Electronic Supplementary Information (ESI) For

A benzothiadiazole-based fluorescent sensor for selective detection of oxalyl chloride and phosgene

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General method and materials

Unless specifically mentioned, all chemicals are commercially available and were used as received. NMR spectra were taken on a Bruker AV400 at room temperature. Mass spectra (EI and HRMS) were obtained in Waters GCT Premier and Bruker MicroToF-Q II spectrometer, respectively. Fluorescence spectra and UV-vis spectra were recorded at room temperature on an Agilent Cary Eclipse spectrofluorophotometer and PerkinElmer Lambda 365, respectively.

Quantum yield measurements

Fluorescence quantum yields were determined in the reference of quinine sulfate ($\Phi = 0.54$) in 0.1M H_2SO_4 at 350 nm excitation.[S1] The quantum yields are calculated according to following equation.

$$\Phi_x = \Phi_s (A_s S_x)/(A_x S_s) (n_x/n_s)^2$$

A_x and A_s are the absorbance of samples and the standard. S_x and S_s are integrated fluorescence emission corresponding to samples and the standard. n is the refractive index of the solvent.

Table S1 Photophysical data of BTA, BTAH and BTAP.

Compound	Absorbance, λ_{max} (nm)	Emission, λ_{max} (nm)	Quantum Yield (Φ)
BTA	438	522	0.06
BTAH	493	516	0.78
BTAP	492	508	0.56

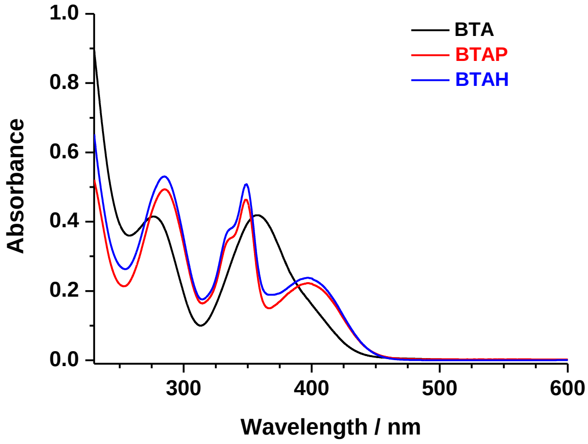


Fig. S1 UV-vis absorption spectra of BTA, BTAP and BTAH (10 μM) in DCM at room temperature.

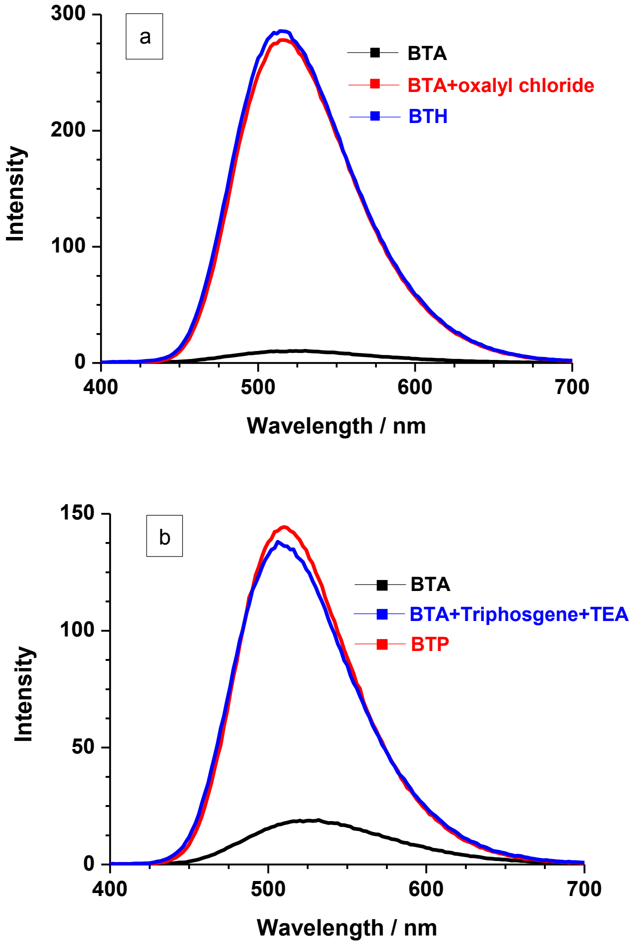


Fig. S2 (a) Fluorescence spectra of BTAH solution (1 μM) and BTA (1 μM) solution upon addition of oxalyl chloride (5 μM) in DCM. (b) Fluorescence spectra of BTAP solution (5 μM) and BTA (5 μM) solution upon addition of triphosgene (50 μM) and TEA (20 μM) in DCM. (λ_{ex} = 380 nm).

Details of Assay Experiments

Preparation of phosgene: As a toxic gas, phosgene is danger to use directly. We employed triphosgene, which is a common nonvolatile and less toxic precursor, to produce phosgene in the presence of tertiary amine in solution. Dichloromethane as the solvent was used all measurements in solutions. In this research, phosgene can be produced in situ in BTA solution containing triethylamine (TEA) upon addition of triphosgene.

Preparation of the Test Paper: Polystyrene (2 g) was dissolved in 50 mL DCM to obtain a sticky homogenous solution and then BTA (2 mg) was added with a magnetic stir bar. A filter paper was cut into strips, and then tied with copper wire. Then, the paper was immersed in the solution and then taken out immediately to dry in air. Finally, the test paper with BTA was made simply to detect oxalyl chloride and phosgene in gas phase.

Detection of oxalyl chloride and phosgene in gas phase:

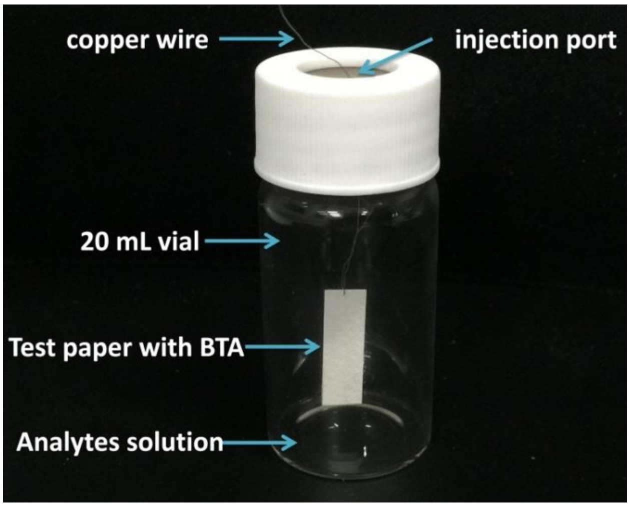


Fig. S3 Schematic diagram of detection device of oxalyl chloride vapor, phosgene and other analytes vapor.

Detection of oxalyl chloride vapor and phosgene in various concentrations: Various concentration of oxalyl chloride ($2*10^{-3}$ M, $1*10^{-2}$ M, $2*10^{-2}$ M and $4*10^{-2}$ M) and triphosgene ($2*10^{-2}$ M, $4*10^{-2}$M, $6*10^{-2}$ M, $8*10^{-2}$ M and $1*10^{-1}$ M) with in DCM solutions were prepared. Using a microliter syringes, 10 μL above solutions were injected to detection devices. Specifically, 10 μL TEA ($4*10^{-2}$) in DCM solution were added into each of triphosgene vials, respectively. After 5 min, the fluorescence of these test papers was taken pictures under 365 nm light.

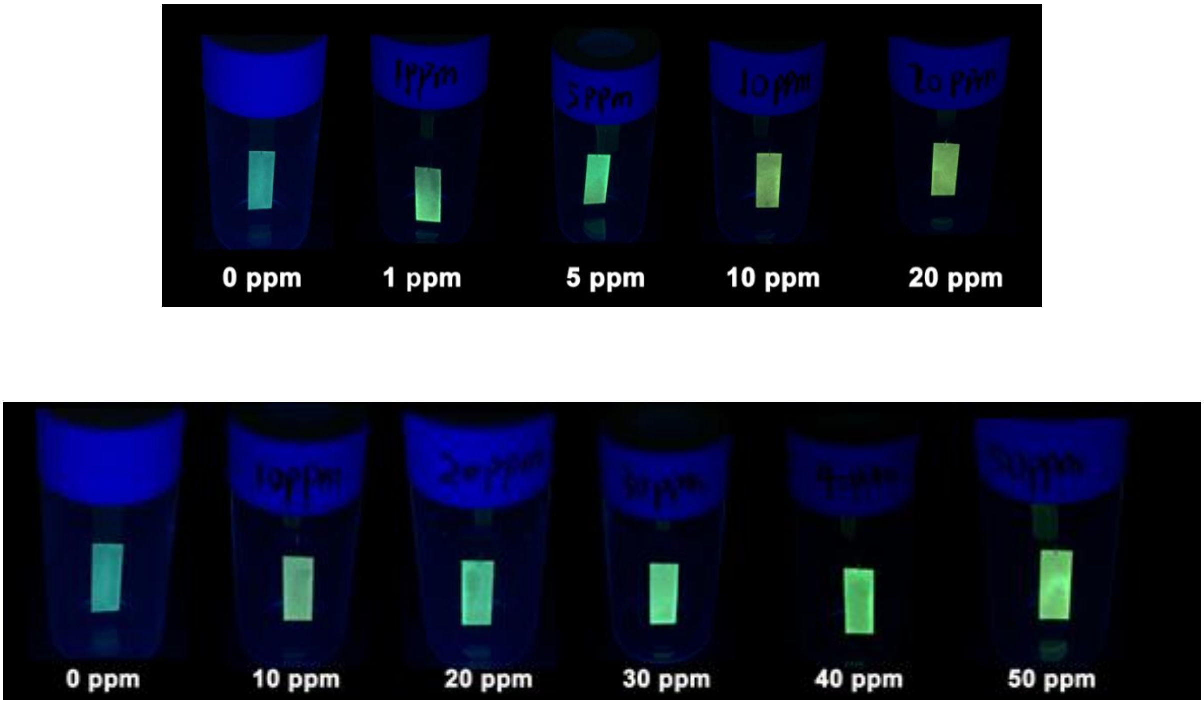


Fig. S4 Fluorescence photo of BTA test papers upon the exposure to various amount of oxalyl chloride (0-20ppm, above) and phosgene (0–50 ppm, bottom).

Selective detection of oxalyl chloride vapor and phosgene over other analytes vapor.

The concentration ($1*10^{-1}$ M) of DCP, $SOCl_2$, SO_2Cl_2, $POCl_3$, CH_3COCl, TsCl, BsCl and BzCl were prepared. Using a microliter syringes, 10 μL above solutions were injected to detection devices respectively. After 5 min, the fluorescence of these test papers were taken pictures under 365 nm light.

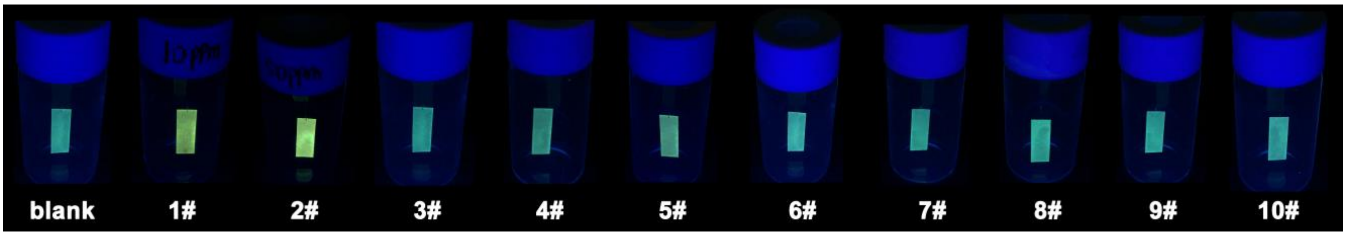


Fig. S5 Fluorescence responses of BTA-based test papers upon exposure to oxalyl chloride (20 ppm) vapor , triphosgene (50 ppm) with TEA (0.01%) vapor and various other analytes vapor (100 ppm) : 0, blank; 1, oxalyl chloride; 2, triphosgene / TEA; 3, DCP; 4, $SOCl_2$; 5, SO_2Cl_2; 6, $POCl_3$; 7, CH_3COCl; 8, TsCl; 9, BsCl; 10, BzCl in vials (20 mL) for 5 min under the irradiation of UV lamp (365 nm).

EI-MS and NMR spectra of related compounds

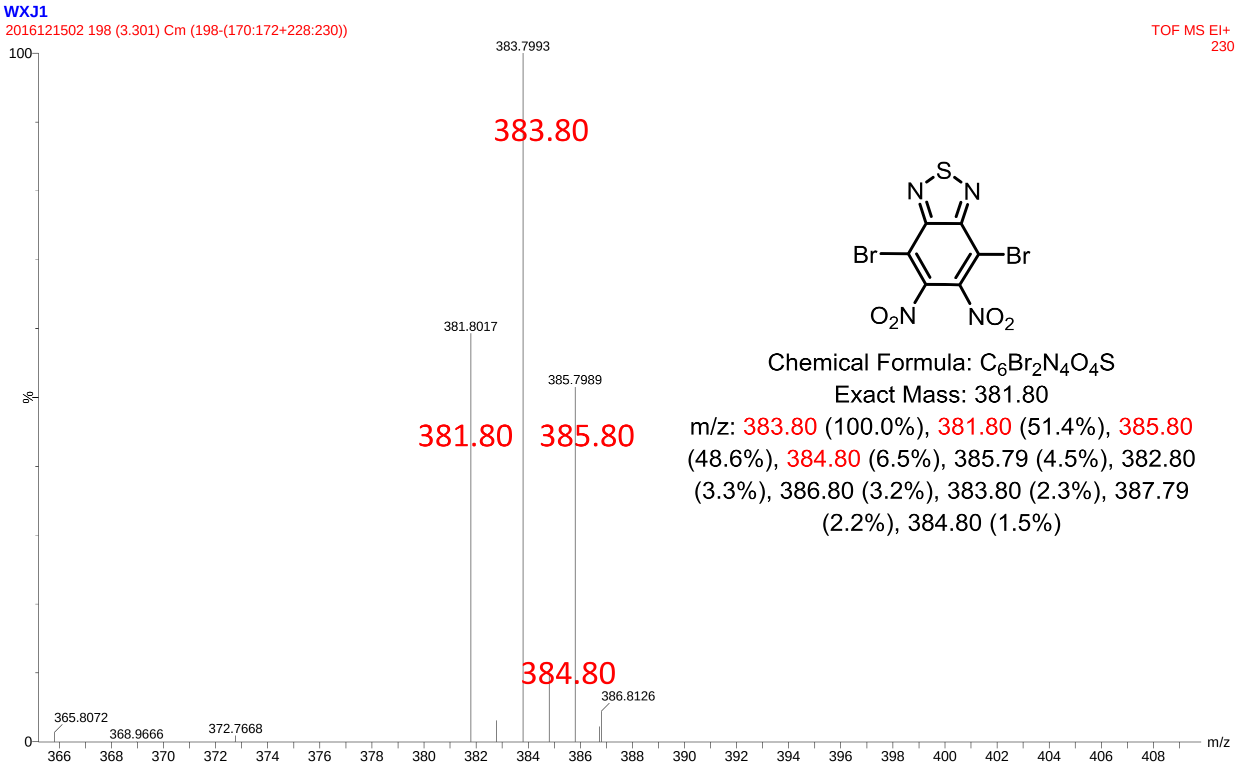


Fig. S6 EI-MS spectra of compound **2**.

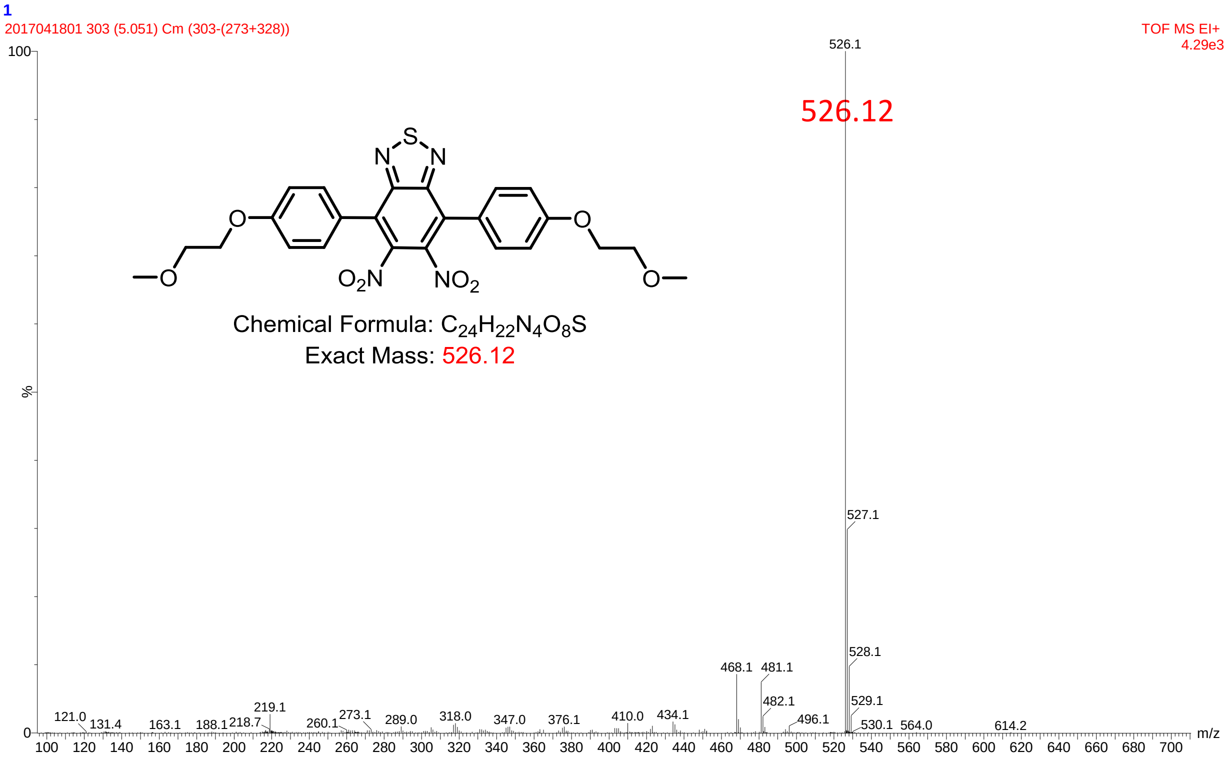


Fig. S7 EI-MS spectra of compound **3**.

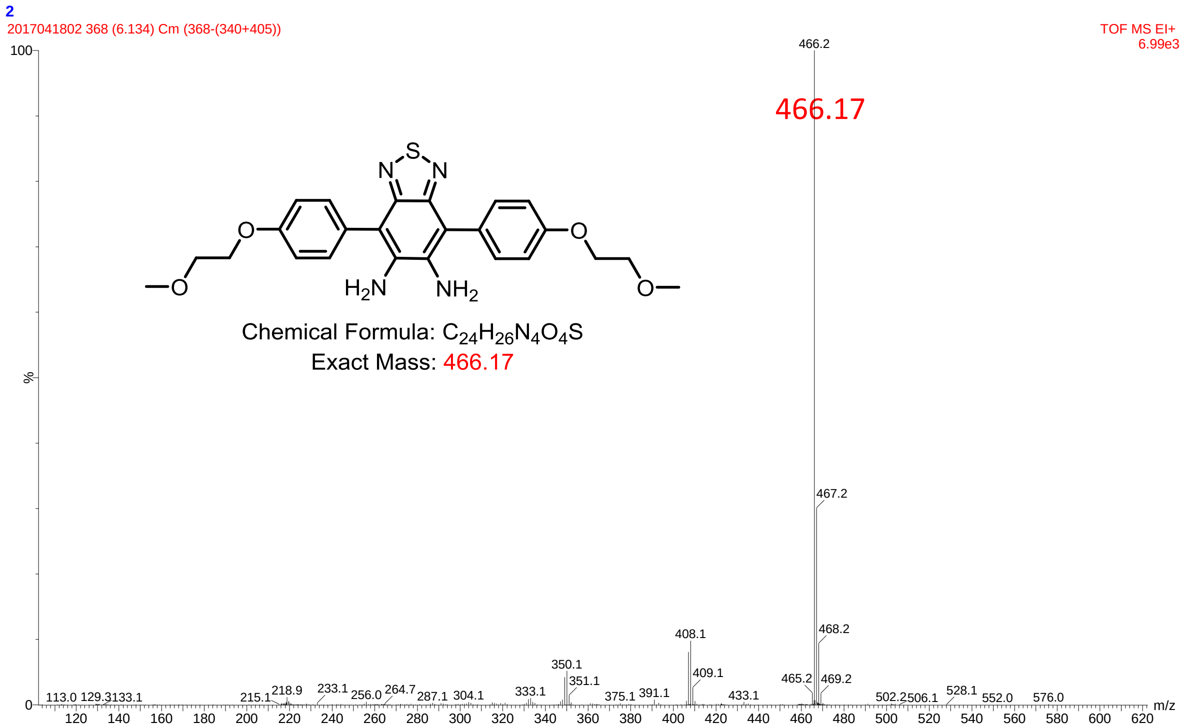


Fig. S8 EI-MS spectra of **BTA**.

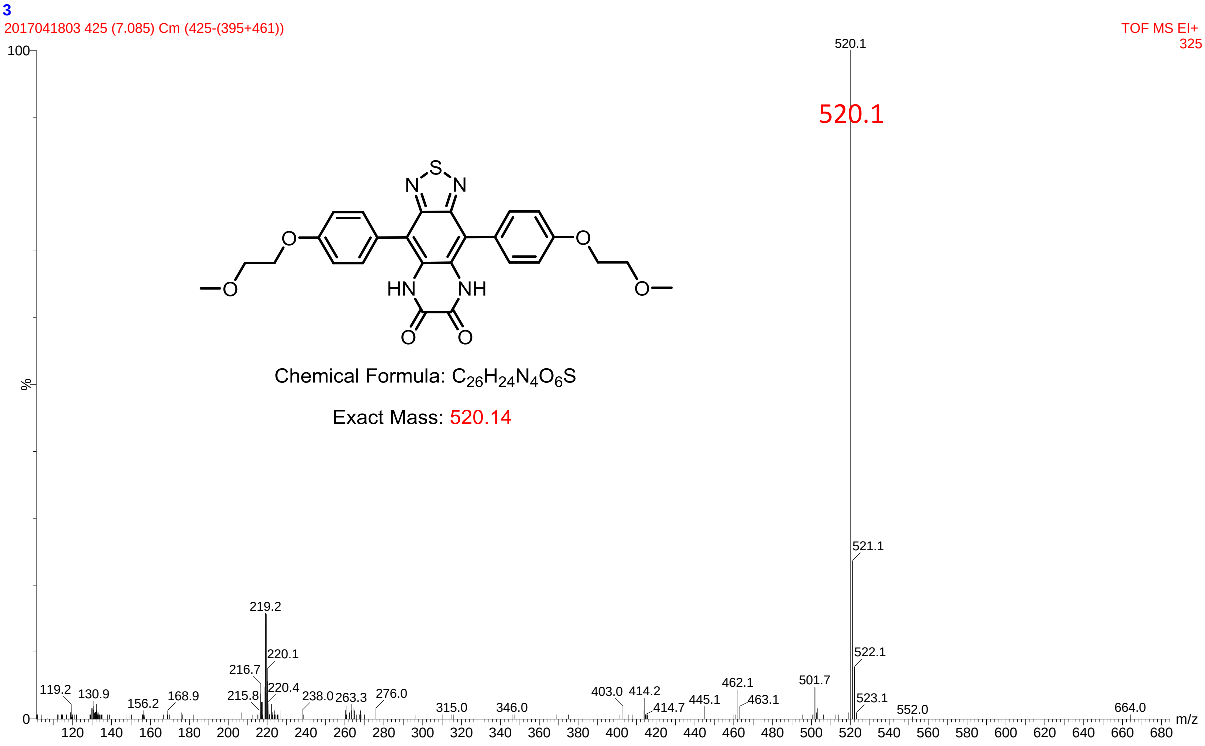


Fig. S9 EI-MS spectra of **BTAH**.

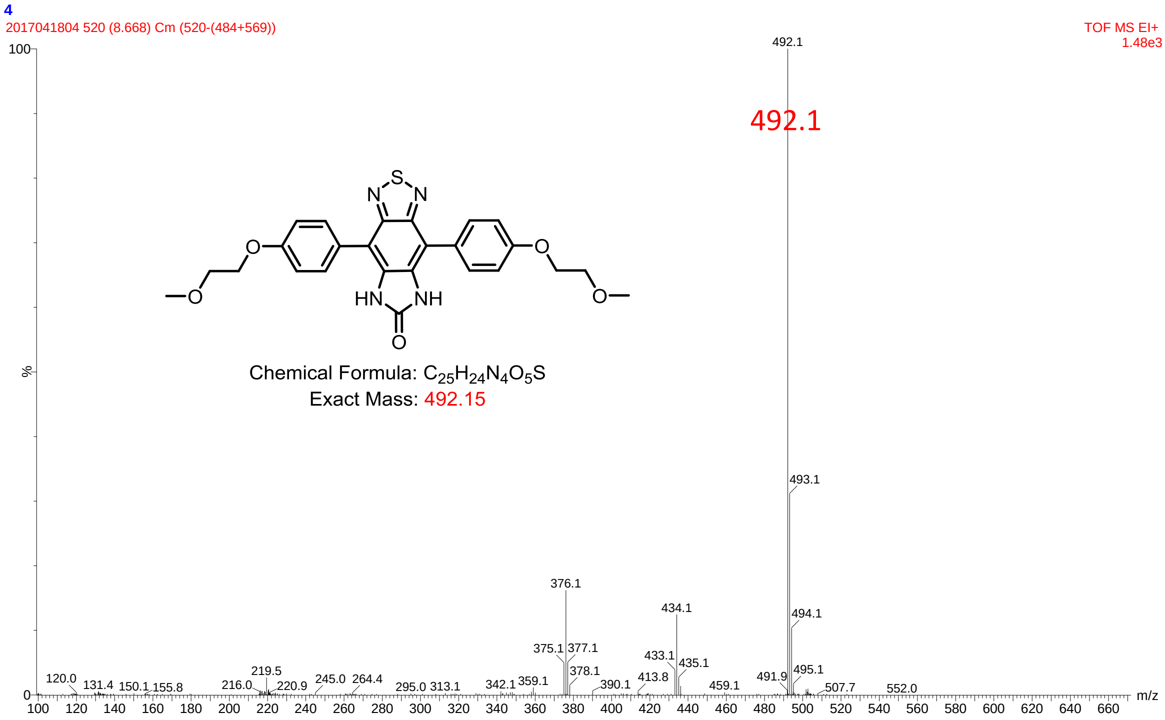


Fig. S10 EI-MS spectra of **BTAP**.

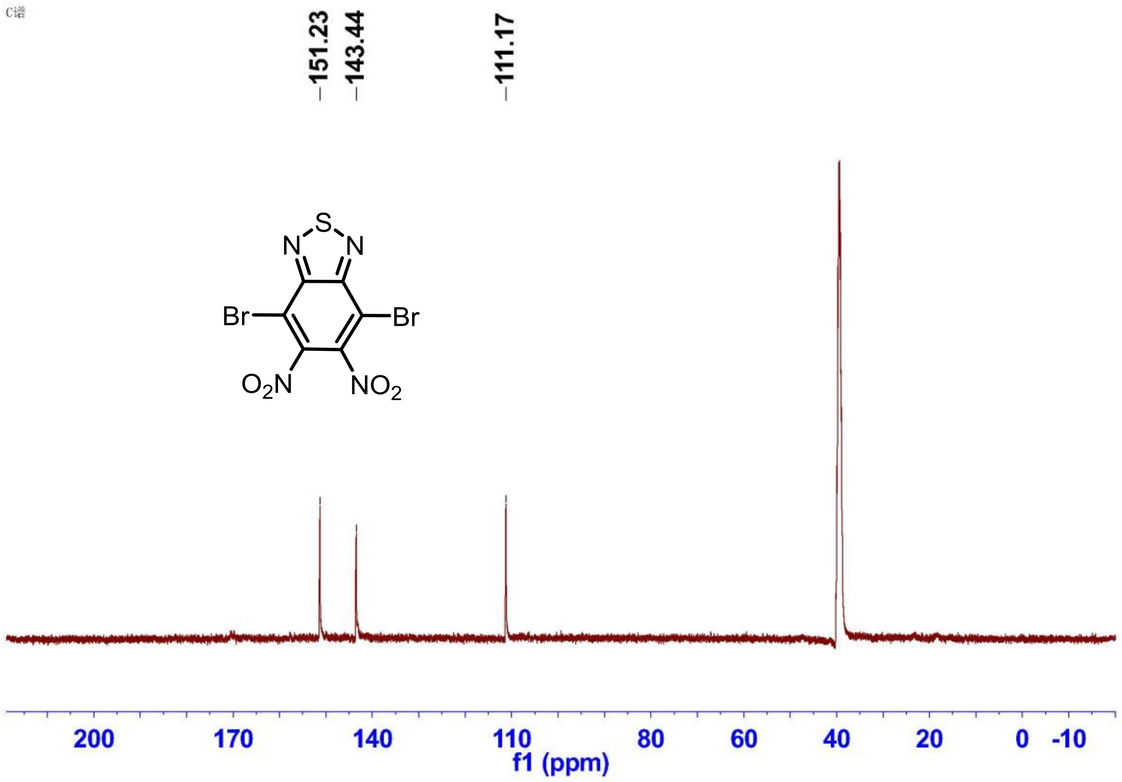


Fig. S11 ^{13}C NMR spectra of compound **2** (DMSO-d_6).

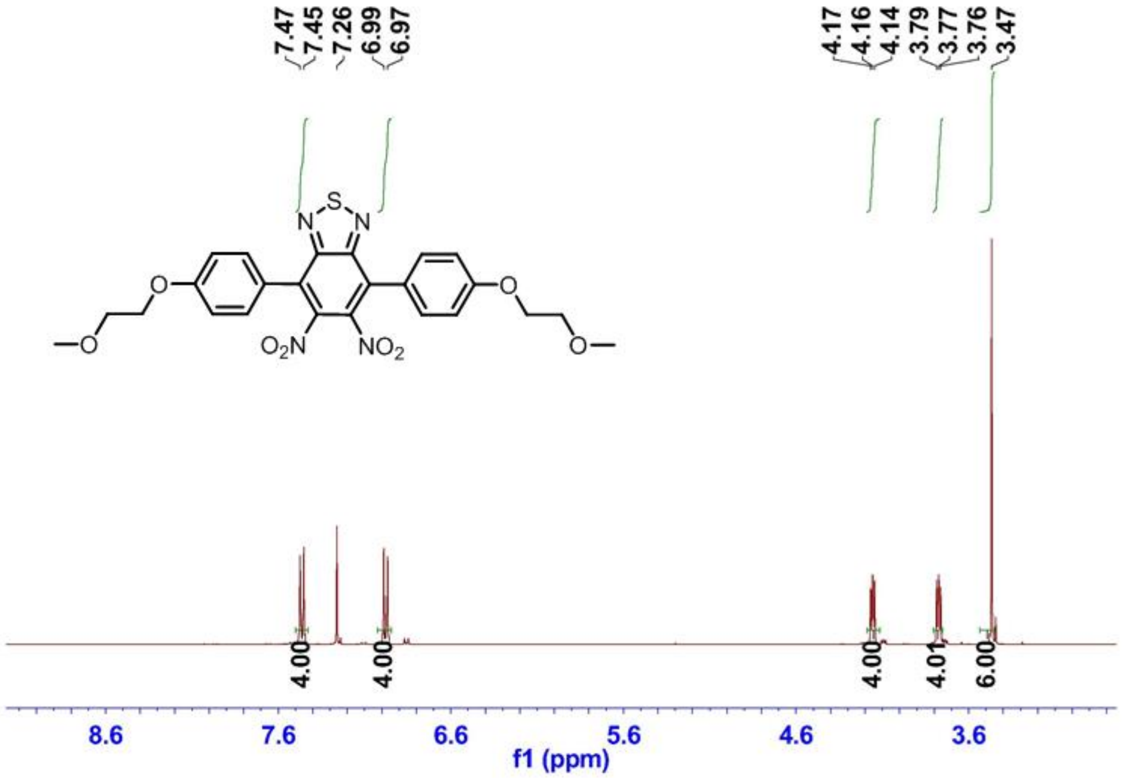


Fig. S12 ^{1}H NMR spectra of compound **3** ($CDCl_3$).

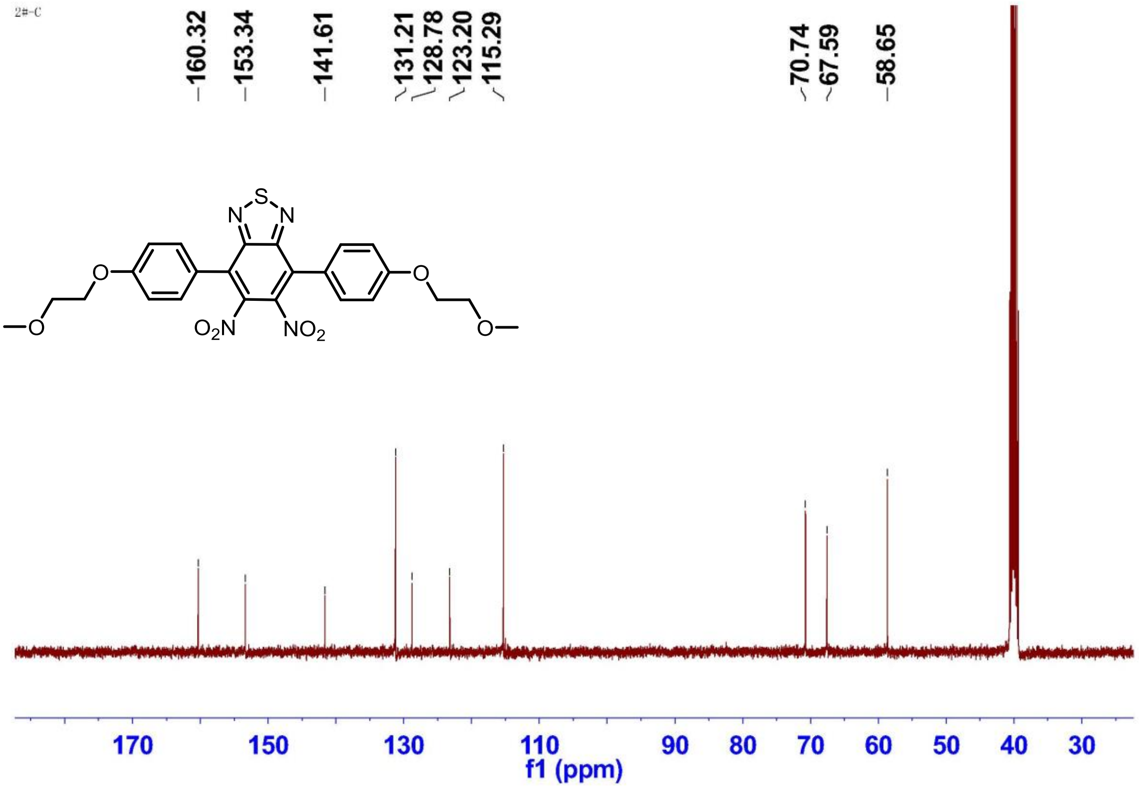


Fig. S13 ^{13}C NMR spectra of compound **3** (DMSO-d_6).

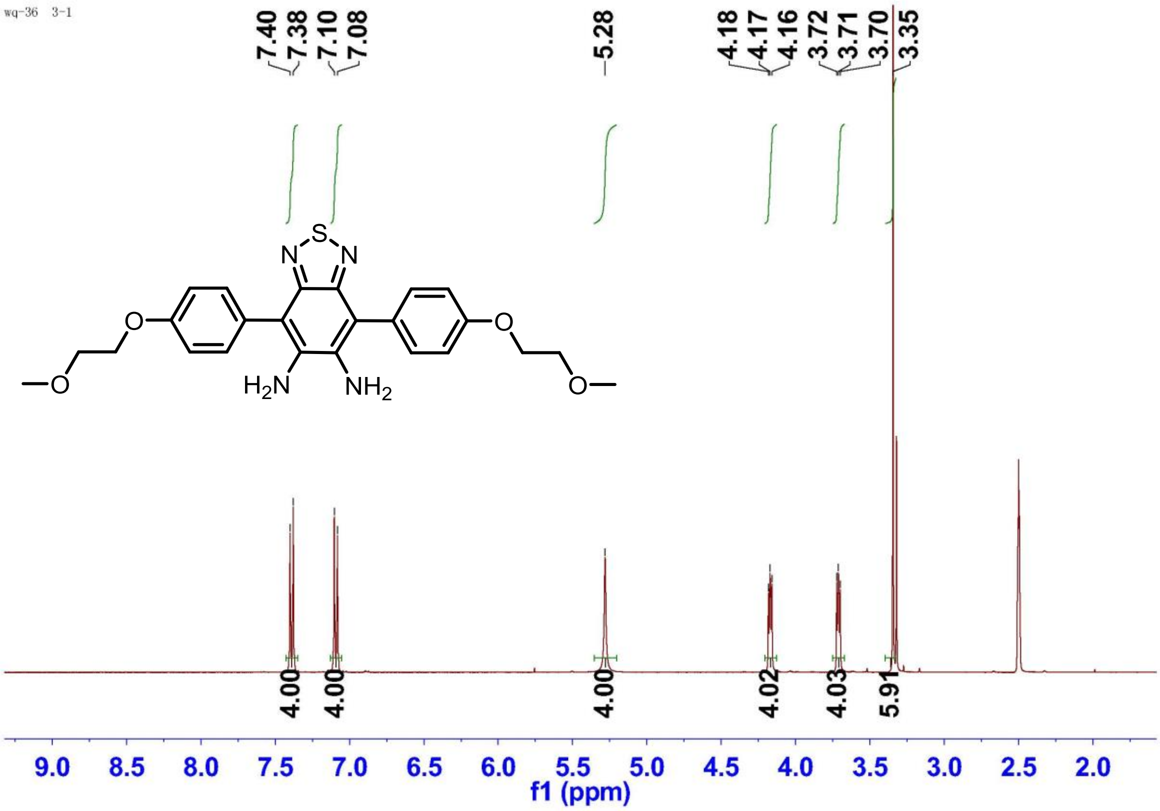


Fig. S14 ^{1}H NMR spectra of **BTA** (DMSO-d_6).

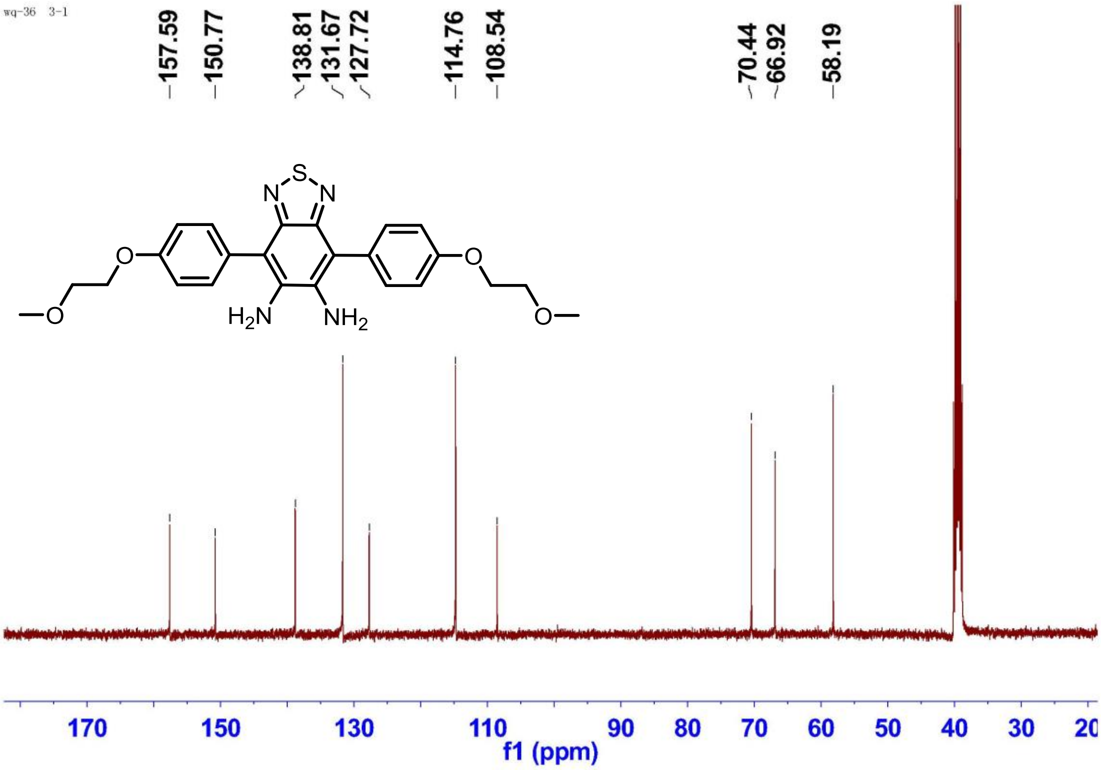


Fig. S15 ^{13}C NMR spectra of **BTA** (DMSO-d_6).

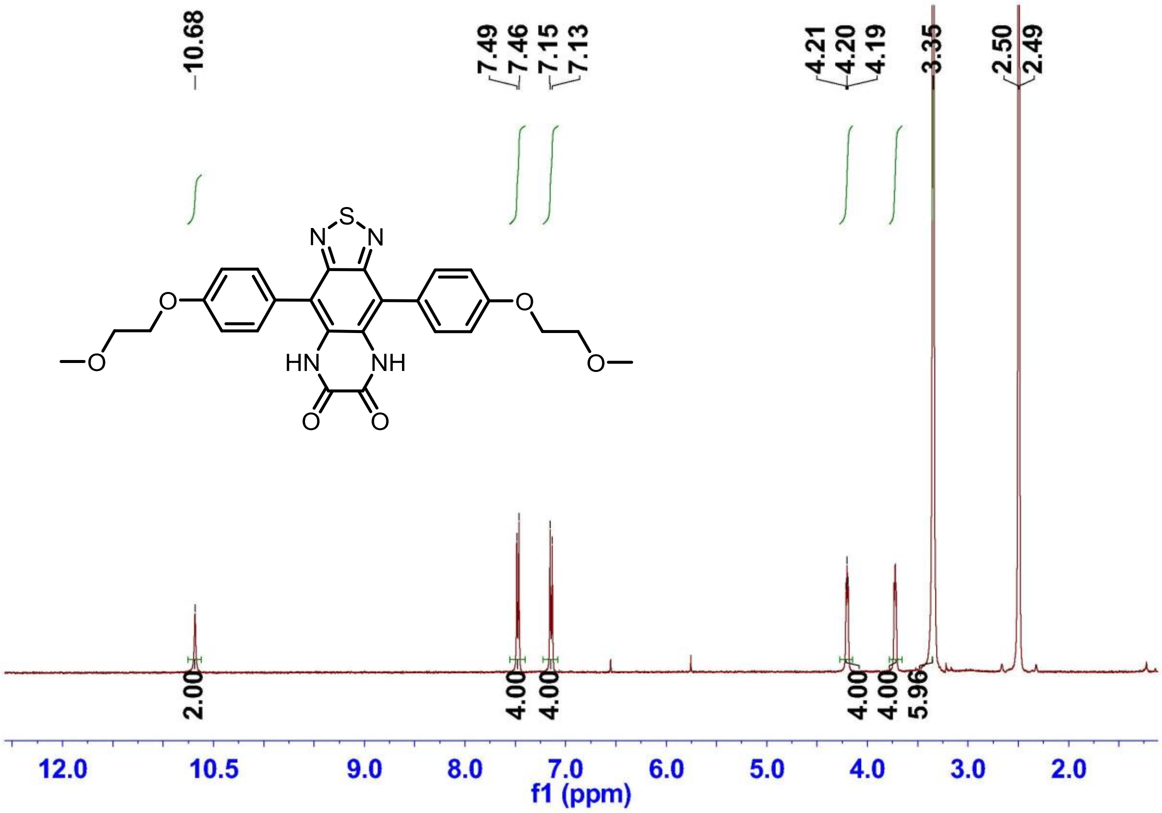


Fig. S16 ^{1}H NMR spectra of **BTAH** (DMSO-d_6).

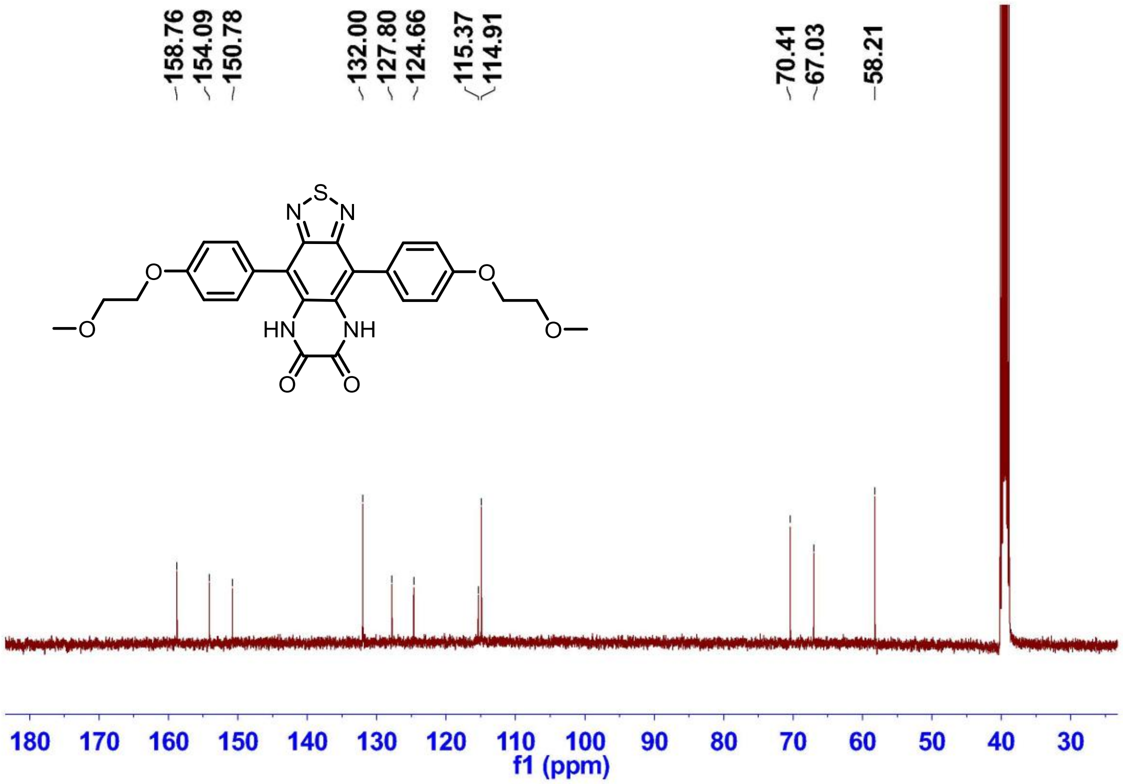


Fig. S17 ^{13}C NMR spectra of **BTAH** (DMSO-d_6).

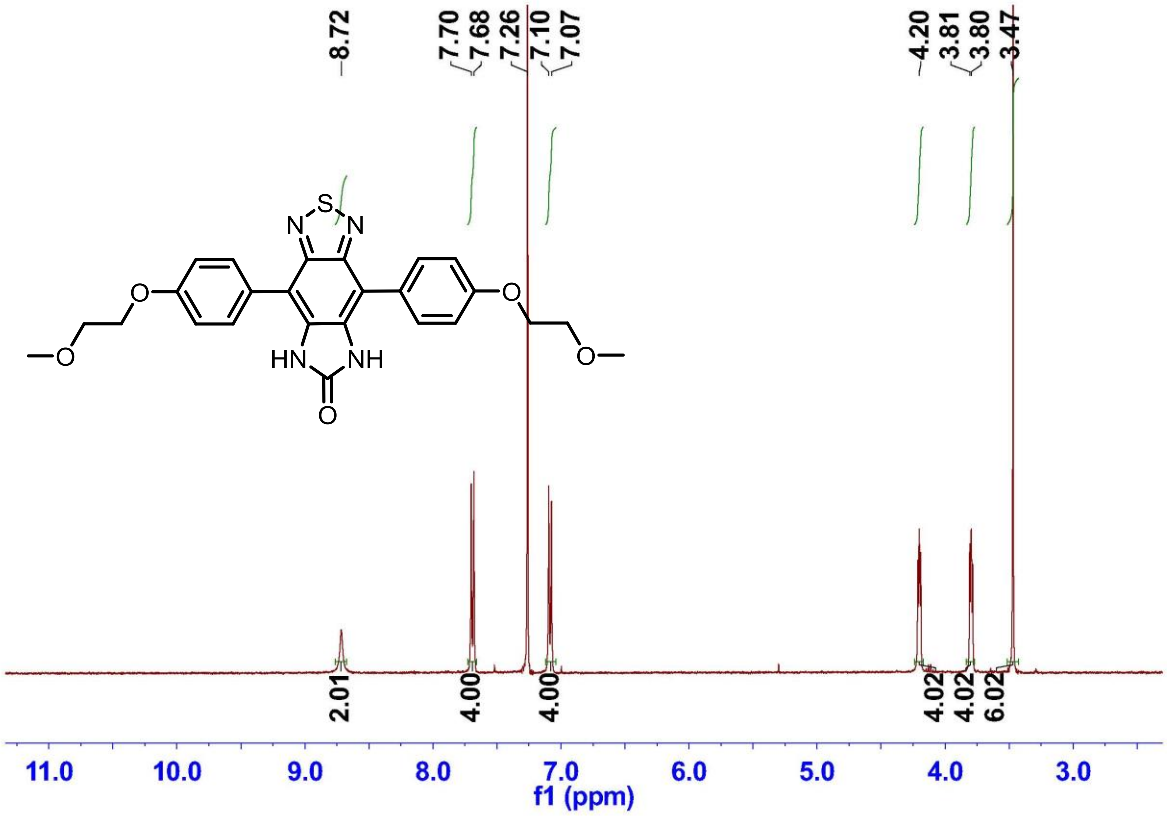


Fig. S18 ^{1}H NMR spectra of **BTAP** ($CDCl_3$).

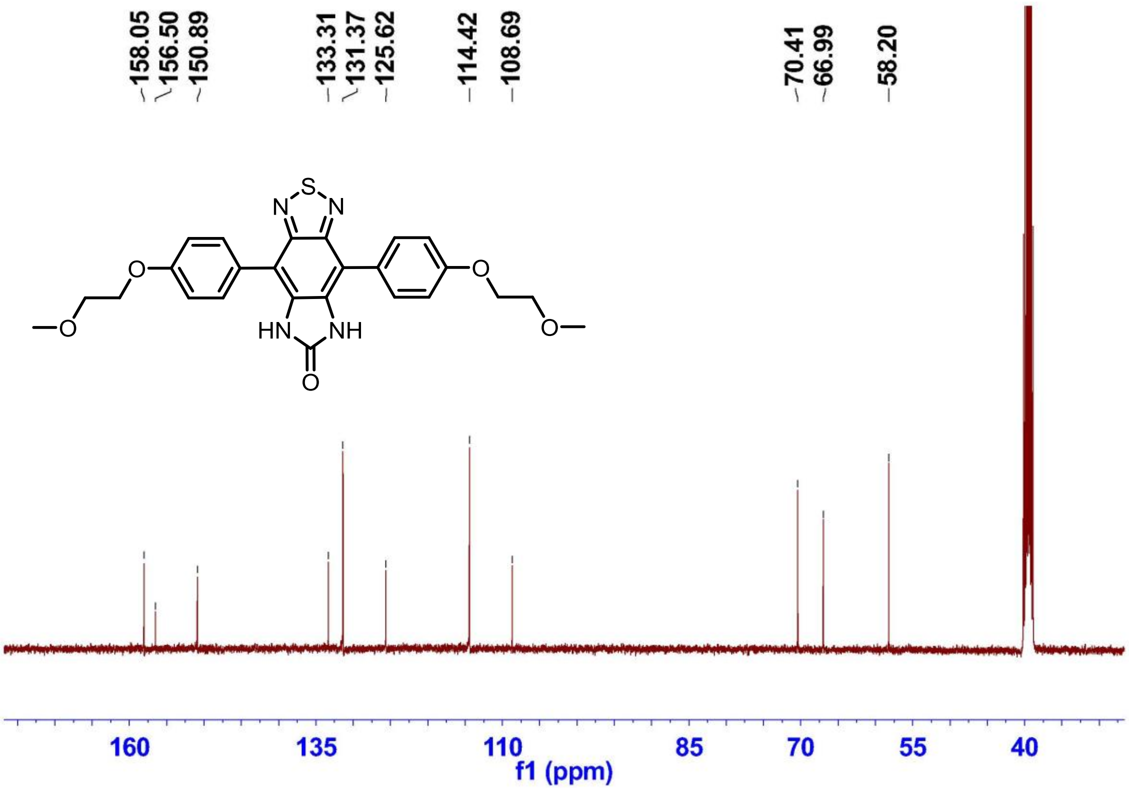
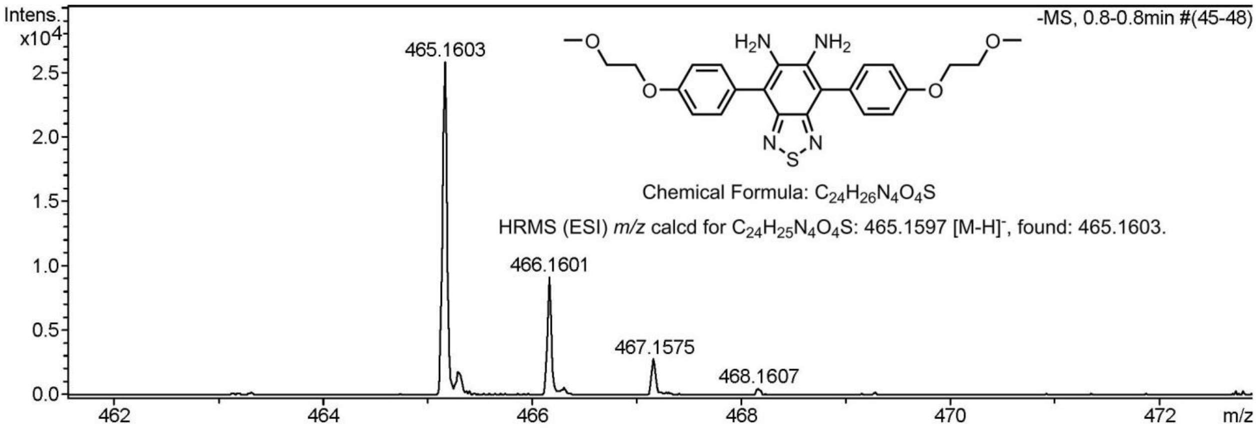
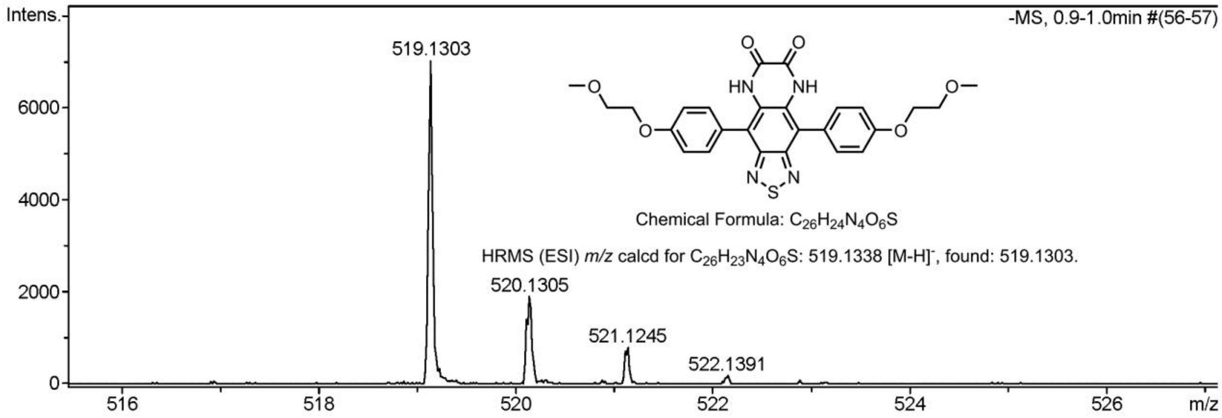


Fig. S19 ^{13}C NMR spectra of **BTAP** (DMSO-d_6).


Chemical Formula: $C_{24}H_{26}N_4O_4S$

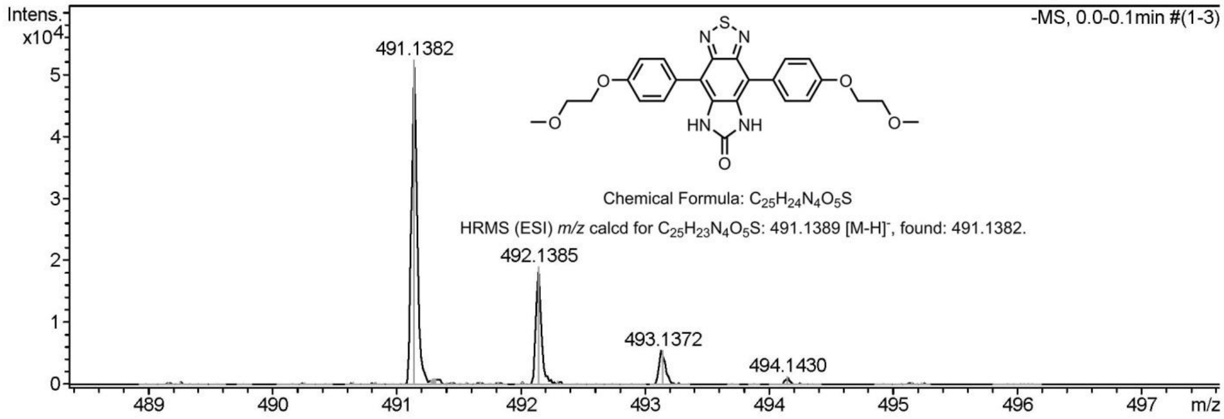
HRMS (ESI) *m/z* calcd for $C_{24}H_{25}N_4O_4S$: 465.1597 [M-H]$^-$, found: 465.1603.

Fig. S20 HR-MS spectra of **BTA**.


Chemical Formula: $C_{26}H_{24}N_4O_6S$

HRMS (ESI) *m/z* calcd for $C_{26}H_{23}N_4O_6S$: 519.1338 [M-H]$^-$, found: 519.1303.

Fig. S21 HR-MS spectra of **BTAH**.


Chemical Formula: $C_{25}H_{24}N_4O_5S$

HRMS (ESI) *m/z* calcd for $C_{25}H_{23}N_4O_5S$: 491.1389 [M-H]$^-$, found: 491.1382.

Fig. S22 HR-MS spectra of **BTAP**.

References:

S1. G. A. Crosby and J. N. Demas, *J. Phy. Chem.*, 1971, **75**, 991-1024.