Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information

Reversible room temperature phosphorescence in response to light stimulation based on photochromic copolymer

*Bingbing Ding, Hao Gao, Chao Wang, and Xiang Ma**

Key Laboratory for Advanced Materials and Joint International Research Laboratory of Precision Chemistry and Molecular Engineering, Feringa Nobel Prize Scientist Joint Research Center, Frontiers Science Center for Materiobiology and Dynamic Chemistry, Institute of Fine Chemicals, School of Chemistry and Molecular Engineering, East China University of Science and Technology, Shanghai 200237, China

E-mail: maxiang@ecust.edu.cn

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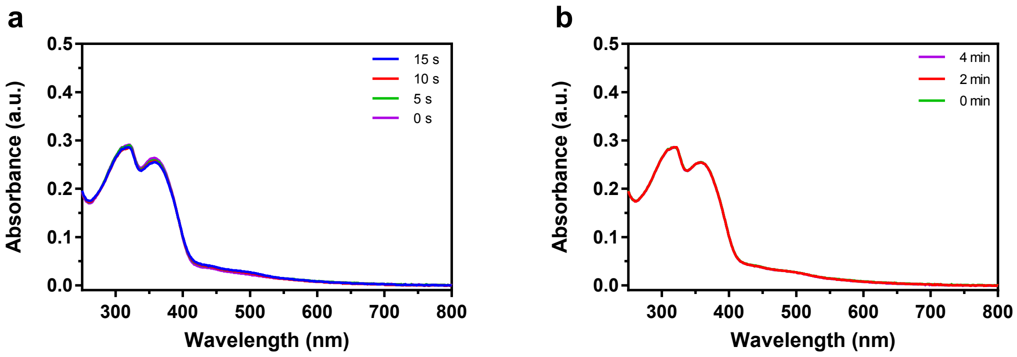


Figure S1. a) Solid-state absorbance spectra of polymer **C7** under UV irradiation for certain time. b) Solid state absorbance spectra of polymer **C7** at various time points post UV irradiation.

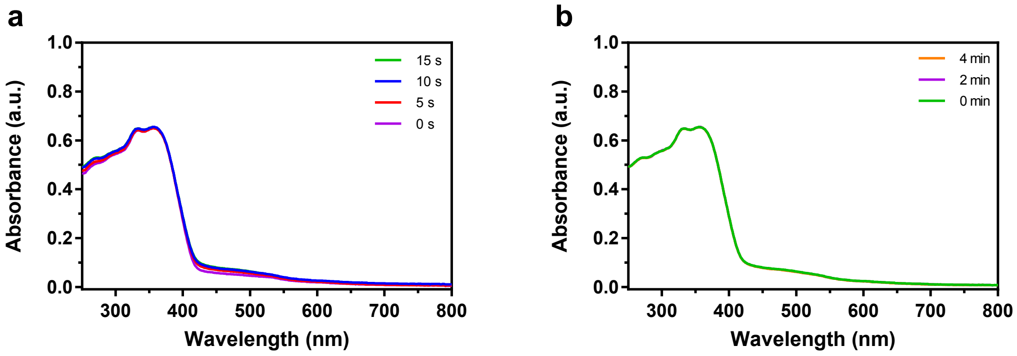


Figure S2. a) Solid state absorbance spectra of polymer **C8** under UV irradiation for certain time. b) Solid state absorbance spectra of polymer **C8** at various time points post UV irradiation.

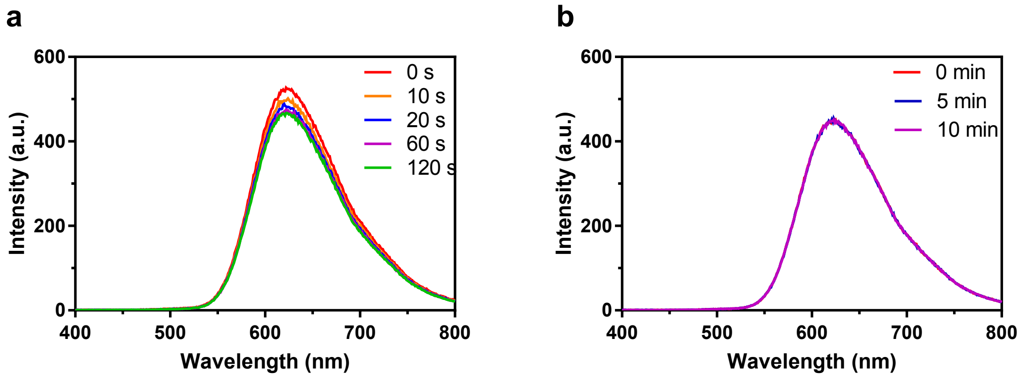


Figure S3. a) RTP spectra of polymer **C7** under continuous 365 nm UV irradiation for certain time. b) RTP spectra of polymer **C7** in dark at various time points post 365 nm UV irradiation.

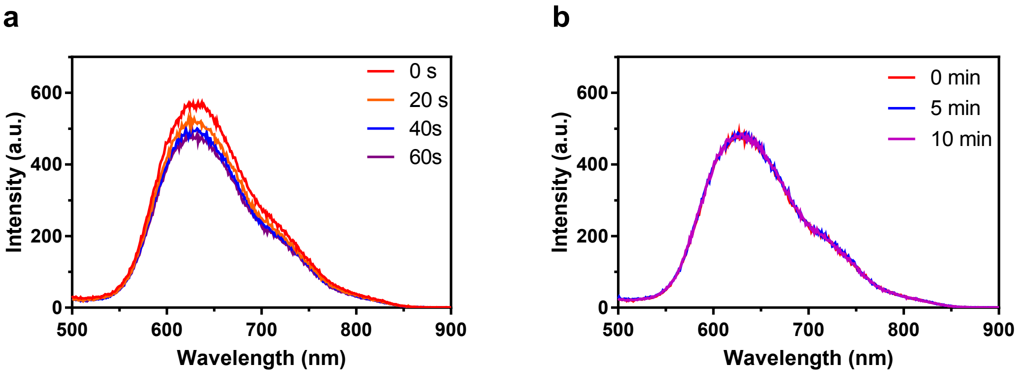


Figure S4. a) RTP spectra of polymer **C8** under continuous 365 nm UV irradiation for certain time. b) RTP spectra of polymer **C8** in dark at various time points post 365 nm UV irradiation.

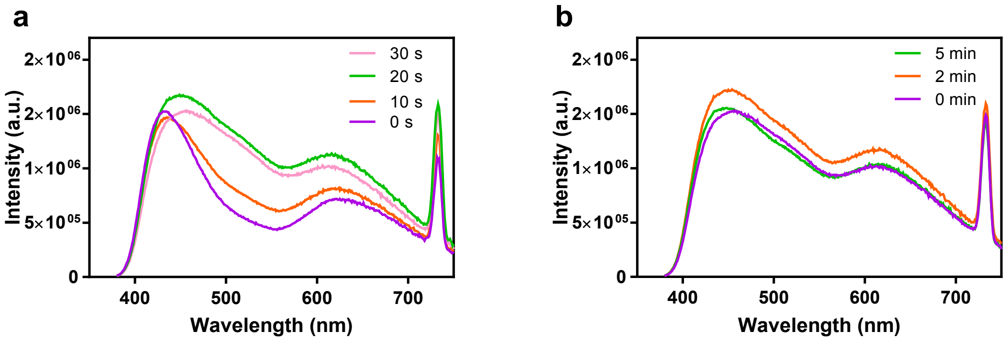


Figure S5. a) Photoluminescence spectra of polymer **C7** under continuous 365 nm excitation for several time. b) Photoluminescence spectra of polymer **C7** at certain time points post UV irradiation.

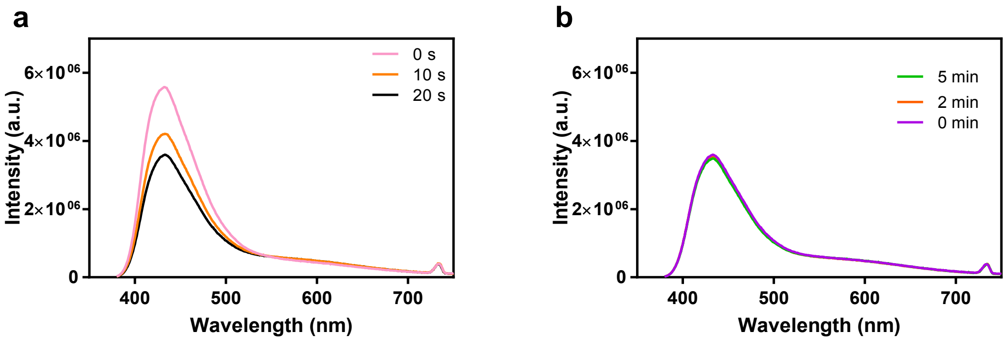


Figure S6. a) Photoluminescence spectra of polymer **C8** under continuous 365 nm excitation for several time. b) Photoluminescence spectra of polymer **C8** at certain time points post UV irradiation.

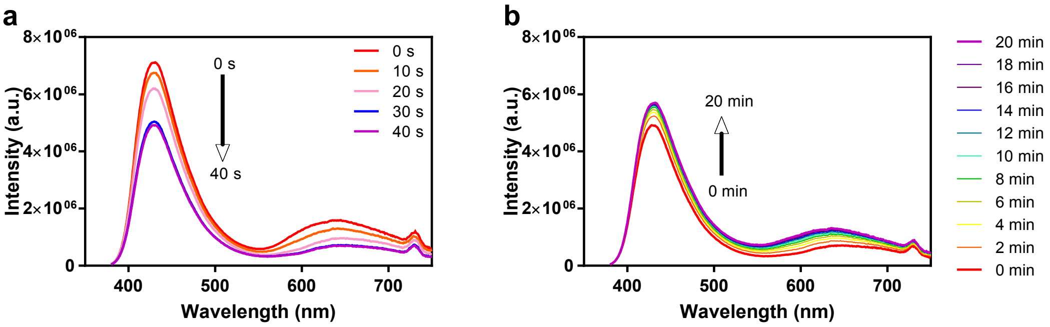


Figure S7. a) Photoluminescence spectra of polymer **C9** under continuous 365 nm excitation for several time. b) Photoluminescence spectra of polymer **C9** at certain time points post UV irradiation.

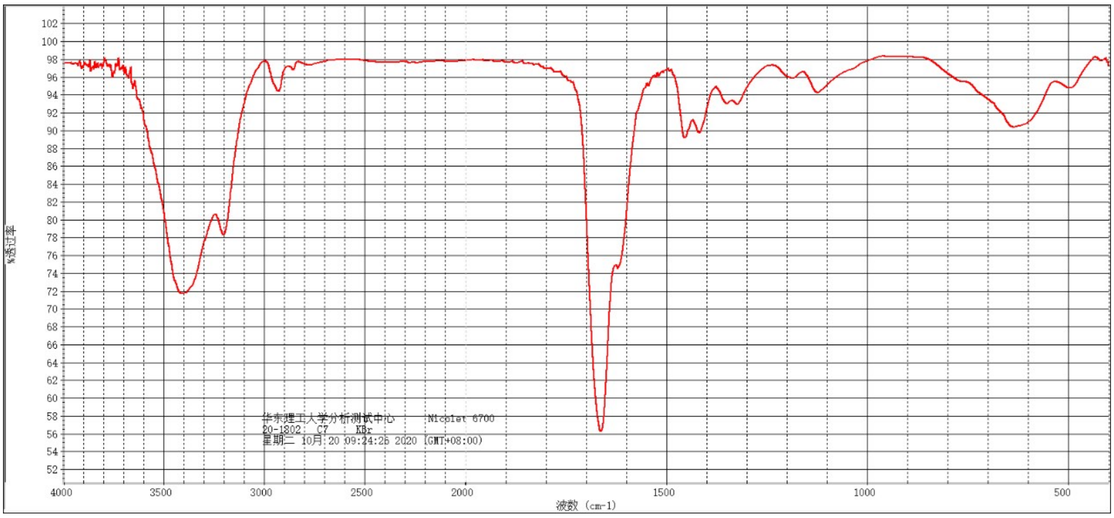


Figure S8. FTIR spectrum of polymer **C7**.

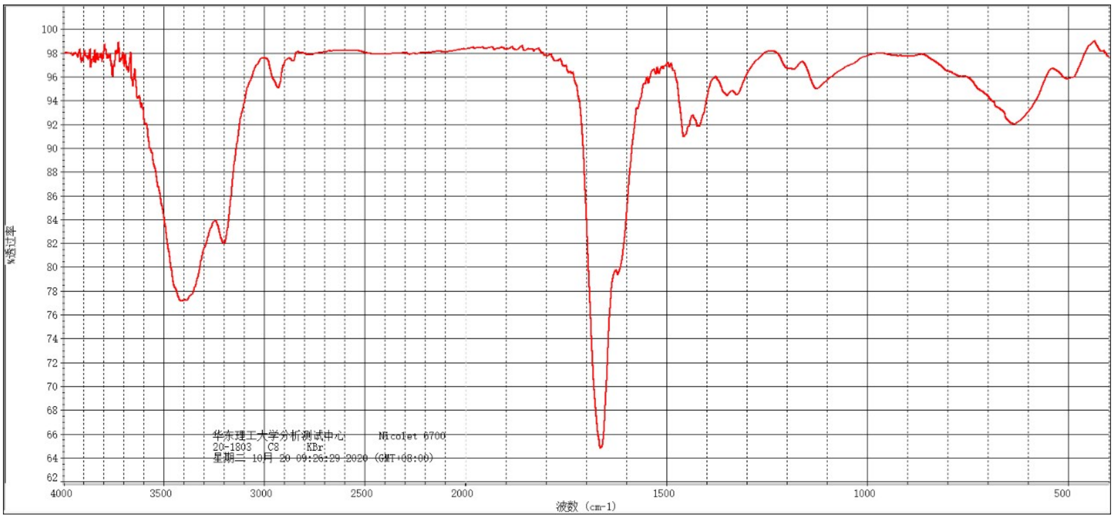


Figure S9. FTIR spectrum of polymer **C8**.

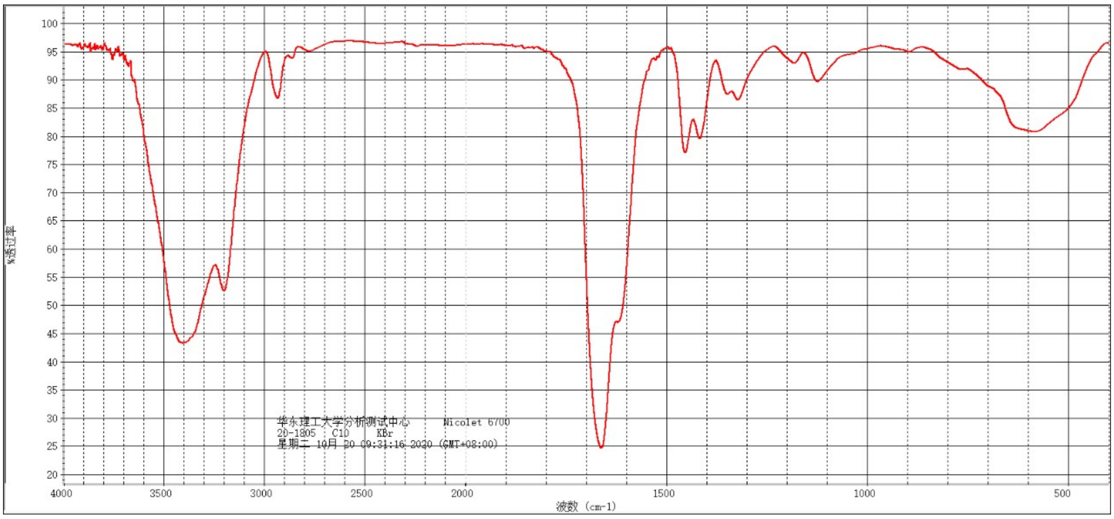


Figure S10. FTIR spectrum of polymer **C9**.

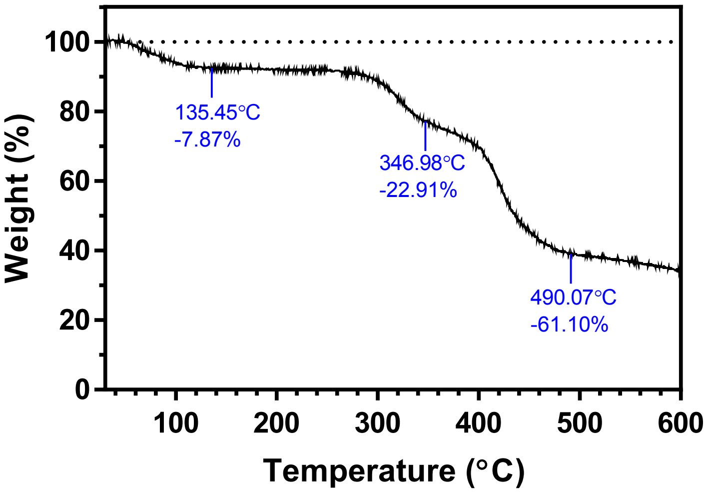


Figure S11. Thermogravimetric analysis of polymer **C7**.

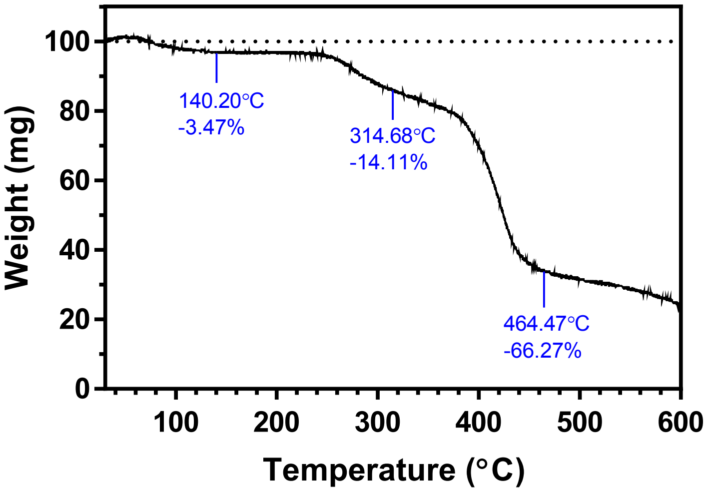


Figure S12. Thermogravimetric analysis of polymer **C8**.

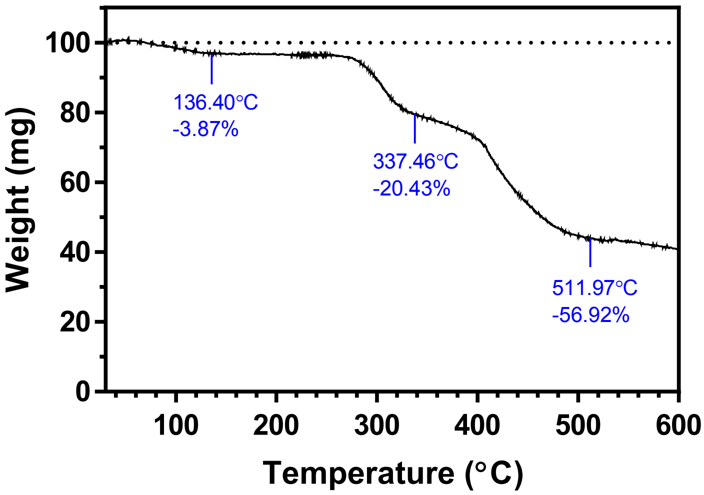


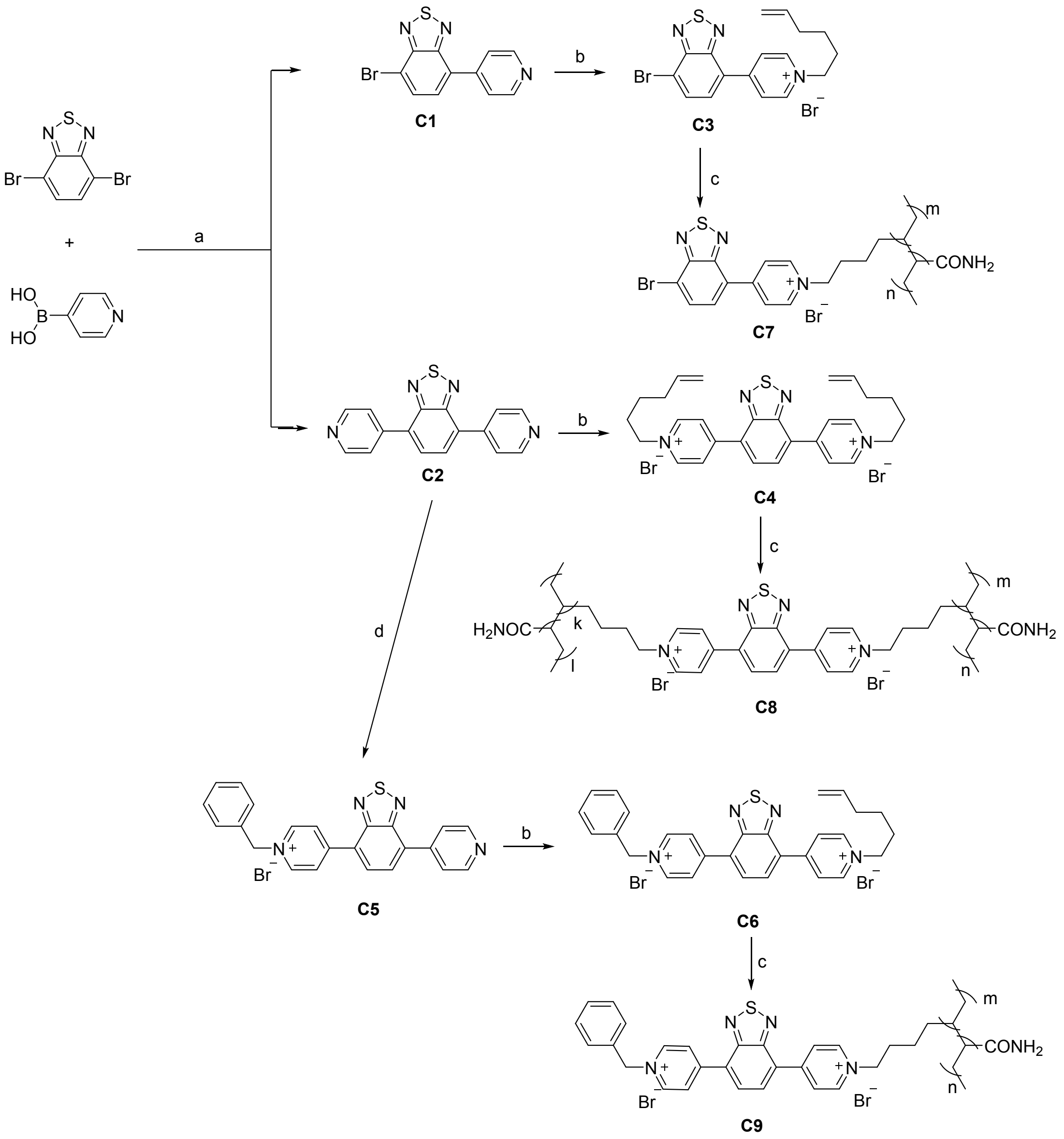
Figure S13. Thermogravimetric analysis of polymer **C9**.

General Methods

All the reagents and solvents were obtained commercially and used as supplied without further purification unless specified otherwise. The UV-Vis absorption spectra of solid sample were obtained on a PerkinElmer Lambda 950 spectrophotometer. The time-resolved photoluminescence spectra and lifetime at room temperature were recorded in air on an Agilent Cary Eclipse spectrophotometer. The photoluminescence quantum yields were measured using a HAMAMATSU absolute PL quantum yield spectrometer (C11347). The integral area ratio of phosphorescence and fluorescence peak is the ratio of phosphorescence and fluorescence quantum yield. Nuclear Magnetic Resonance (NMR) spectra were measured on a Bruker AV-400 spectrometer and processing on MestReNova (Mestralab Research, version: 14.0.0) software. Reversed phase chromatography was performed on SepaBean^{TM} machine (Santai Technology Inc., China) equipped with C18-bonded Sepaflash$^{®}$ columns. GPC was recorded using a Waters Breeze at 25 °C with water as the eluent. The ESI+ mass spectra were tested on a Waters GCT Premier spectrometer.

Chemistry

Scheme 1. Synthetic route of polymers **C7**, **C8** and **C9**.



a) K_2CO_3, $Pd(PPh_3)_4$, Dioxane/H_2O, reflux; b) 6-Bromo-1-hexene, DMF, 100°C; c) Acrylamide, AIBN, DMF, 70°C; d) Benzyl bromide, Acetonitrile, reflux.

4-bromo-7-(4-pyridyl)-2,1,3-benzothiadiazole (C1). The mixture of 4-pyridylboronic acid (244 mg, 2 mmol), 4,7-dibromobenzothiadiazole (647 mg, 2.2 mmol), $Pd(PPh_3)_4$ (116 mg, 0.1 mmol), and K_2CO_3 (832mg, 6 mmol) in 1,4-dioxane/ H_2O (3/1, v/v, 20 mL) was heated to reflux under a nitrogen atmosphere for 18 h. After cooling to room temperature, the reaction was extracted with DCM (3 × 20 ml). The organic phase was combined and dried over sodium sulfate. Then the solvent was removed under reduce pressure. The residue was purified by flash column chromatography on silica gel to yield yellow solid (234 mg, 40%). ^1H NMR (400 MHz, $CDCl_3$) δ 8.77 (d, J = 5.2 Hz, 1H), 7.97 (d, J = 7.5 Hz, 1H), 7.85 (d, J = 5.2 Hz, 1H), 7.68 (d, J = 7.6 Hz, 1H). HRMS(EI): m/z $[M]^+$, calcd for $C_{16}H_{10}N_4S$: 290.0626; found: 374.0337.

Compound C3. Compound **C1** (58 mg, 0.2 mmol) and 6-bromo-1-hexene (65 mg, 0.053 mL, 0.4 mmol) was dissolved in anhydrous DMF (1 mL). The reaction was stirred at 100℃ overnight. After cooling to room temperature, the mixture was poured into diethyl ether (10 mL). Participate was separated and purified by reversed phase chromatography on C18-bonded silica gel to yield white solid (87 mg, 96%). ^{1}H NMR (400 MHz, CD_3OD) δ 9.10 (d, J = 7.0 Hz, 2H), 8.87 (d, J = 7.0 Hz, 2H), 8.26 – 8.16 (m, 2H), 5.90 – 5.76 (m, 1H), 5.06 (dd, J = 17.1, 1.8 Hz, 1H), 5.02 – 4.97 (m, 1H), 4.69 (t, J = 7.6 Hz, 2H), 2.23 – 2.05 (m, 4H), 1.60 – 1.49 (m, 2H); ^{13}C NMR (101 MHz, CD_3OD) δ 155.3, 153.8, 153.0, 145.7, 138.9, 133.6, 133.1, 128.4, 127.4, 120.2, 115.9, 62.4, 34.1, 31.9, 26.5. HRMS(ESI+): *m/z* $[M\text{-}Br]^+$, calcd for $C_{17}H_{17}BrN_3S^+$: 374.0327; found: 374.0337.

Polymer C7. Compound **C3** (23 mg, 0.05 mmol), acrylamide (178 mg, 2.5 mmol) and 2,2'-azobis(2-methylpropionitrile) (AIBN, 7 mg) was heat at 70 ℃ under a nitrogen atmosphere in DMF (1 mL) for 12 h. After cooling to room temperature, the reaction was poured into MeOH (10 mL) to participate the polymer solid. The participate was filter off and washed with MeOH and dried to yield a white solid. GPC (H_2O): Mn (PDI) = 5888 Da (2.318).

4,7-di(4-pyridyl)-2,1,3-benzothiadiazole (C2). The mixture of 4-pyridylboronic acid (537 mg, 4.4 mmol), 4,7-dibromobenzothiadiazole (588 mg, 2 mmol), $Pd(PPh_3)_4$ (232 mg, 0.2 mmol), and K_2CO_3 (1108mg, 8 mmol) in 1,4-dioxane/ H_2O (3/1, v/v, 20 mL) was heated to reflux under a nitrogen atmosphere for 18 h. After cooling to room temperature, the reaction was extracted with DCM (3 × 30 ml). The organic phase was combined and dried over sodium sulfate. Then the solvent was removed under reduce pressure. The residue was purified by flash column chromatography on silica gel to yield yellow solid (445 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (d, J = 6.2 Hz, 4H), 7.94 (d, J = 6.2 Hz, 4H), 7.93 (s, 2H).

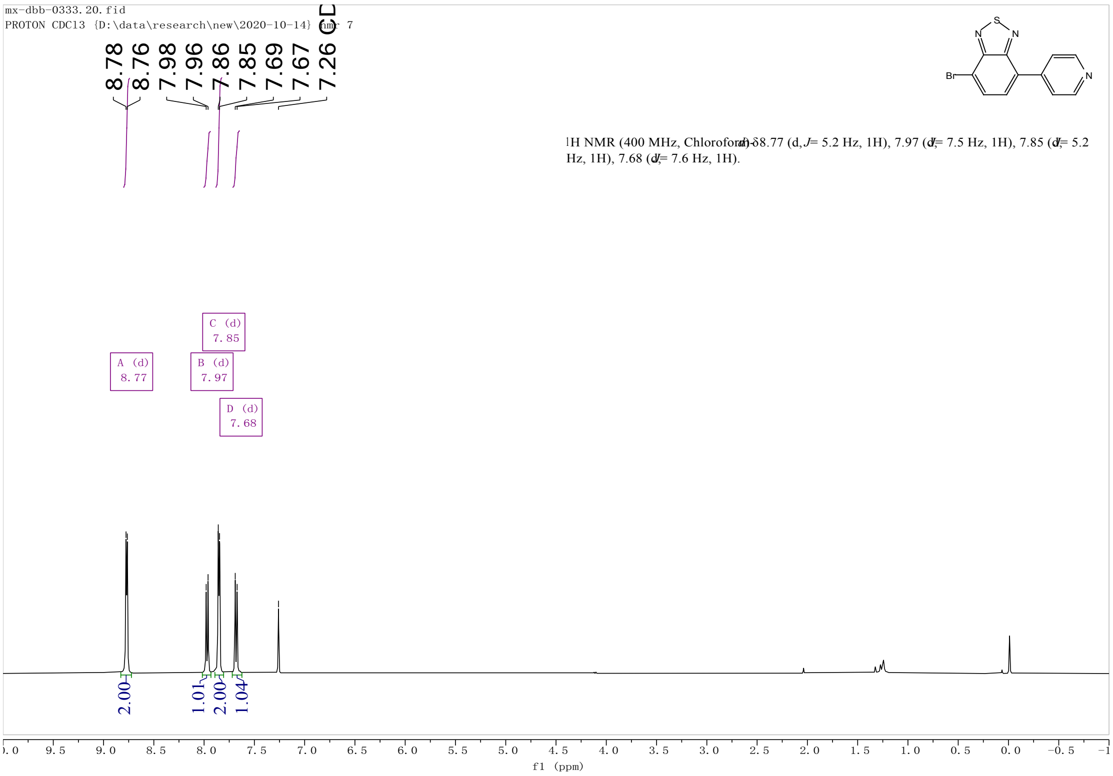
Compound C4. Compound **C2** (48 mg, 0.165 mmol) and 6-bromo-1-hexene (107 mg, 0.088 mL, 0.66 mmol) was dissolved in anhydrous DMF (1 mL). The reaction was stirred at 100℃ overnight. After cooling to room temperature, the mixture was poured into diethyl ether (10 mL). Participate was separated and purified by reversed phase chromatography on C18-bonded silica gel to yield white solid (93 mg, 91%). ^{1}H NMR (400 MHz, CD_3OD) δ 9.17 (d, J = 7.0 Hz, 4H), 8.95 (d, J = 6.9 Hz, 4H), 8.56 (s, 2H), 5.92 – 5.77 (m, 2H), 5.08 (dd, J = 17.1, 1.8 Hz, 2H), 5.03 – 4.98 (m, 2H), 4.73 (t, J = 7.6 Hz, 4H), 2.25 – 2.07 (m, 8H), 1.63 – 1.51 (m, 4H); ^{13}C NMR (101 MHz, CD_3OD) δ 154.2, 153.5, 145.9, 138.9, 132.4, 131.2, 129.0, 115.9, 62.6, 34.1, 31.9, 26.5. HRMS(ESI+): *m/z* $[M\text{-}2Br]^{2+}$, calcd for $C_{28}H_{32}N_4S^{2+}$: 228.1168; found: 228.1170.

Polymer C8. The polymer **C8** was synthesized follow a similar method as polymer **C7**. Polymer **C8** was achieved as a white solid. GPC (H_2O): Mn (PDI) = 4770 Da (2.410).

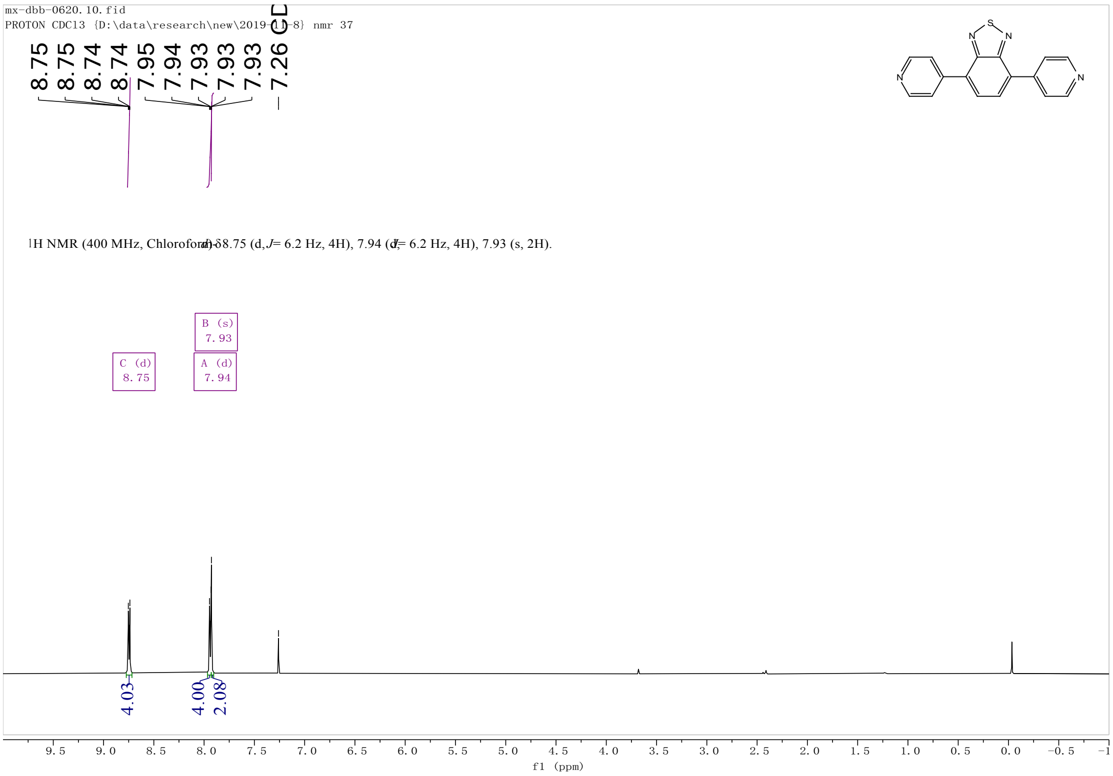
Compound C5. Compound **C4** (290 mg, 1.0 mmol) and benzyl bromide (171 mg, 0.119 mL, 1 mmol) were dissolved in acetonitrile (30 mL). The mixture was heated to reflux overnight. After cooling to room temperature, the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel to yield yellow solid (216 mg, 47%). ^{1}H NMR (400 MHz, CD_3OD) δ 9.20 (d, J = 6.4 Hz, 2H), 8.96 (d, J = 6.3 Hz, 2H), 8.73 (d, J = 4.6 Hz, 2H), 8.49 (dd, J = 7.5, 1.9 Hz, 1H), 8.23 (dd, J = 7.5, 2.0 Hz, 1H), 8.16 (d, J = 4.4 Hz, 2H), 7.61 (d, J = 7.0 Hz, 2H), 7.54 – 7.48 (m, 3H), 5.93 (s, 2H); ^{13}C NMR (101 MHz, CD_3OD) δ 154.7, 154.3, 154.2, 150.5, 146.1, 145.7, 135.6, 134.8, 133.0, 131.1, 130.8, 130.19, 130.1, 128.7, 128.4, 125.6, 65.2. HRMS(ESI+): *m/z* $[M\text{-}Br]^+$, calcd for $C_{23}H_{17}N_4S^+$: 381.1174; found: 381.1177.

Compound C6. The compound **C6** was synthesized similar as compound **C3**. The compound **C6** was achieved as white solid. ^{1}H NMR (400 MHz, CD_3OD) δ 9.28 (d, J = 6.7 Hz, 2H), 9.21 (d, J = 6.9 Hz, 2H), 9.01 – 8.94 (m, 4H), 8.59 (s, 2H), 7.68 – 7.60 (m, 2H), 7.57 – 7.45 (m, 3H), 5.98 (s, 2H), 5.93 – 5.79 (m, 1H), 5.08 (dd, J = 17.1, 1.8 Hz, 1H), 5.01 (dd, J = 10.2, 1.7 Hz, 1H), 4.77 (t, J = 7.6 Hz, 2H), 2.27 – 2.16 (m, 2H), 2.19 – 2.09 (m, 2H), 1.64 – 1.52 (m, 2H); ^{13}C NMR (101 MHz, CD_3OD) δ 154.2, 153.8, 153.4, 145.9, 138.9, 134.7, 132.7, 132.5, 131.2, 131.1, 131.0, 130.8, 130.3, 129.2, 129.0, 115.9, 65.3, 62.5, 34.1, 31.9, 26.5. HRMS(ESI+): *m/z* $[M\text{-}2Br]^{2+}$, calcd for $C_{29}H_{28}N_4S^{2+}$: 232.1012; found: 232.1006.

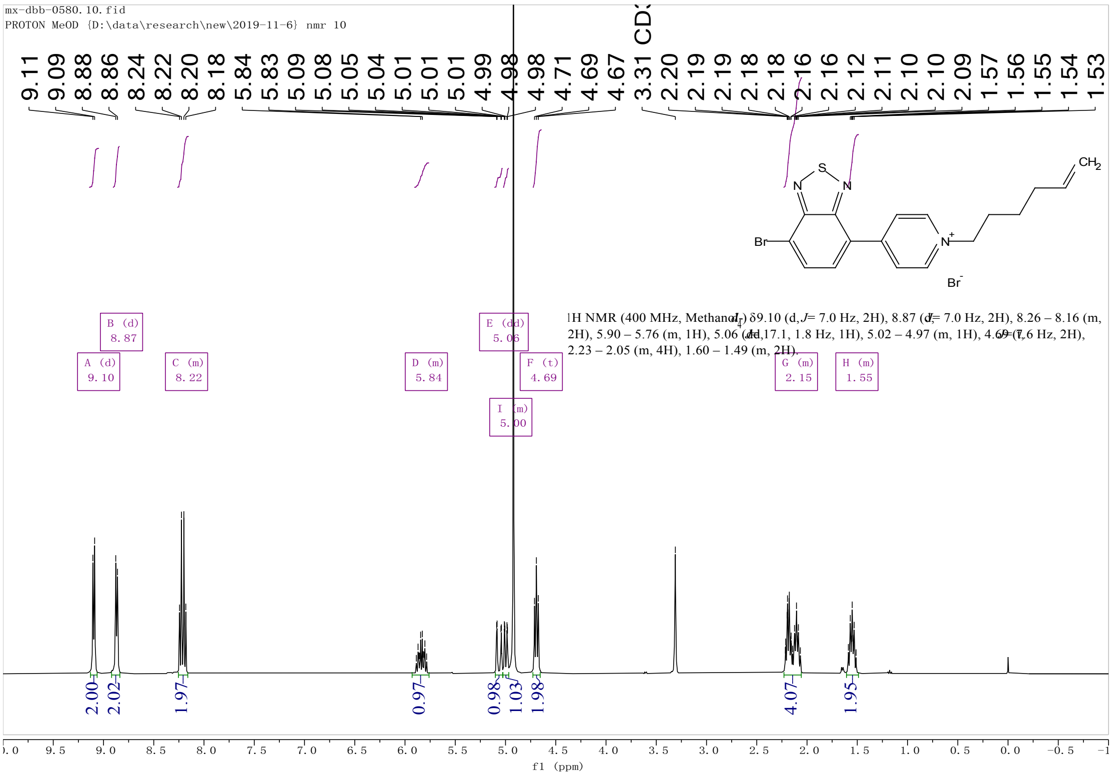
Polymer C9. The polymer **C9** was synthesized follow a similar method as polymer **C7**. Polymer **C9** was achieved as a white solid. GPC (H_2O): Mn (PDI) = 3567 Da (1.835).



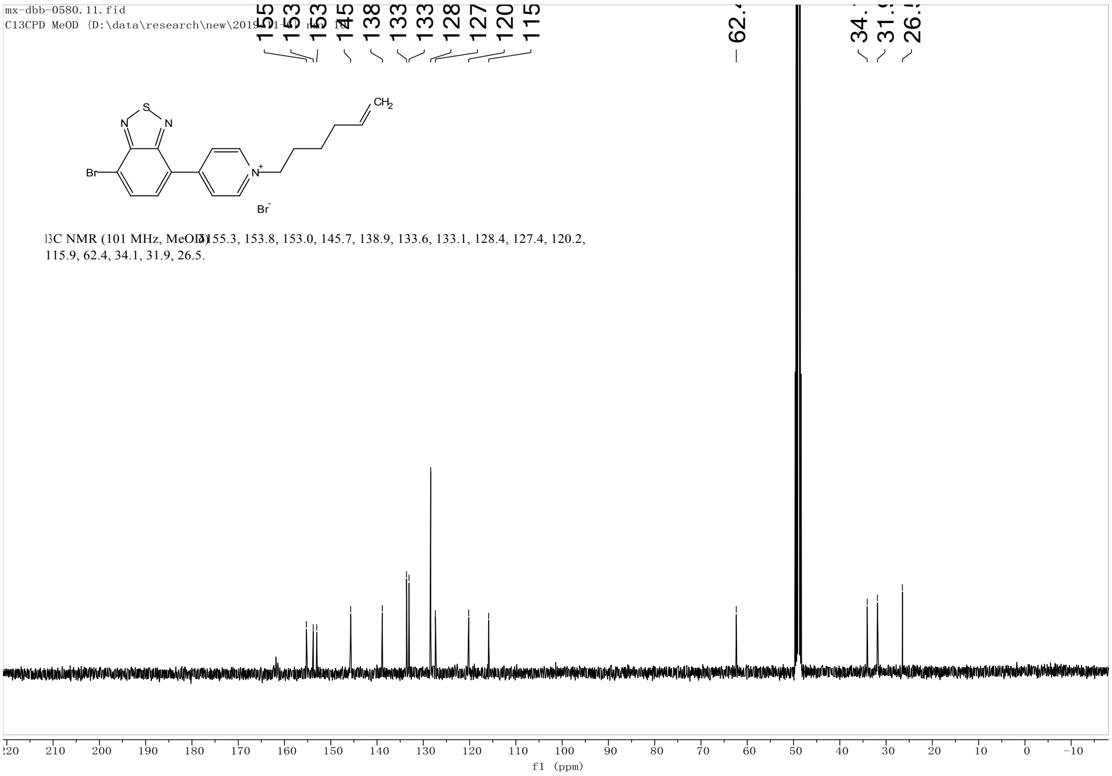
1H NMR (400 MHz, Chloroform-d) δ 8.77 (d, J = 5.2 Hz, 1H), 7.97 (d, J = 7.5 Hz, 1H), 7.85 (d, J = 5.2 Hz, 1H), 7.68 (d, J = 7.6 Hz, 1H).



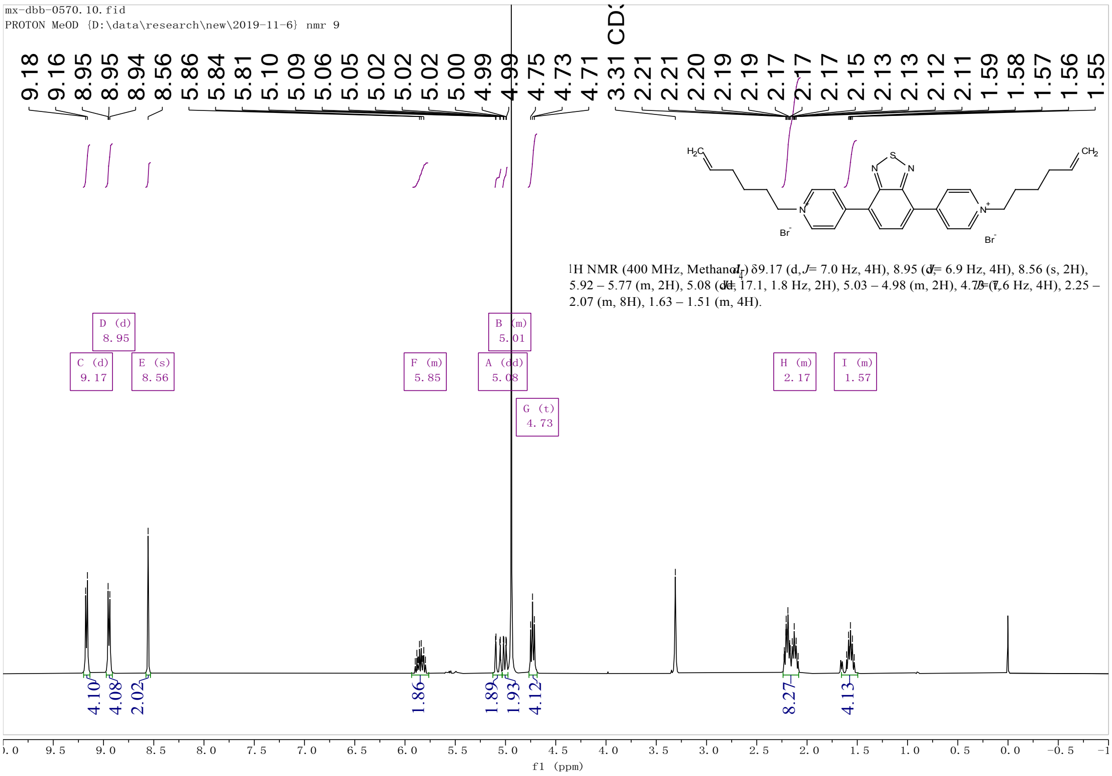
1H NMR (400 MHz, Chloroform-d) δ 8.75 (d, J = 6.2 Hz, 4H), 7.94 (d, J = 6.2 Hz, 4H), 7.93 (s, 2H).



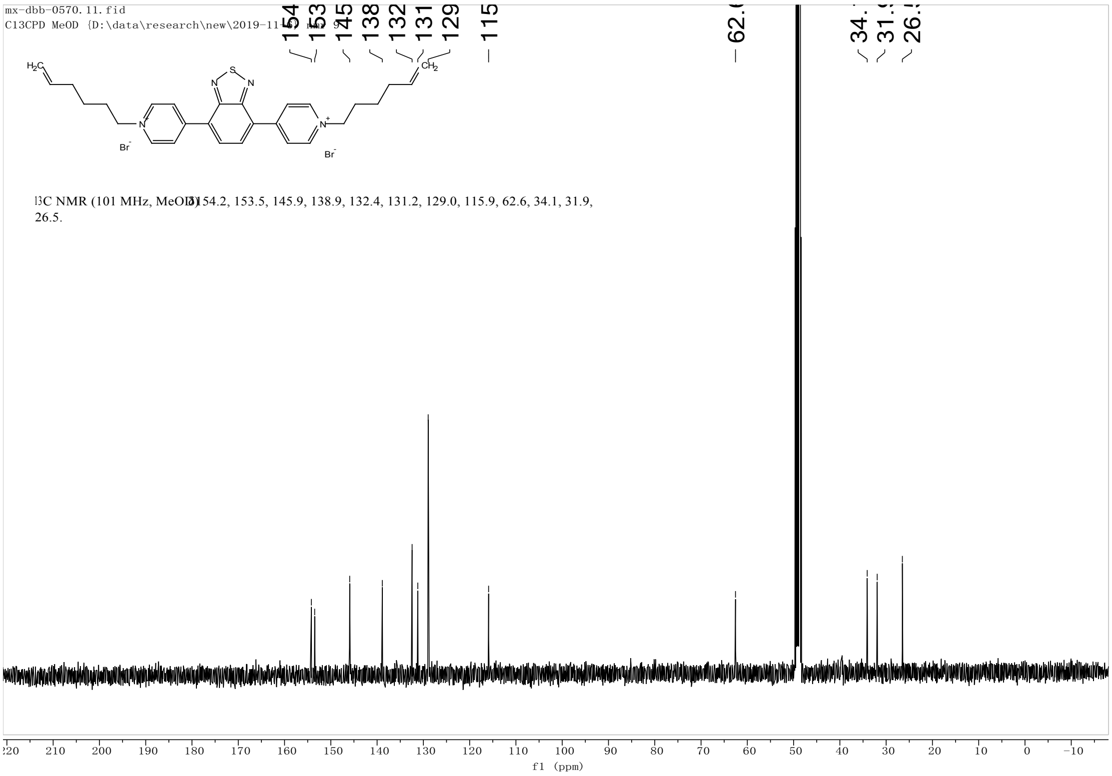
1H NMR (400 MHz, Methanol-d_4) δ 9.10 (d, J = 7.0 Hz, 2H), 8.87 (d, J = 7.0 Hz, 2H), 8.26 – 8.16 (m, 2H), 5.90 – 5.76 (m, 1H), 5.06 (dd, J = 17.1, 1.8 Hz, 1H), 5.02 – 4.97 (m, 1H), 4.69 (t, J = 7.6 Hz, 2H), 2.23 – 2.05 (m, 4H), 1.60 – 1.49 (m, 2H).



13C NMR (101 MHz, MeOD) δ 155.3, 153.8, 153.0, 145.7, 138.9, 133.6, 133.1, 128.4, 127.4, 120.2, 115.9, 62.4, 34.1, 31.9, 26.5.

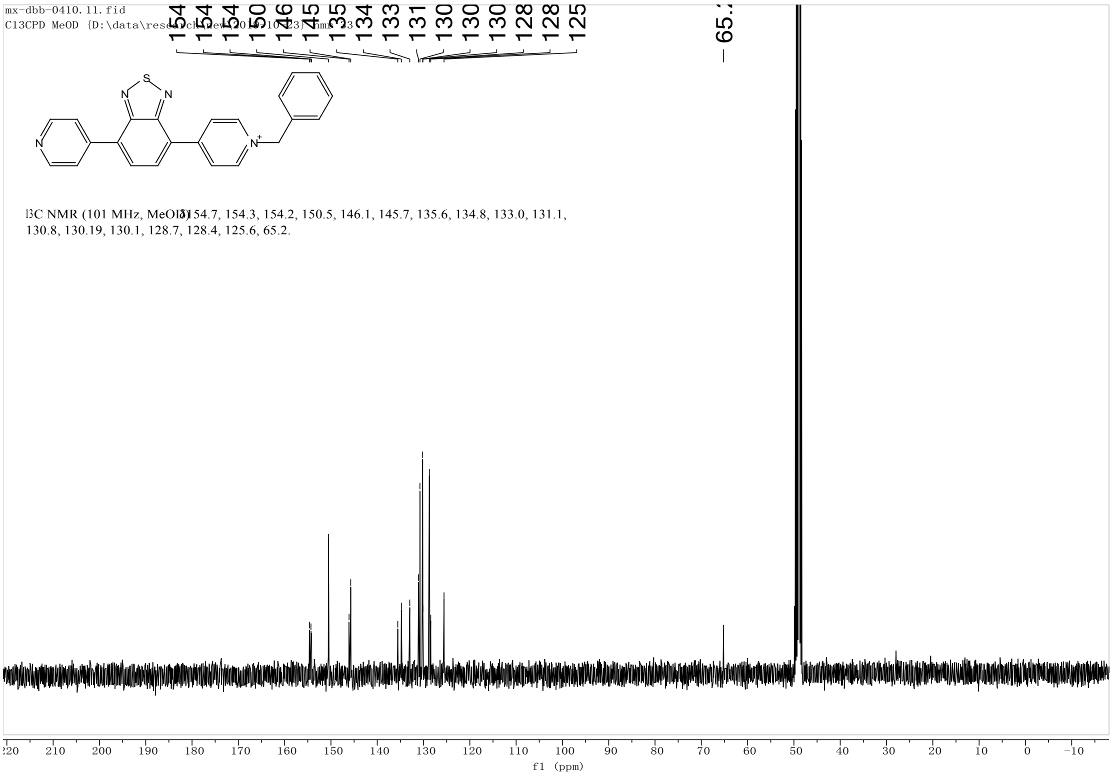


^{1}H NMR (400 MHz, Methanol-d_4) δ 9.17 (d, J = 7.0 Hz, 4H), 8.95 (d, J = 6.9 Hz, 4H), 8.56 (s, 2H), 5.92 – 5.77 (m, 2H), 5.08 (dd, J = 17.1, 1.8 Hz, 2H), 5.03 – 4.98 (m, 2H), 4.73 (t, J = 7.6 Hz, 4H), 2.25 – 2.07 (m, 8H), 1.63 – 1.51 (m, 4H).



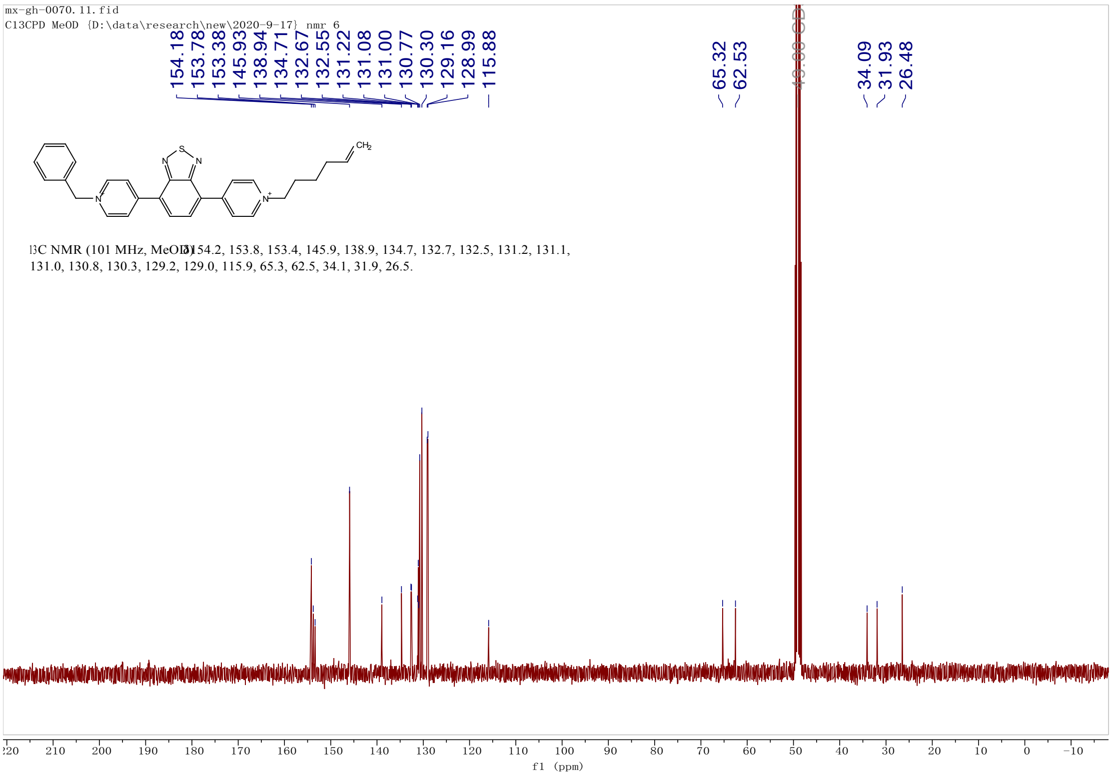
^{13}C NMR (101 MHz, MeOD) δ 154.2, 153.5, 145.9, 138.9, 132.4, 131.2, 129.0, 115.9, 62.6, 34.1, 31.9, 26.5.

^{1}H NMR (400 MHz, Methanol-d_4) δ 9.20 (d, *J* = 6.4 Hz, 2H), 8.96 (d, *J* = 6.3 Hz, 2H), 8.73 (d, *J* = 4.6 Hz, 2H), 8.49 (dd, *J* = 7.5, 1.9 Hz, 1H), 8.23 (dd, *J* = 7.5, 2.0 Hz, 1H), 8.16 (d, *J* = 4.4 Hz, 2H), 7.61 (d, *J* = 7.0 Hz, 2H), 7.54 – 7.48 (m, 3H), 5.93 (s, 2H).

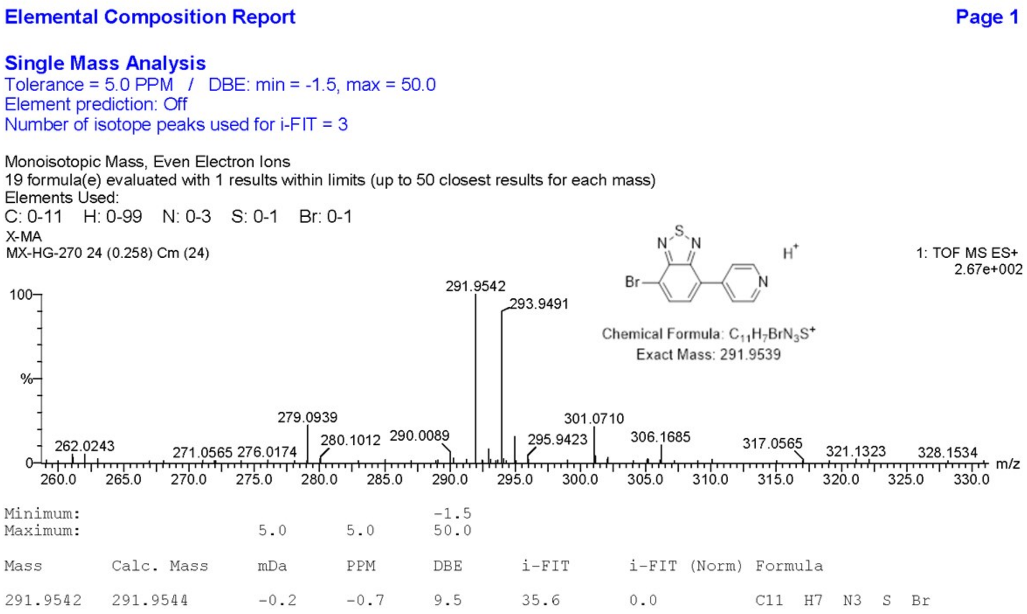


^{13}C NMR (101 MHz, MeOD) δ 154.7, 154.3, 154.2, 150.5, 146.1, 145.7, 135.6, 134.8, 133.0, 131.1, 130.8, 130.19, 130.1, 128.7, 128.4, 125.6, 65.2.

1H NMR (400 MHz, Methanol-d_4) δ 9.28 (d, J = 6.7 Hz, 2H), 9.21 (d, J = 6.9 Hz, 2H), 9.01 – 8.94 (m, 4H), 8.59 (s, 2H), 7.68 – 7.60 (m, 2H), 7.57 – 7.45 (m, 3H), 5.98 (s, 2H), 5.93 – 5.79 (m, 1H), J, 5.0 = 17.1, 1.8 Hz, 1H), 5.01 (dd, J = 10.2, 1.7 Hz, 1H), 4.77 (t, J = 7.6 Hz, 2H), 2.27 – 2.16 (m, 2H), 2.19 – 2.09 (m, 2H), 1.64 – 1.52 (m, 2H).



13C NMR (101 MHz, MeOD) δ 154.2, 153.8, 153.4, 145.9, 138.9, 134.7, 132.7, 132.5, 131.2, 131.1, 131.0, 130.8, 130.3, 129.2, 129.0, 115.9, 65.3, 62.5, 34.1, 31.9, 26.5.



Elemental Composition Report **Page 1**

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Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
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Elements Used:
C: 0-11 H: 0-99 N: 0-3 S: 0-1 Br: 0-1
X-MA
MX-HG-270 24 (0.258) Cm (24)

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Minimum:                                    -1.5
Maximum:                   5.0       5.0    50.0

Mass       Calc. Mass      mDa       PPM    DBE       i-FIT      i-FIT (Norm) Formula

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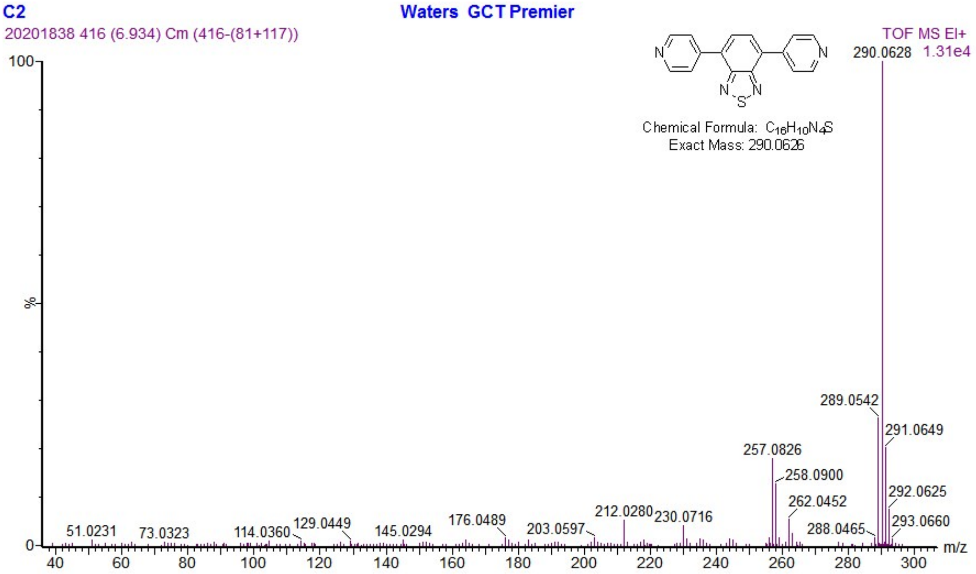
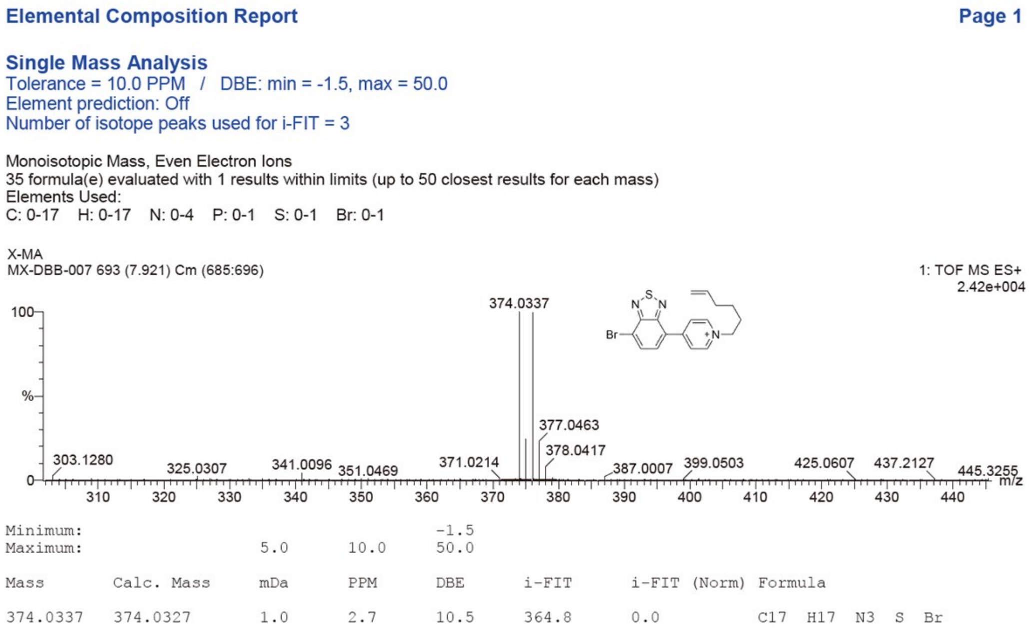
HRMS (ESI+) spectra of **C1**.



HRMS (EI+) spectra of **C2**.



Elemental Composition Report **Page 1**

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Monoisotopic Mass, Even Electron Ions
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X-MA
MX-DBB-007 693 (7.921) Cm (685:696) 1: TOF MS ES+ 2.42e+004

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Minimum:                                 -1.5
Maximum:                  5.0    10.0    50.0

Mass      Calc. Mass      mDa    PPM     DBE     i-FIT     i-FIT (Norm)  Formula

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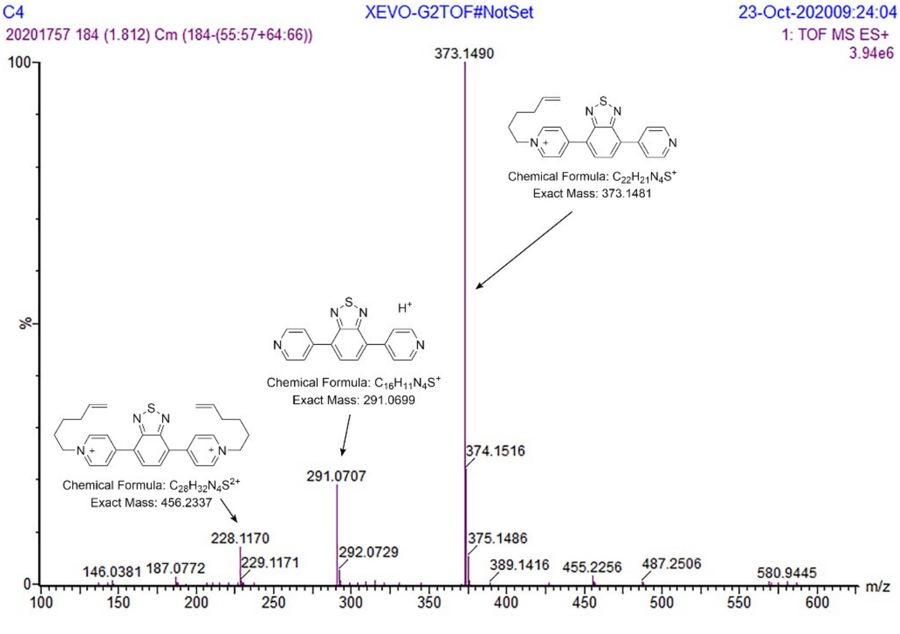
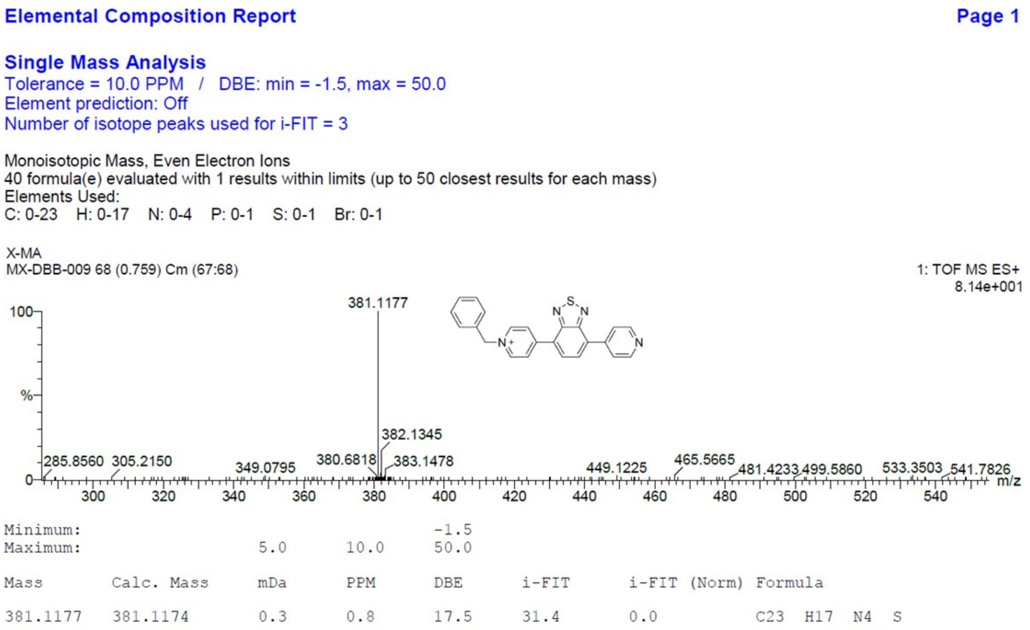
HRMS (ESI+) spectra of **C3**.



HRMS (ESI+) spectra of **C4**.



Elemental Composition Report **Page 1**

Single Mass Analysis
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Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
40 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-23 H: 0-17 N: 0-4 P: 0-1 S: 0-1 Br: 0-1

X-MA
MX-DBB-009 68 (0.759) Cm (67:68)

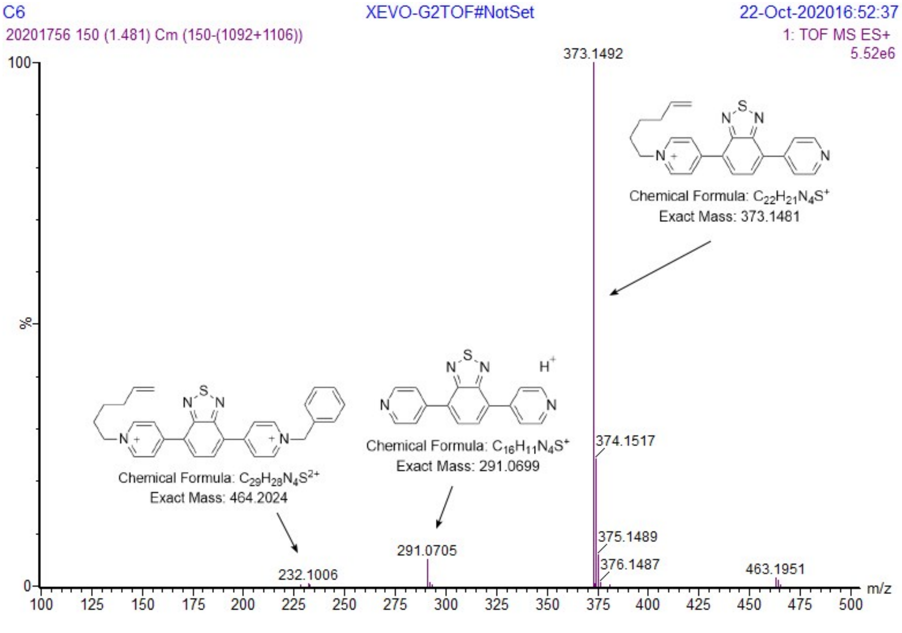
1: TOF MS ES+
8.14e+001

```
Minimum:                                   -1.5
Maximum:                   5.0      10.0   50.0

Mass      Calc. Mass       mDa      PPM    DBE      i-FIT      i-FIT (Norm) Formula

381.1177  381.1174         0.3      0.8    17.5     31.4       0.0          C23  H17  N4  S
```

HRMS (ESI+) spectra of **C5**.



HRMS (ESI+) spectra of **C6**.