ Hz, 8H), 7.47 (d, $J = 8.4$ Hz, 4H), 7.29 (t, $J = 8.4$ Hz, 6H), 1.37 (s, 16H). ^{13}C NMR (150 MHz, CDCl_3) δ 188.82, 154.07, 153.90, 150.15, 149.19, 145.96, 139.91, 137.63, 136.63, 132.60, 130.60, 129.51, 127.95, 126.43, 125.79, 125.75, 125.43, 122.37, 34.53, 31.38.

Parallel experiments of A1 with different substrates



Scheme S2. Three parallel experiments of A1 with different substrates.

Synthesis of compound A2



Scheme S3. The synthetic route for A2.

Synthesis of compound A2-1

Compound A2-1 were synthesized according to previous reported method.^[2]

Synthesis of compound A2-2

Compound A2-1 (500 mg, 0.96 mmol), (4-(*tert*-butyl) phenyl) boronic acid (514 mg, 2.88 mmol), $\text{Pd}(\text{PPh}_3)_4$ (66.7 mg, 0.058 mmol) were loaded into 100 ml Schlenk flask. A mixture of aqueous solution of K_2CO_3 (4.80 ml, 2 M) and THF (30 ml) were added to flask and stirred at reflux (65 °C) for overnight under argon ambience. After the reaction was complete, the reaction mixture was

poured into water and then extracted with CH₂Cl₂, and evaporated under reduced pressure. The remaining crude product was purified by column chromatography using a dichloromethane/hexanes (3:2) mixture as the eluent. Compound **A2-2** was isolated as an orange powder in 95% yield. ¹H NMR (600 MHz, CDCl₃) δ 9.91 (s, 1H), 7.70 (d, *J* = 9.0 Hz, 2H), 7.52 (dd, *J* = 8.4, 4.2 Hz, 8H), 7.47 (d, *J* = 8.4 Hz, 4H), 7.22 (d, *J* = 8.4 Hz, 4H), 7.16 (d, *J* = 9.0 Hz, 2H), 4.42 (m, *J* = 7.8 Hz, 2H), 4.38 (m, *J* = 8.4 Hz, 2H), 1.36 (s, 18H). ¹³C NMR (150 MHz, CDCl₃) δ 179.36, 150.08, 148.18, 145.98, 137.59, 137.03, 136.37, 132.48, 128.00, 127.92, 127.88, 126.40, 125.74, 125.11, 122.74, 114.92, 65.15, 64.54, 34.53, 31.38.

Synthesis of compound **A2**

To a solution of **A2-1** (300 mg, 0.45 mmol) and malononitrile (90 mg, 1.36 mmol) in 15 mL of toluene was added 0.20 mL of triethylamine. After being stirred at 90 °C for 1 h under argon atmosphere, the reaction mixture was poured into water and then extracted with CH₂Cl₂. The organic extract was dried over anhydrous Na₂SO₄ and was further purified by column chromatography using a dichloromethane/hexanes (1:1) mixture as the eluent. Compound **A2** was isolated as a dark powder in 53% yield. ¹H NMR (600 MHz, CDCl₃) δ 7.83 (s, 1H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.53 (dd, *J* = 8.4, 1.8 Hz, 8H), 7.46 (d, *J* = 8.4 Hz, 4H), 7.22 (d, *J* = 8.4 Hz, 4H), 7.13 (d, *J* = 8.4 Hz, 2H), 4.42 (d, *J* = 3.0 Hz, 2H), 4.36 (s, 2H), 1.36 (s, 24H). ¹³C NMR (150 MHz, CDCl₃) δ 150.22, 149.45, 149.03, 145.60, 144.76, 137.48, 136.95, 136.88, 132.07, 128.40, 127.98, 126.44, 125.77, 125.49, 124.13, 121.96, 115.47, 114.54, 109.65, 65.60, 64.48, 34.55, 31.38. HRMS (APCI): calcd for C₄₈H₄₄N₃O₂S [M + H]⁺: 726.3149, found 726.3155.

HPLC analysis

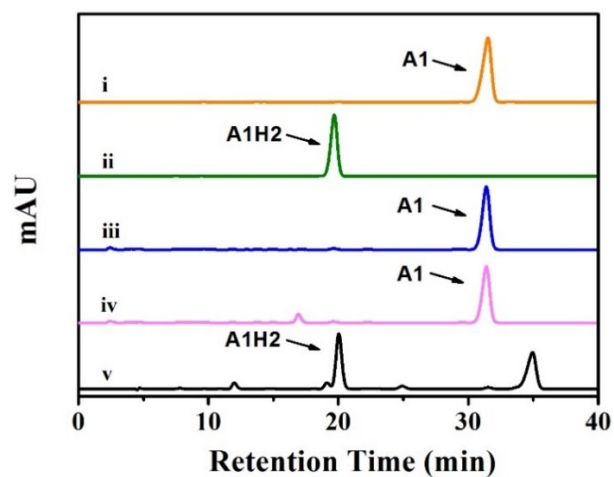


Fig. S1 HPLC profile showing the reactions of A1 with different substrates: (i) A1 alone, (ii) A1H2 alone, (iii) A1+toluene, (iv) A1+toluene+malononitrile, (v) A1+toluene+triethylamine.

TLC plate

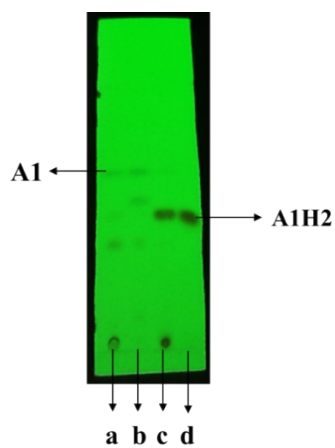


Fig. S2 a, b and c correspond to the reactions using piperidine, diethylamine and hexylamine as base, respectively; d represents the pure A1H2.

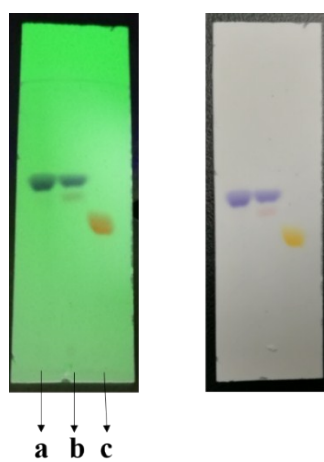


Fig. S3 a and c represent the pure A1 and A1H2, respectively. b is the reaction of A1 with amantadine.

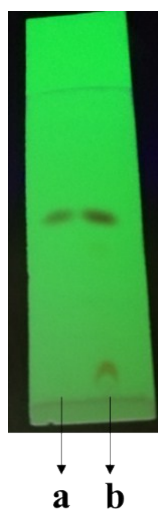


Fig. S4 a represents the pure A2. b is the reaction using the hexylamine as the base.

PL spectra of A1 and A1H2 in solid state

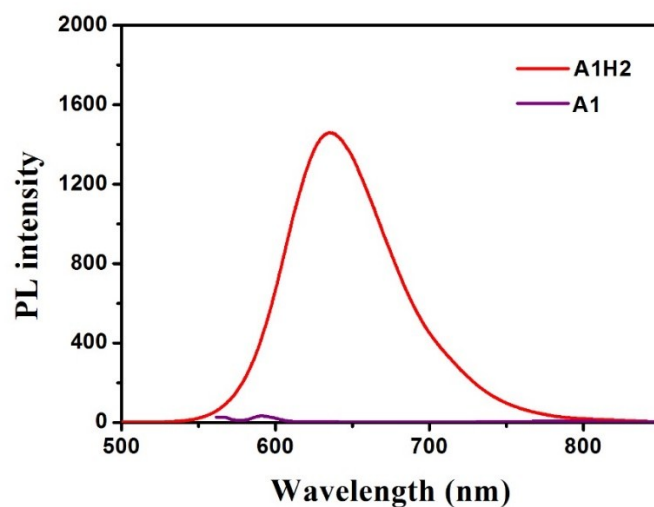


Fig. S5 PL spectra of A1 (purple line) and A1H2 (red line) in solid state (excitation wavelength for A1: 550 nm, excitation wavelength for A1H2: 385 nm).

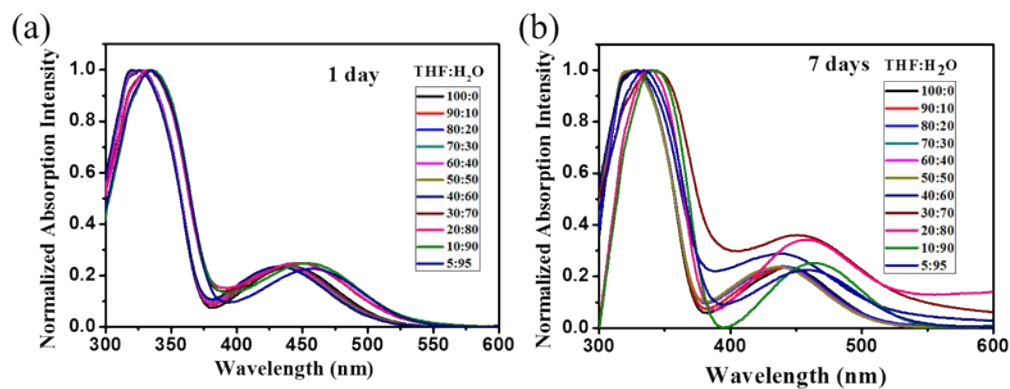


Fig. S6 Normalized Absorption spectra of A1H2-NPs at different water fractions aged for (a) 1 day and (b) 7 days.

Table S1. The maximum absorption wavelength of A1H2-NPs at different water fractions after aging for 1 day and 7 days.

	λ_{abs} (nm)										
	0%	10%	20%	30%	40%	50%	60%	70%	80%	90%	95%
1day	441	438	436	436	435	433	433	447	447	454	459
7days	443	441	439	437	437	437	439	449	457	463	459

Data calculated at the B3LYP/6-31G (d)* level

Table S2. Data calculated at the B3LYP/6-31G (d)* level

Sample	f^a	Orb: Compos (%)	$\lambda_{\text{calc em}}^b/\text{nm}$
A1H2	0.2760	HOMO→LUMO:98.4	672.98
A1	0.5136	HOMO→LUMO:99.2	914.33

^a Oscillator strength. ^b Emission maximum (λ_{em}) derived from theoretical DFT calculations.

Influence of pH on fluorescent intensity of A1H2-NPs

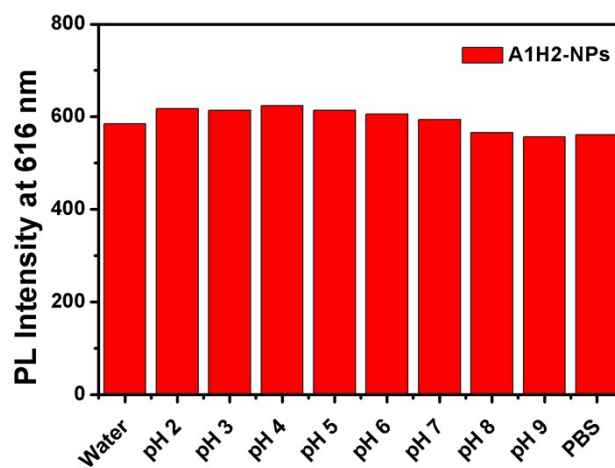
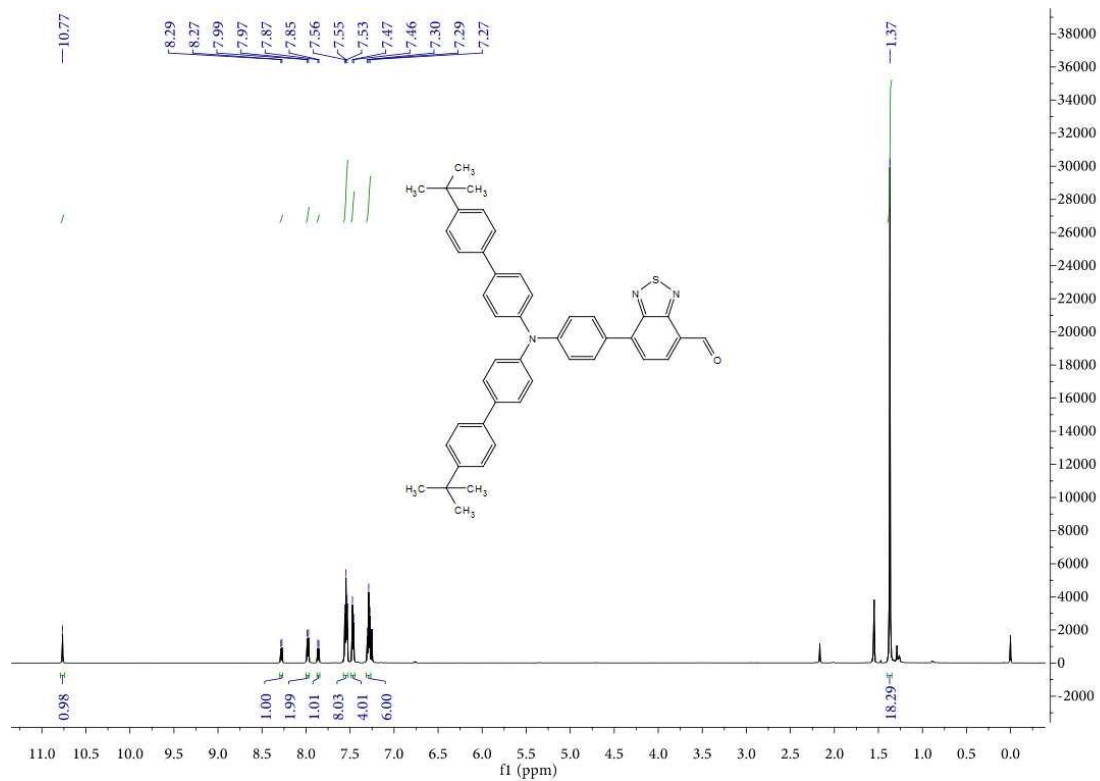
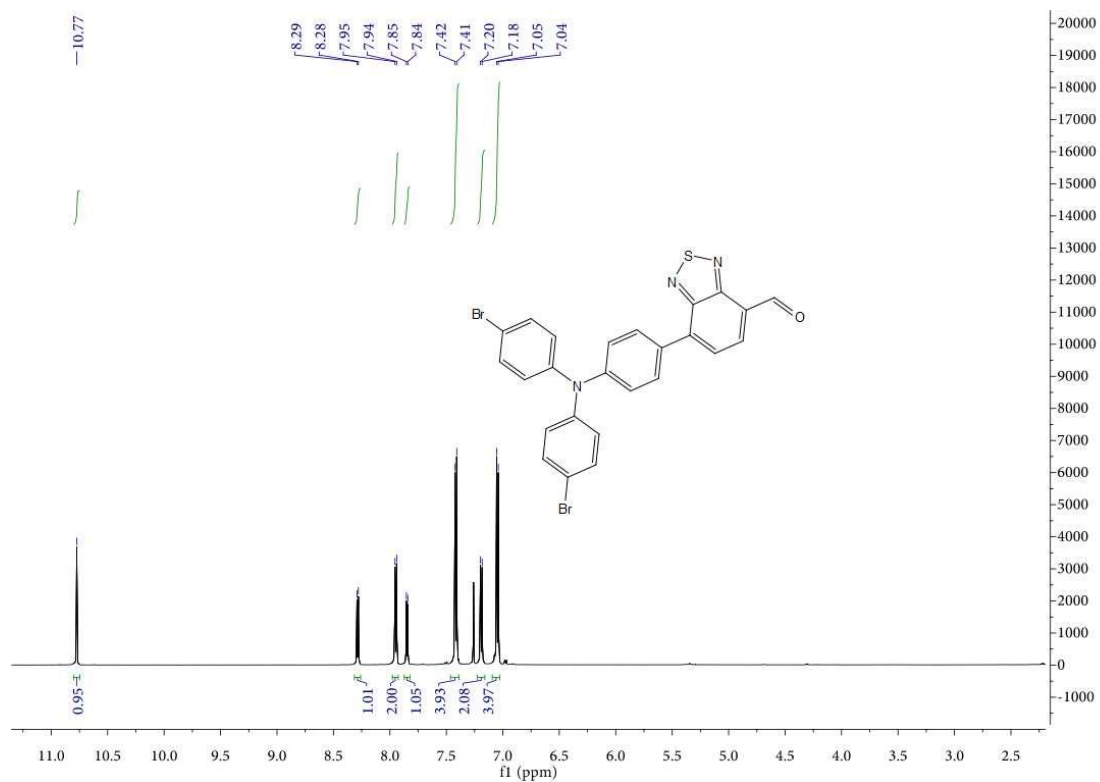
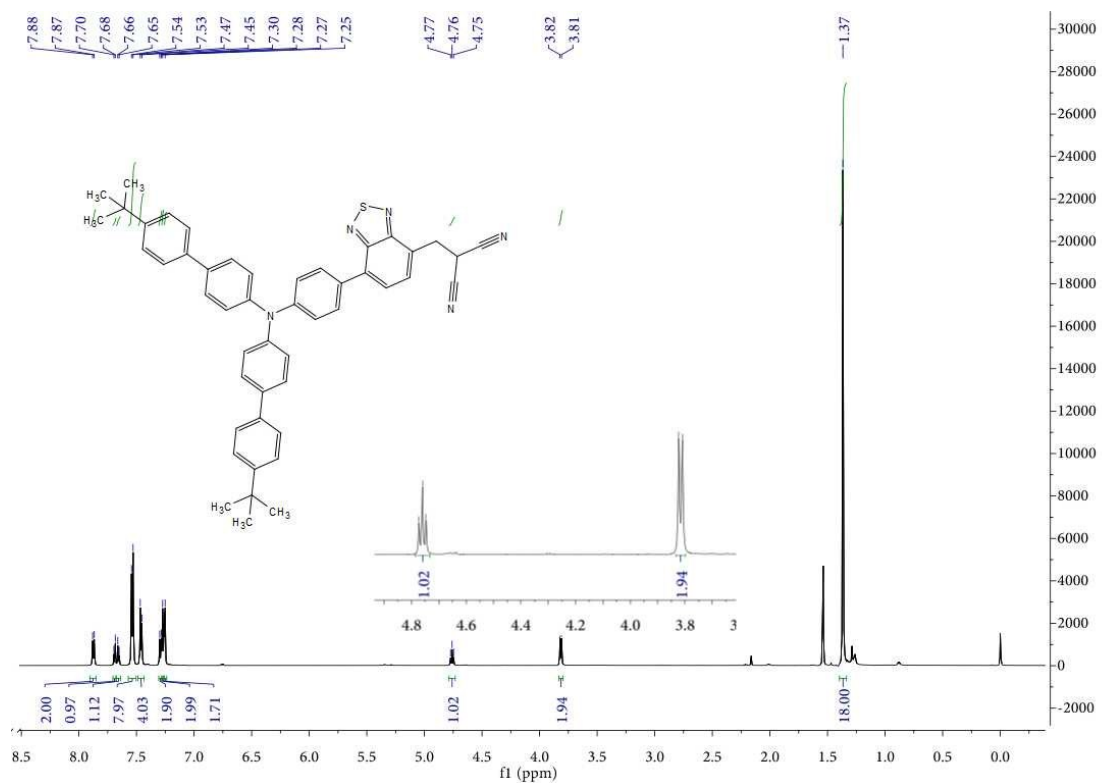
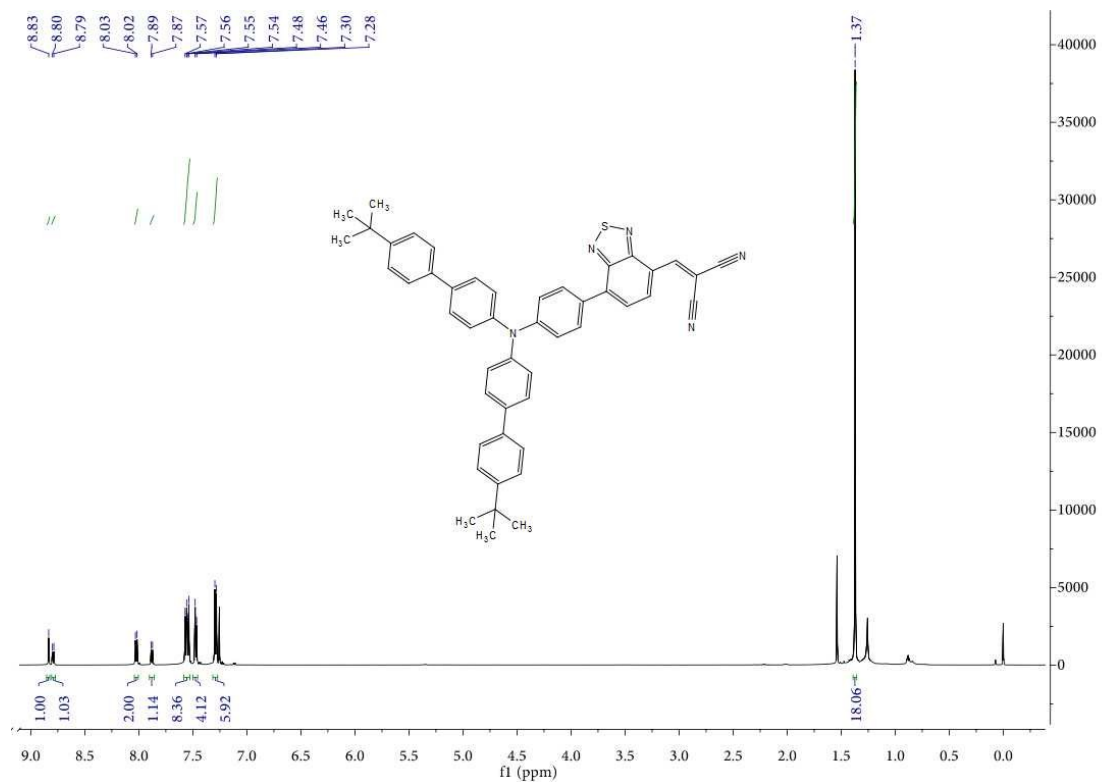


Fig. S7 Fluorescence intensity of the A1H2-NPs at 616 nm in PBS (pH 7.4), and other buffer solutions with pH ranging from 2 to 9, compared with that in deionized water.

^1H -NMR, ^{13}C -NMR, and MS spectra





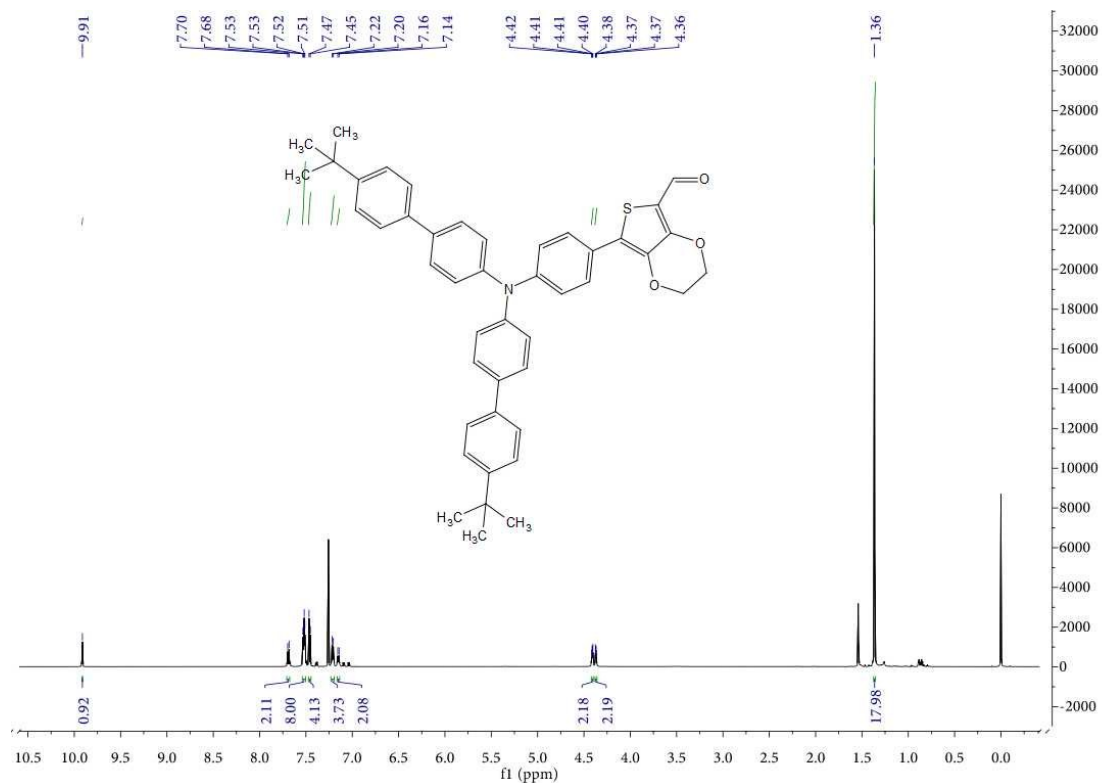


Fig. S12 ^1H NMR spectrum of A2-2 in CDCl_3

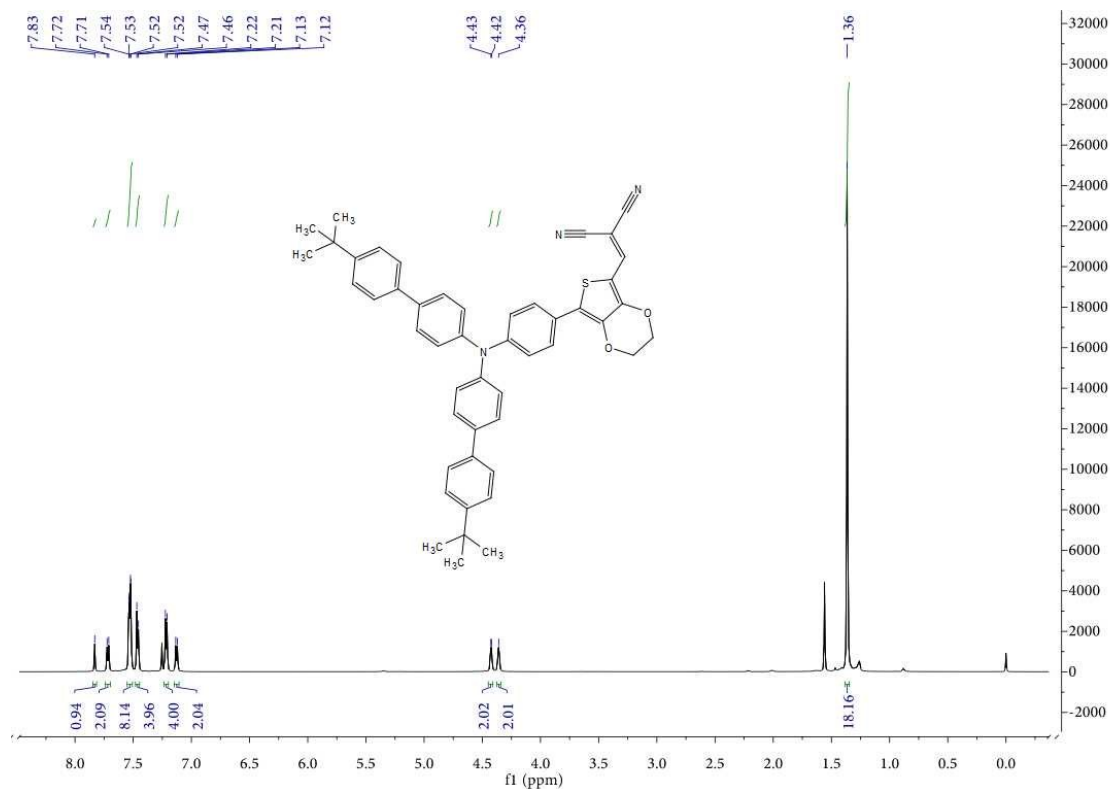


Fig. S13 ^1H NMR spectrum of A2 in CDCl_3

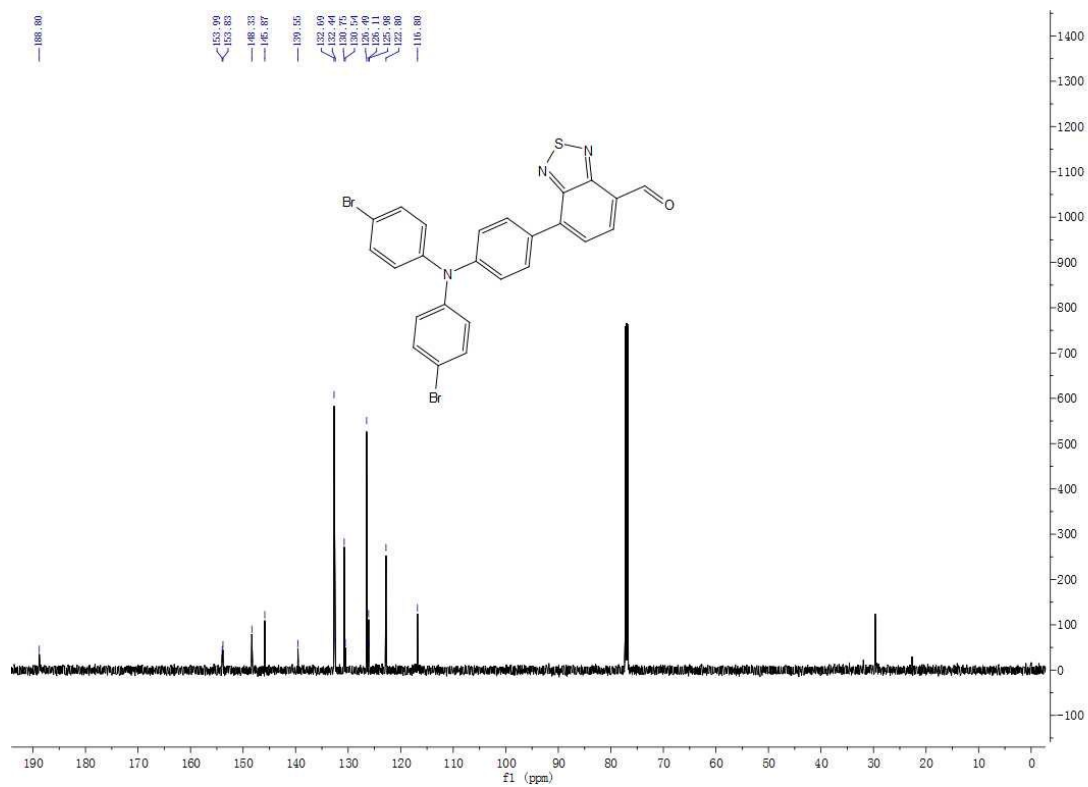


Fig. S14 ^{13}C NMR spectrum of A1-2 in CDCl_3

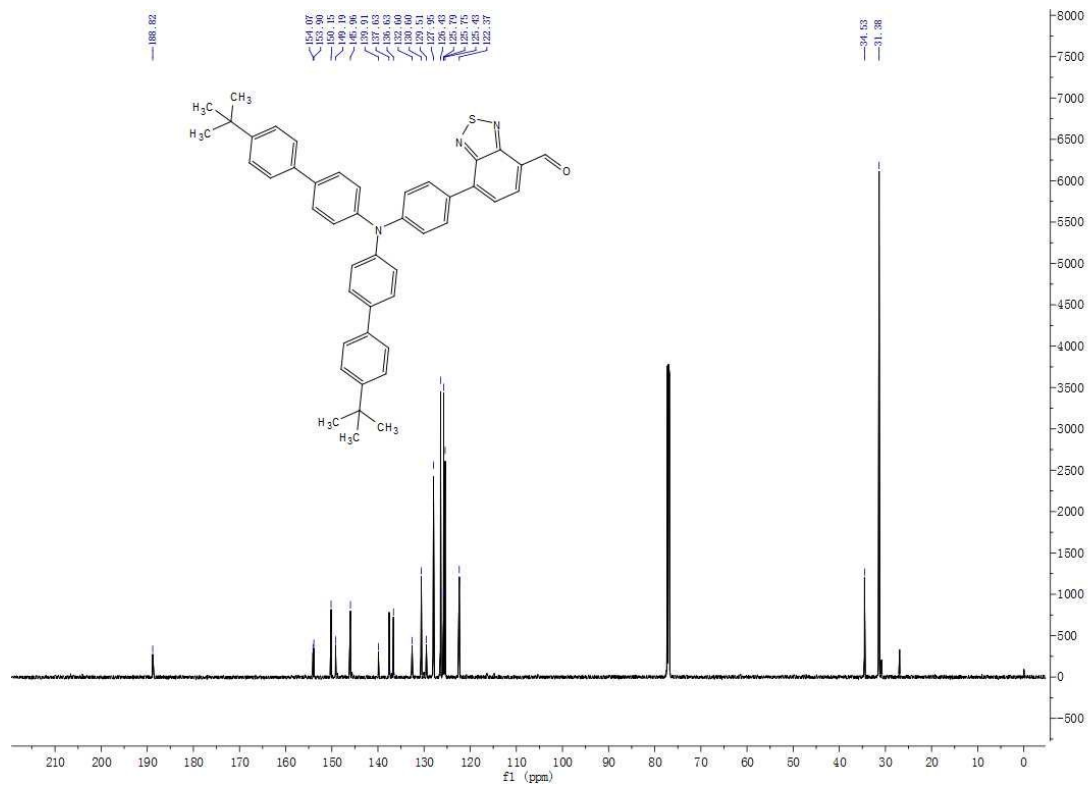


Fig. S15 ^{13}C NMR spectrum of BT-CHO in CDCl_3

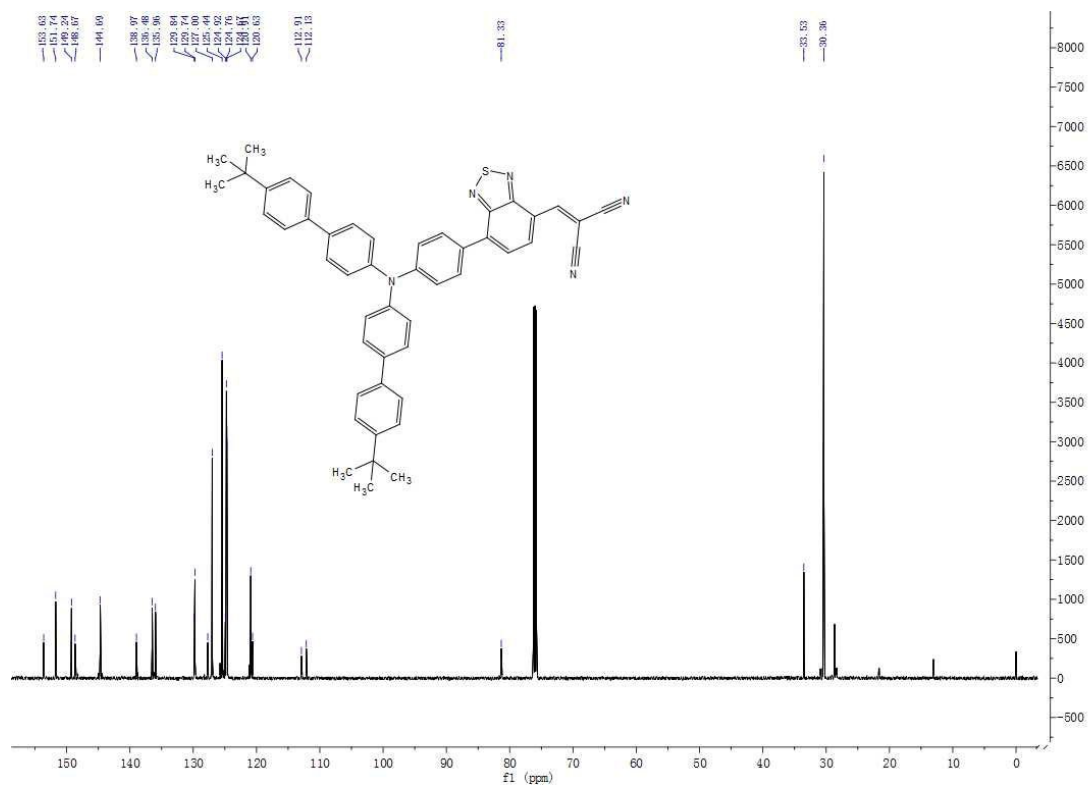


Fig. S16 ¹³C NMR spectrum of A1 in CDCl₃

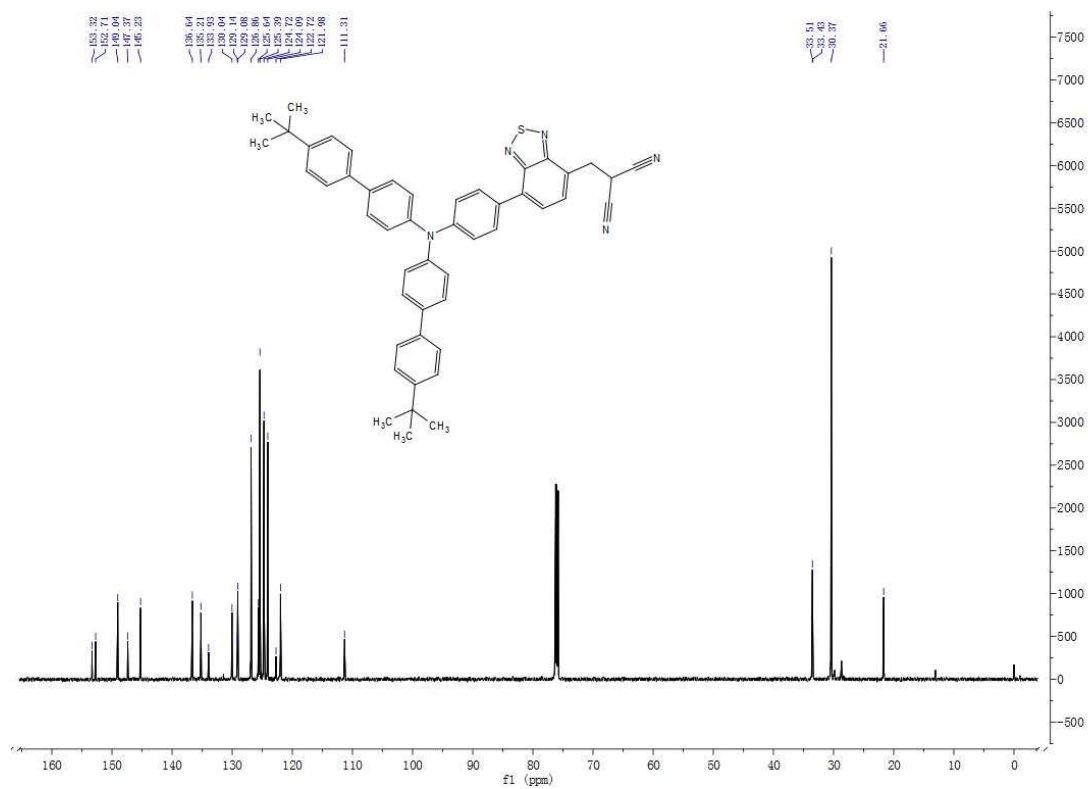


Fig. S17 ¹³C NMR spectrum of A1H2 in CDCl₃

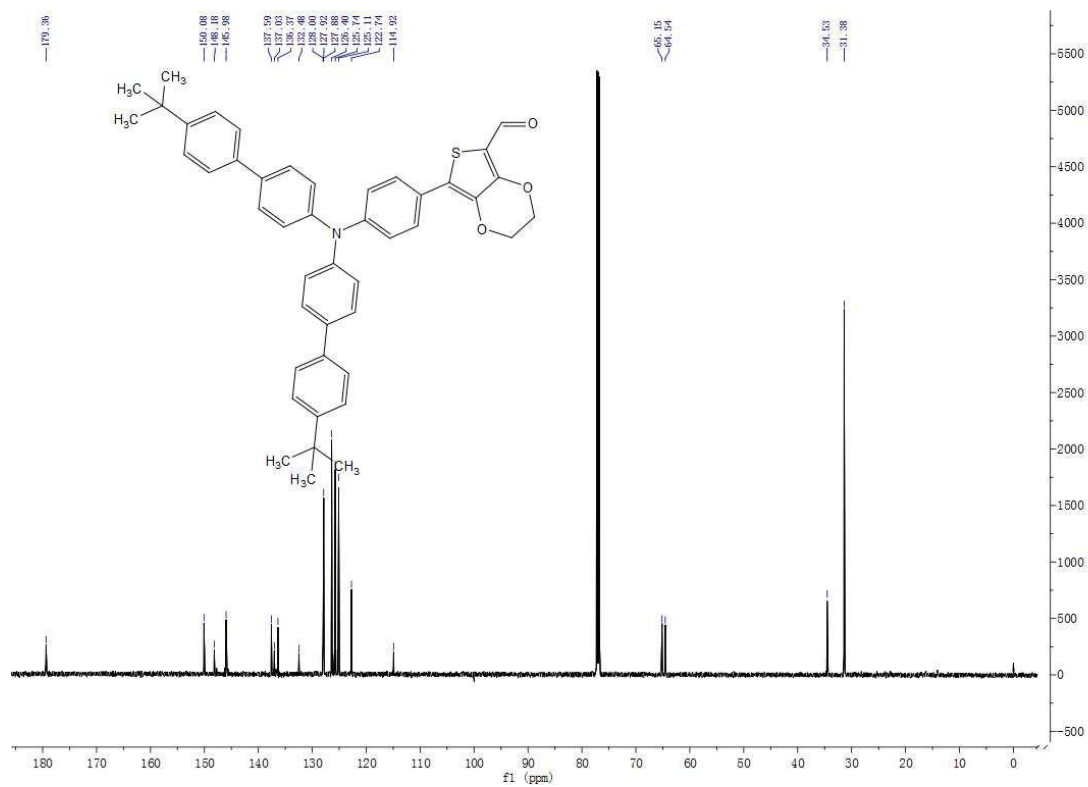


Fig. S18 ¹³C NMR spectrum of A2-2 in CDCl₃

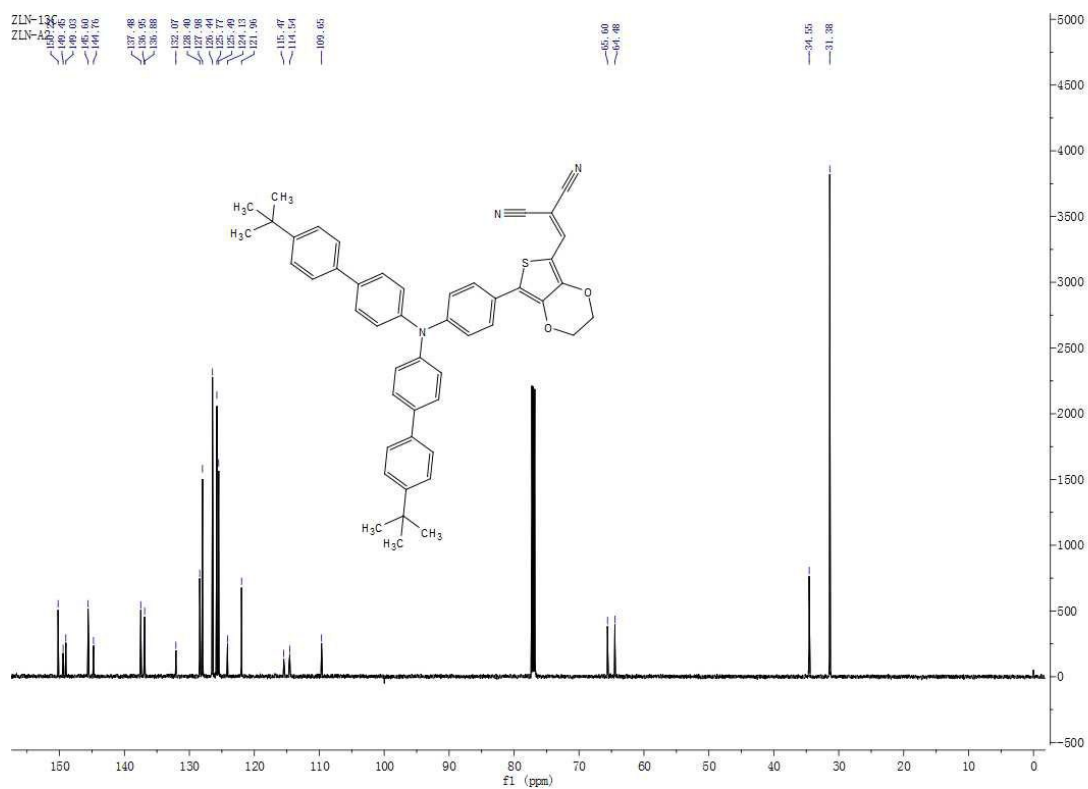


Fig. S19 ¹³C NMR spectrum of A2 in CDCl₃

MALDI,A1,20170411

Analysis Info

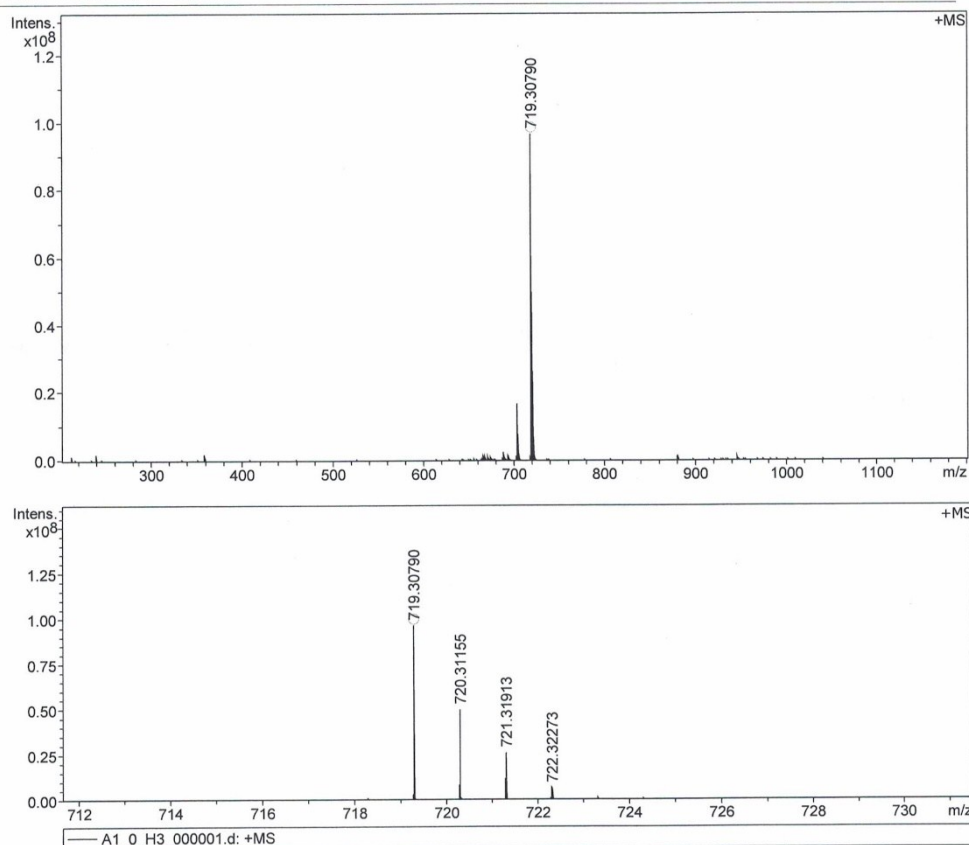
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Method MALDI_P_100-3000
Sample Name
Comment

Acquisition Date 4/11/2017 3:43:22 PM

Operator
Instrument solariX

Acquisition Parameter

Acquisition Mode	Single MS	Acquired Scans	2	Calibration Date	Mon Apr 10 04:54:22
Polarity	Positive	No. of Cell Fills	1	Data Acquisition Size	2097152
Broadband Low Mass	202.1 m/z	No. of Laser Shots	10	Data Processing Size	4194304
Broadband High Mass	1200.0 m/z	Laser Power	23.8 lp	Apodization	Sine-Bell Multiplication
Source Accumulation	0.001 sec	Laser Shot Frequency	0.020 sec		
Ion Accumulation Time	0.300 sec				



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e ⁻ Conf	N-Rule
719.307905	1	C48H41N5S	100.00	719.307719	0.3	-0.5	77.0	31.0	odd	ok

Fig. S20 MALDI-TOF-MS of A1

Sample No.	Formula (M)	Ion Formula	Measured m/z	Calc m/z	Diff (ppm)
A1H2	C ₄₈ H ₄₃ N ₅ S	C ₄₈ H ₄₄ N ₅ S	722.3331	722.3319	1.66

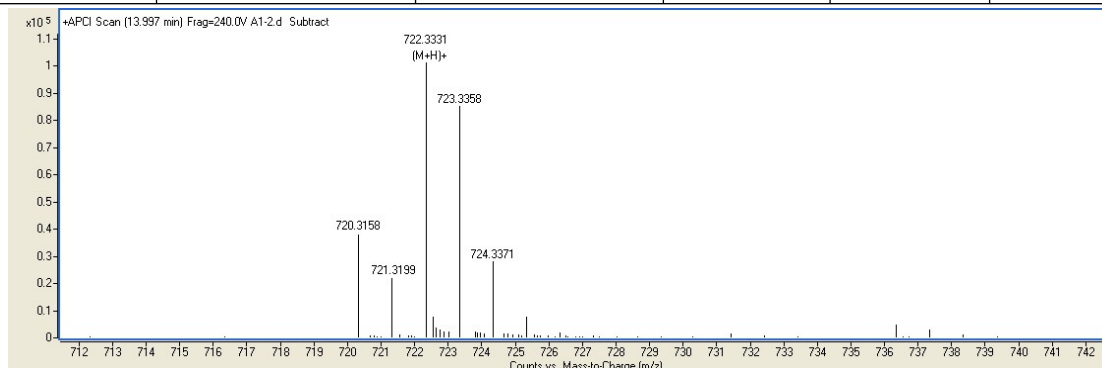


Fig. S21 HRMS of A1H2

Sample No.	Formula (M)	Ion Formula	Measured m/z	Calc m/z	Diff (ppm)
A2	C ₄₈ H ₄₃ N ₃ O ₂ S	C ₄₈ H ₄₄ N ₃ O ₂ S	726.3155	726.3149	0.97

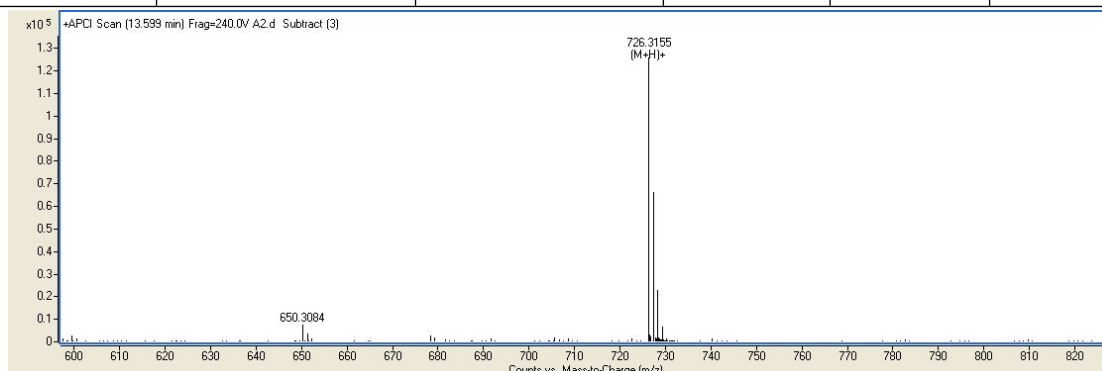


Fig. S22 HRMS of A2

References

- [1] Roh, D.-H.; Kim, K. M.; Nam, J. S.; Kim, U.-Y.; Kim, B.-M.; Kim, J. S.; Kwon, T.-H. *J. Phys. Chem. C*, 2016, **120**, 24655.
- [2] Hua, Y.; Jin, B.; Wang, H.; Zhu, X.; Wu, W.; Cheung, M.-S.; Lin, Z.; Wong, W.-Y.; Wong, W.-K. *J Power Sources*, 2013, **237**, 195.