Supporting Information

An AIE-Based Fluorescent Probe for Selective and Sensitive Detection of N-Bromosuccinimide

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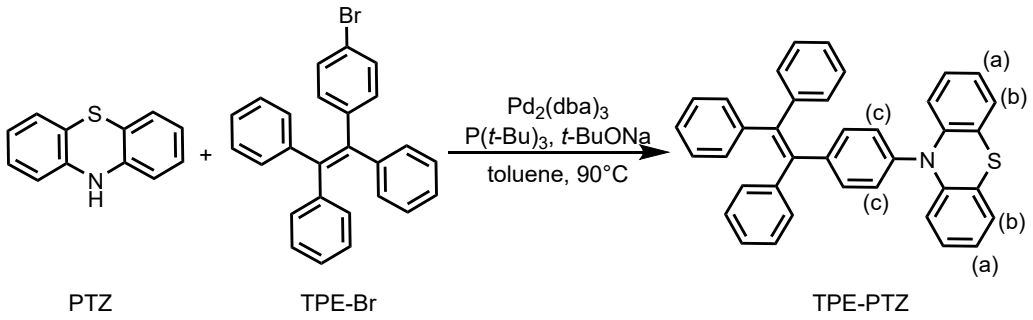
Part I Experimental Section

1.1 General information

^{1}H NMR and ^{13}C NMR were recorded on Bruker-500 MHz Spectrometer (^{1}H NMR: 500MHz, ^{13}C NMR: 125MHz). The chemical shifts (δ) and coupling constants (J) were expressed in ppm and Hz respectively. The Photoluminescence (PL) spectra were obtained on Hitachi F-4600 Fluorescence Spectrometer. Commercially available compounds were used without further purification. The UV-vis spectra were obtained on Shimadzu UV-VIS-NIR Spectrophotometer (UV-2700). HRMS data were obtained on Waters Xevo G2-S QTof Mass Spectrometer. DLS measurements were performed on Zetasizer Nano Instrument. All solvents were purified according to the standard procedures unless otherwise noted.

1.2 Synthesis of TPE-PTZ



Scheme S1. Synthetic route of TPE-PTZ

Tris(dibenzylideneacetone)dipalladium(0) ($Pd_2(dba)_3$) (87 mg, 0.095 mmol) and tri-tert-butylphosphane (P(*t*-Bu)$_3$) (0.02 mL, 0.095 mmol) were dissolved in dry toluene (20 mL) under argon and stirred for 10 min at room temperature (preformation of the catalyst). The catalyst was then added to a mixture of 10H-phenothiazine (1.53 g, 7.66 mmol), TPE-Br (3.0 g, 7.29 mmol), and sodium tert-butylate (*t*-BuONa) (1.05 g, 10.94 mmol) in dry toluene (90 mL). The reaction mixture was stirred at 90°C overnight. The reaction mixture was cooled to room temperature and treated with water. The mixture was extracted with chloroform three times. The organic phases were collected, dried over $MgSO_4$, and concentrated under vacuum. The residue was purified by silica gel chromatography (eluent: dichloromethane/hexane = 3/7) to give desired compound as a light green solid in 91% yield (3.5 g). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28-7.28 (m, 2H), 7.20-7.08 (m, 17H), 7.00 (dd, J = 7.5, 1.7 Hz, 2H), 6.88 (td, J = 7.8, 1.7 Hz, 2H, H_c), 6.82 (td, J = 7.4, 1.3 Hz, 2H, H_b), 6.16 (dd, J = 8.1, 1.3 Hz, 2H, H_a). ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.1, 144.0, 143.6, 143.2, 142.9, 142.1, 140.2, 138.9, 133.6, 131.4, 131.3, 131.3, 130.0, 127.9, 127.8, 127.6, 126.8, 126.7, 126.6, 122.4, 120.1, 117.8, 116.0. HRMS (ESI) m/z calcd. $[M+H]^+$ for $C_{38}H_{28}NS^+$ 530.1937, found 530.1938.

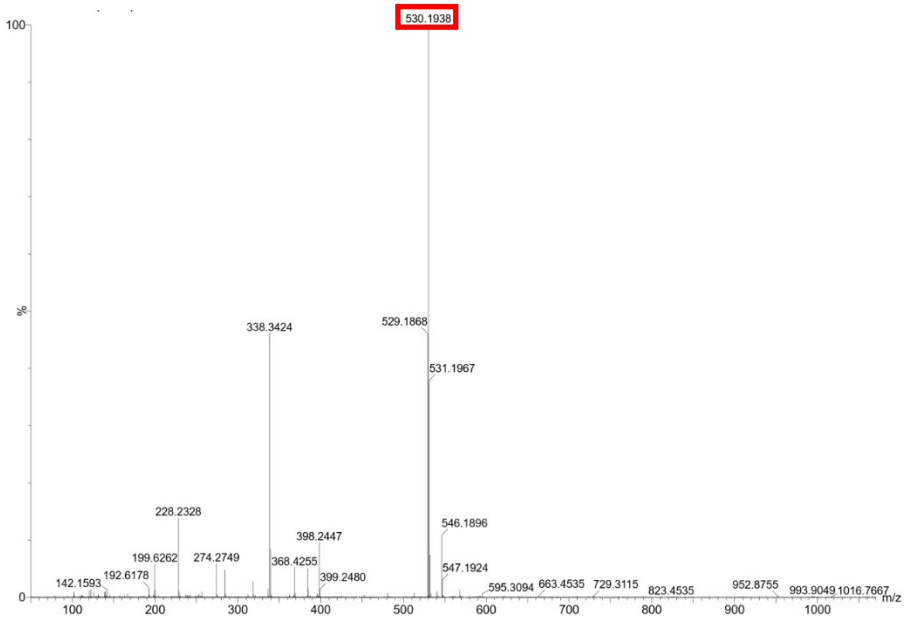


Fig.S1 HRMS Spectrum of TPE-PTZ

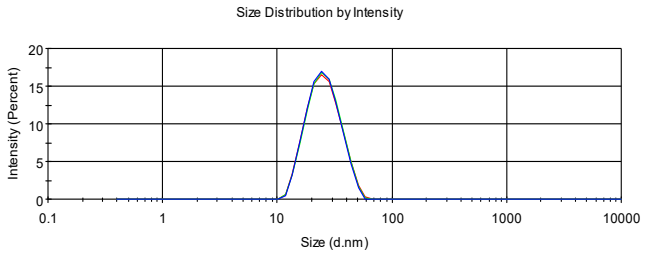


Fig.S2 Particle sizes of 10^{-5} M TPE-PTZ in pure CH_3CN measured by DLS analysis.

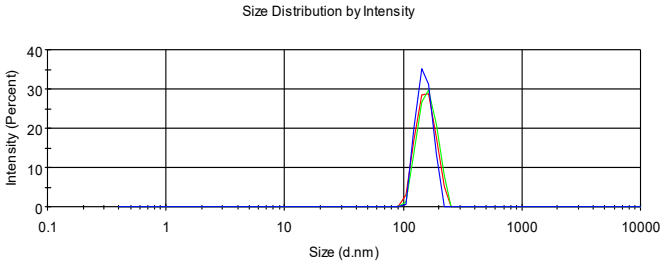


Fig.S3 Particle sizes of 10^{-5} M TPE-PTZ in CH_3CN/water mixtures with 70% water fraction measured by DLS analysis.

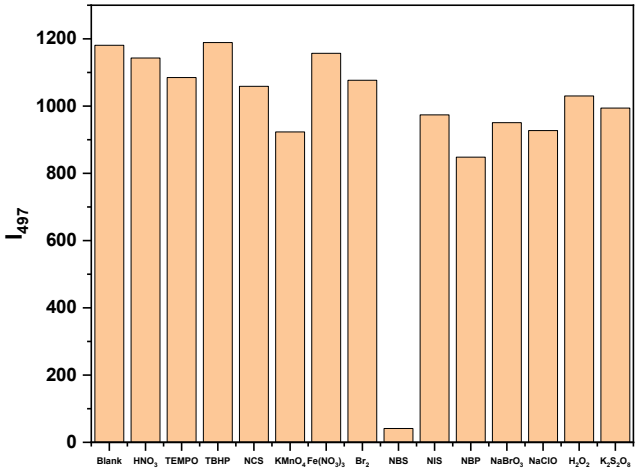


Fig.S4 Changes of fluorescence intensity (I_{497}) of TPE-PTZ upon addition of various analytes.

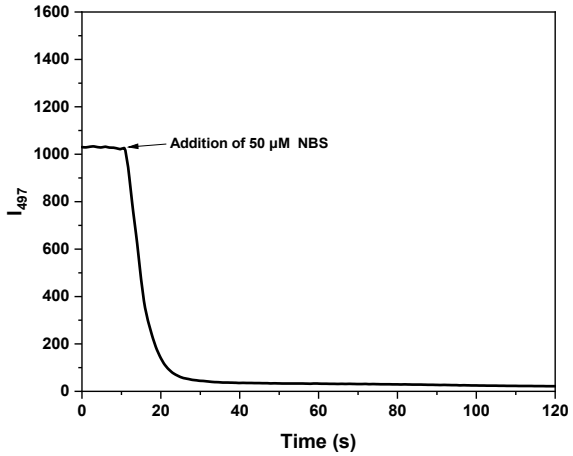


Fig.S5 The detection of response time of TPE-PTZ with 50 μM NBS

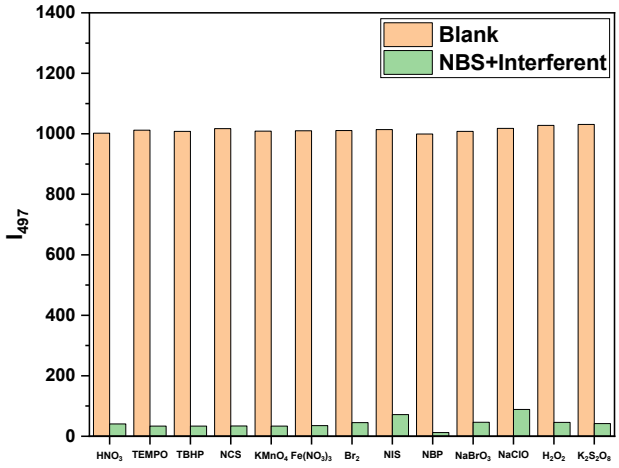


Fig.S6 Changes of fluorescence intensity (I_{497}) of TPE-PTZ upon addition of NBS and various interferents.

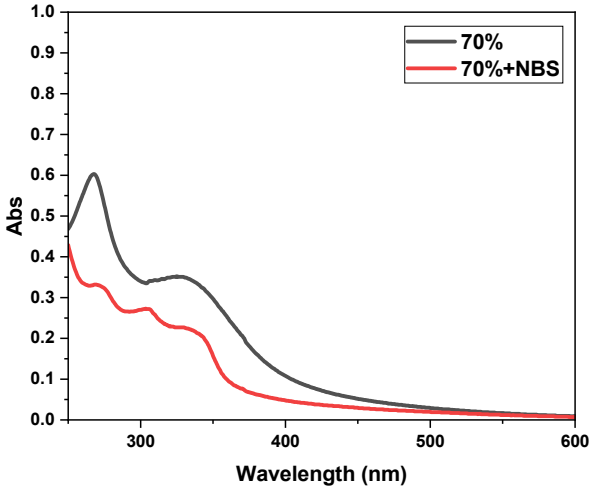


Fig.S7 UV-Vis absorption spectra of 10^{-5} M TPE-PTZ in CH_3CN/water mixtures with 70% water before and after of NBS addition.

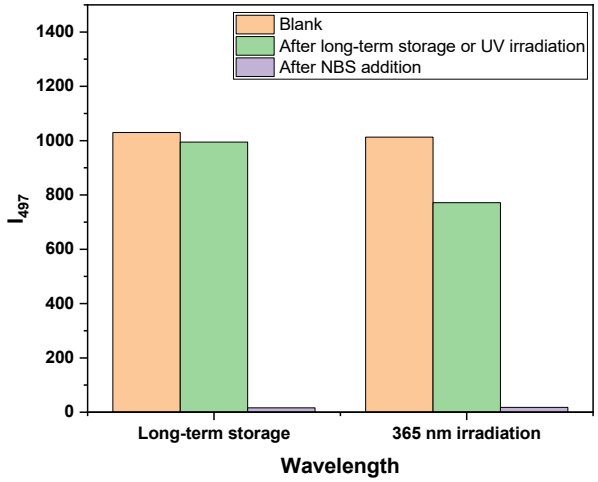


Fig.S8 Stability assessment experiment of the probe

1.3 Mechanism study.

Cyclic voltammetry experiments Cyclic voltammetry experiments were conducted in dry acetonitrile with 2 mM TPE-PTZ and 0.1 M NBu_4PF_6. Working electrode: Glassy carbon electrode. Reference electrode: Ag/AgCl. Corresponding electrode: Platinum. Two pairs of reversible redox peaks were observed at +0.81 V and +1.54 V (vs. Ag/Ag^+), which are assigned to two consecutive one-electron oxidation steps: TPE-PTZ → $TPE\text{-}PTZ^{\bullet+}$ (radical cation) and $TPE\text{-}PTZ^{\bullet+}$ → $TPE\text{-}PTZ^{2+}$ (dication). These findings provide direct evidence for the generation of the $TPE\text{-}PTZ^{2+}$ species upon NBS oxidation.

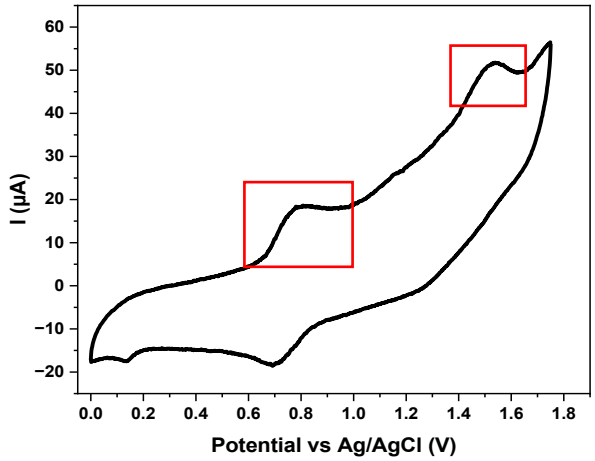


Fig.S9 Cyclic voltammetry traces of TPE-PTZ

HRMS analysis of TPE-PTZ after treatment with two equivalents of NBS revealed two distinct peaks at m/z = 529.1861 and 264.5935. The latter matches the dication species $TPE\text{-}PTZ^{2+}$ (calcd for $C_{38}H_{27}NS^{2+}/2$: 264.5927), while the former corresponds to the radical cation $TPE\text{-}PTZ^{\bullet+}$ (calcd for $C_{38}H_{27}NS^{\bullet+}$: 529.1859). The absence of any signal from the neutral species confirms complete oxidation to the radical cation and dication.

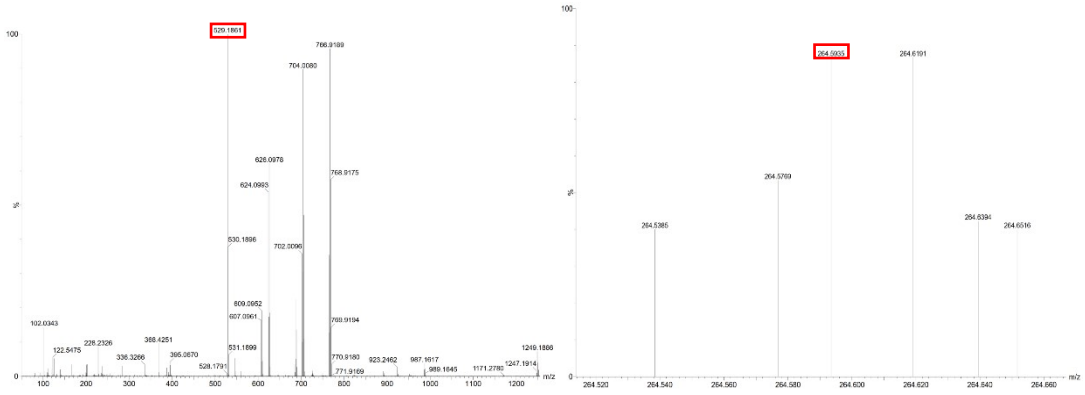


Fig.S10 HRMS Spectrum of $TPE\text{-}PTZ^{\bullet+}$ and $TPE\text{-}PTZ^{2+}$

Sample	NBS added/μM	Results/μM	Recovery /%	RSD /% (n = 3)
River water 1	12	12.78	106.5	0.86
River water 2	18	17.42	96.7	0.96
River water 3	32	31.49	98.4	0.99

Table S1. NBS detection results of TPE-PTZ in river water samples.

1.4 TD-DFT calculation

All the calculations were performed using Gaussian 16 software packages[1]. The geometry of all reactants were optimized using the M062X. In these geometry optimizations, basis set of 6-311+G(d,p) was used.

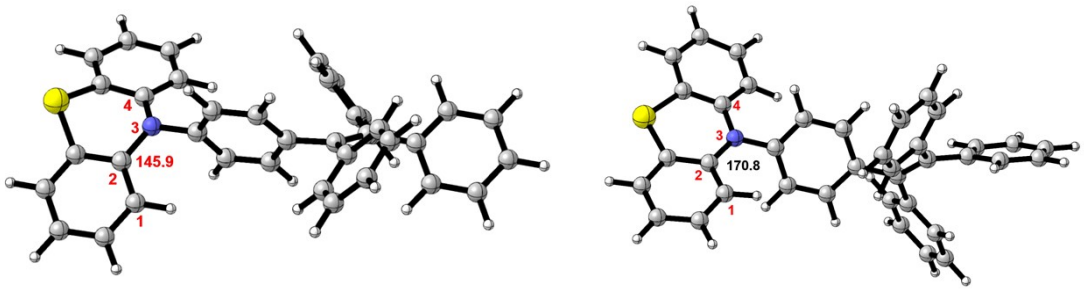


Fig.S11 The dihedral angles of TPE-PTZ and TPE-PTZ^{2+}

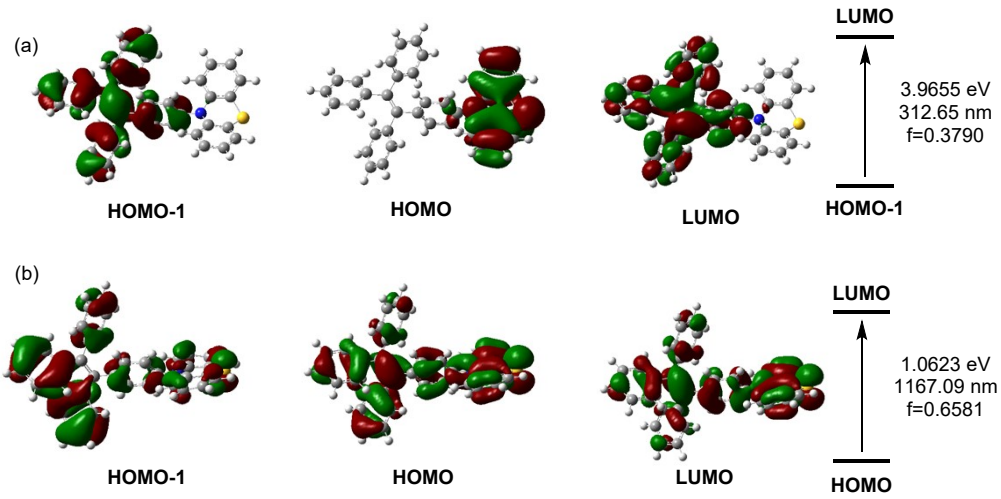


Fig. S12 Time dependent M062X/6-311+G(d,p) calculated frontier molecular orbitals, selected electronic transitions and oscillator strengths of TPE-PTZ(a) and TPE-PTZ^{2+}(b)

Coordinates:

TPE-PTZ

C	4.99050900	3.49480300	-0.92825200
C	3.62522100	3.37204100	-0.71159700
C	3.05298800	2.12979000	-0.45758200
C	3.83952500	0.97286900	-0.43913200
C	5.21182200	1.10240000	-0.69880700
C	5.78173500	2.35174000	-0.91158800
N	3.28655600	-0.30849400	-0.19363000
C	4.03314700	-1.28540900	0.50813500
C	5.42286800	-1.36159700	0.33503100
S	6.20891600	-0.34871200	-0.88564300

C	3.42313100	-2.20882000	1.36290900
C	4.18050900	-3.16538500	2.03105300
C	5.55988100	-3.20743800	1.88385800
C	6.17733600	-2.29270700	1.03811000
C	1.85658500	-0.40734400	-0.15054100
C	1.13937400	0.03217100	0.96125800
C	-0.24577700	-0.02304300	0.95706200
C	-0.93683800	-0.52331900	-0.15247900
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C	1.18508500	-0.94240400	-1.24218500
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C	-3.15083700	0.56902100	0.12057800
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C	-4.62927900	0.53968800	0.30499300
C	-2.51686000	1.90823400	0.29643700
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H	-1.38115400	1.81639600	-1.52441300
H	-0.86018900	5.38764200	0.79383100

TPE-PTZ^{2+}

C	5.43895500	0.84766900	-3.42133300
C	4.04692800	1.01589200	-3.35446700
C	3.35911800	0.71464600	-2.20295600
C	4.02858900	0.20055800	-1.06928900
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C	6.12757800	0.45626500	-2.29737500
N	3.30086600	-0.18570800	0.06987600
C	3.89383200	-0.52814400	1.29775500
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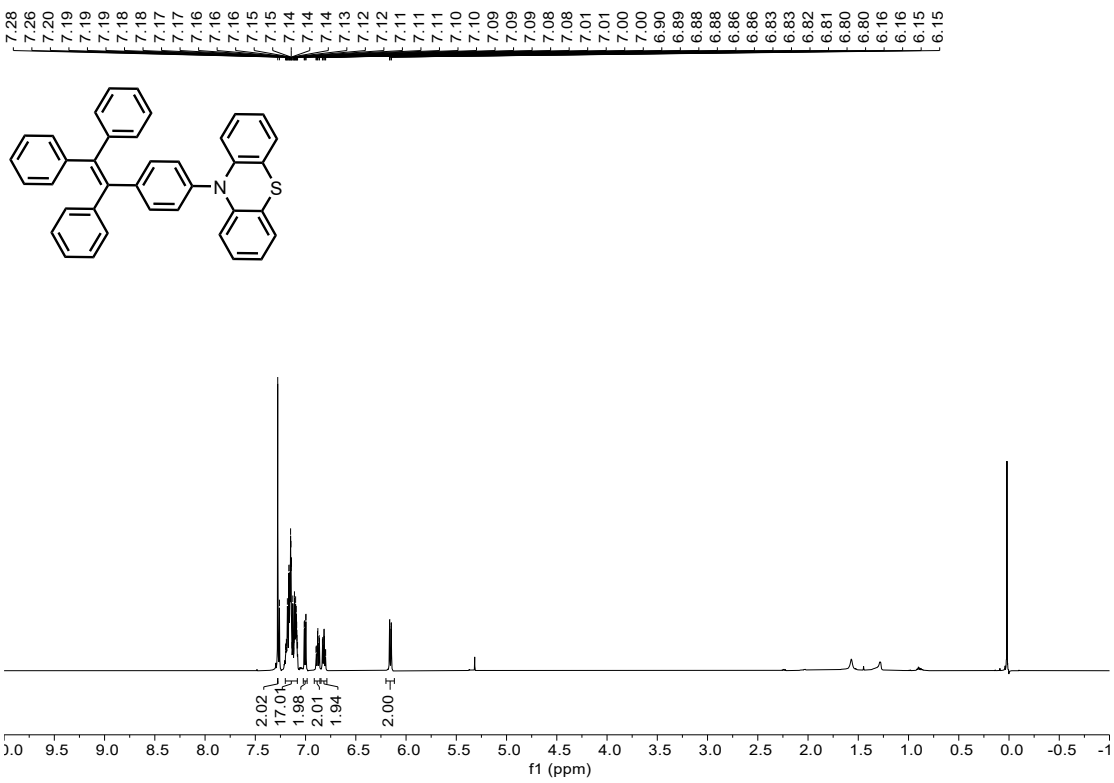
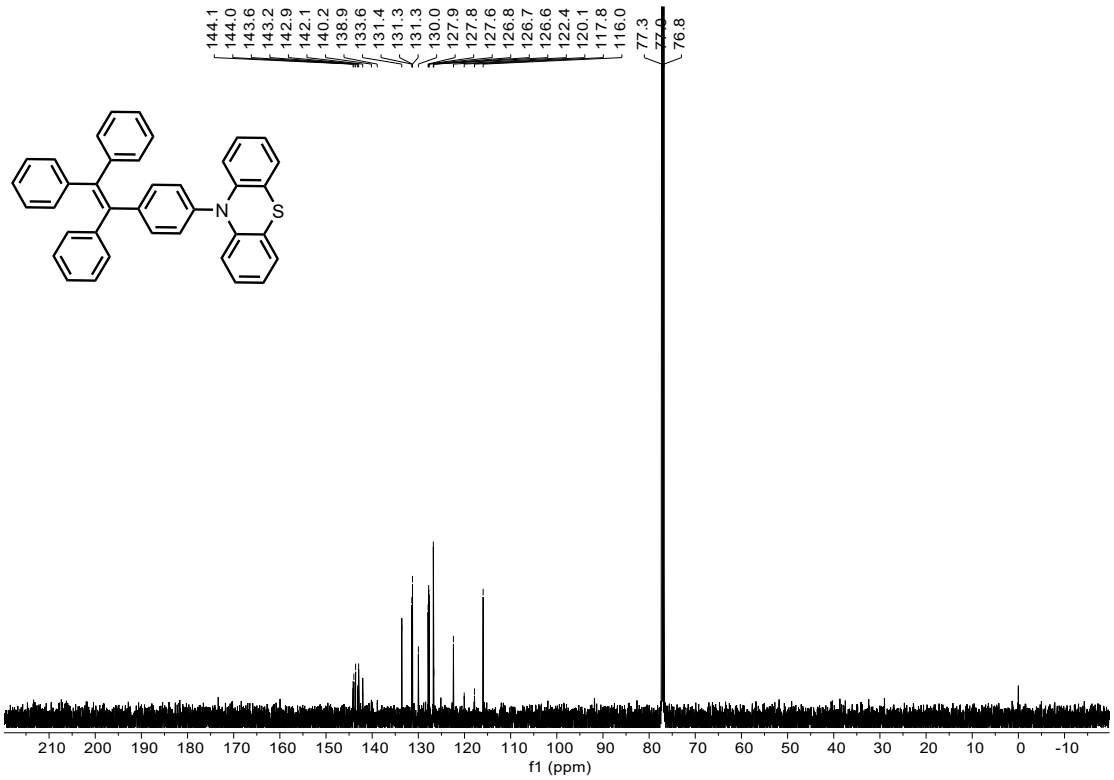
Part II NMR spectra



^{1}H NMR of TPE-PTZ



^{13}C NMR of **TPE-PTZ**

Reference:

[1] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, Gaussian 16, Revision C.01, Gaussian, Inc., Wallingford CT 2016.