Electronic Supporting Information (ESI) for

Pyrazinium-based Fluorescent Chemosensor for Selective Detection of 2,4,6-trinitrophenol in Aqueous Medium

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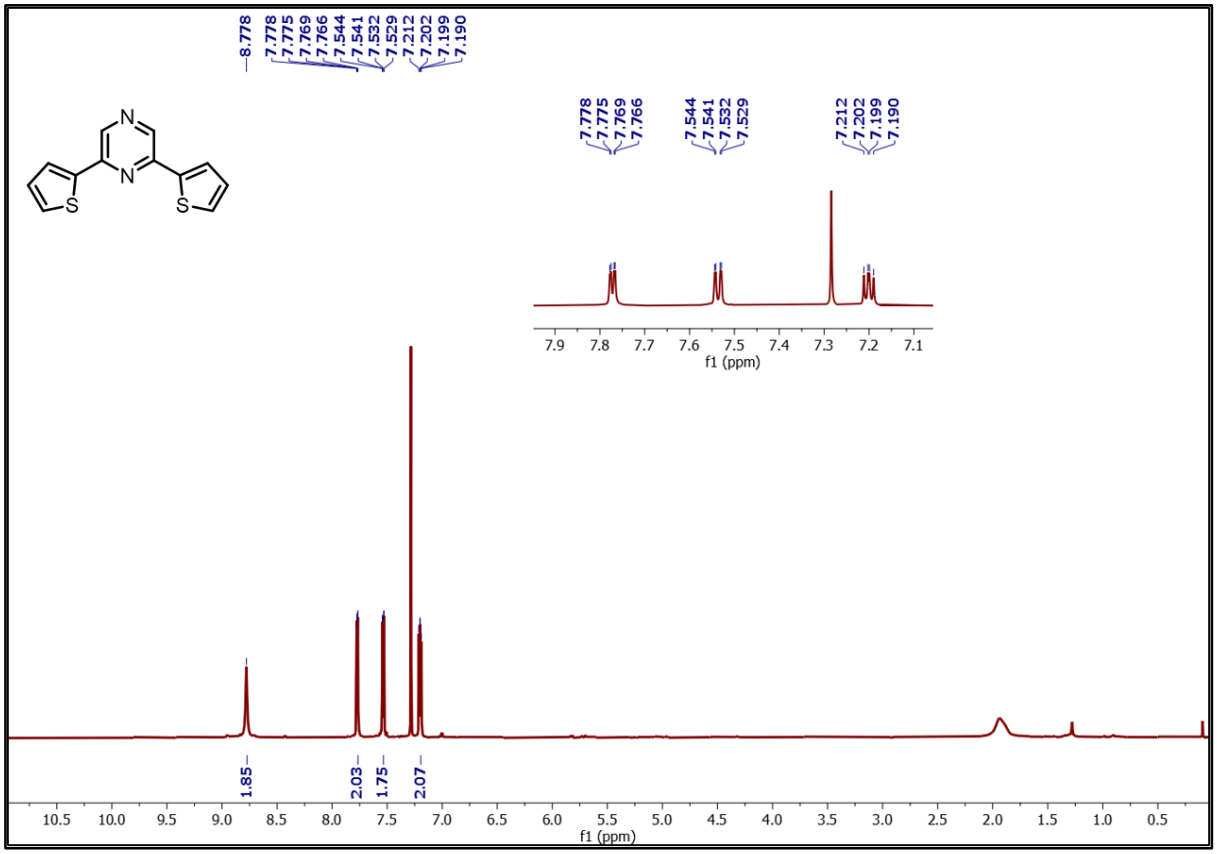

Fig. S1 ^{1}H NMR of **TPyz**

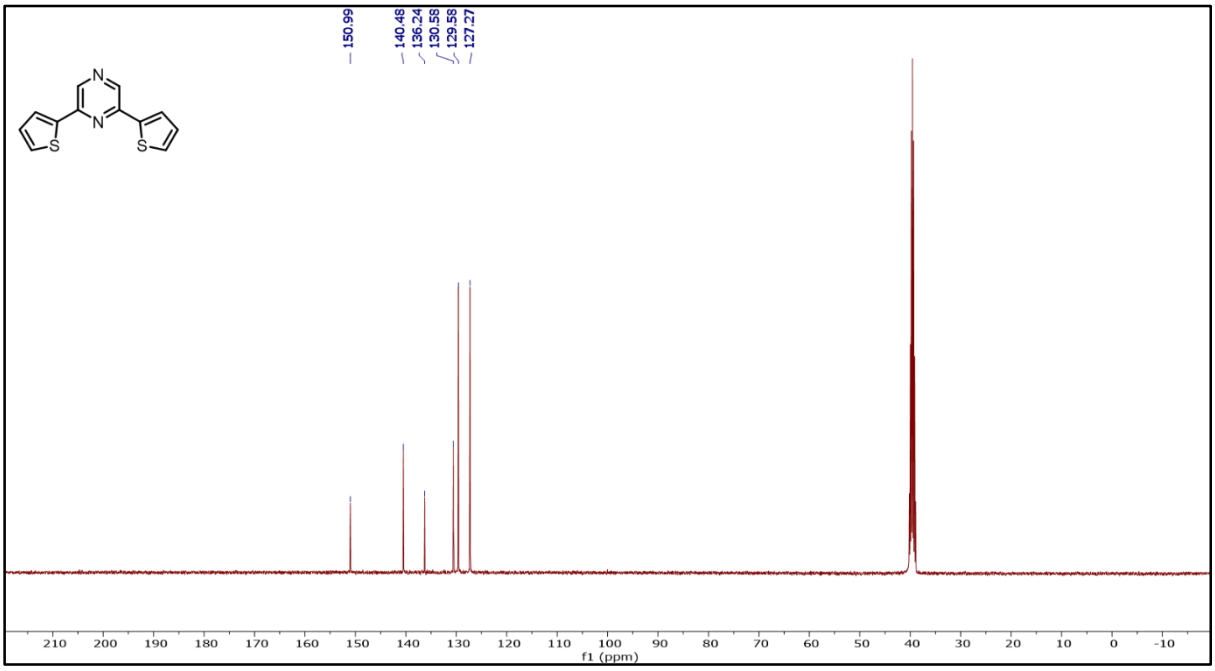

Fig. S2 ^{13}C NMR of **Tpyz**

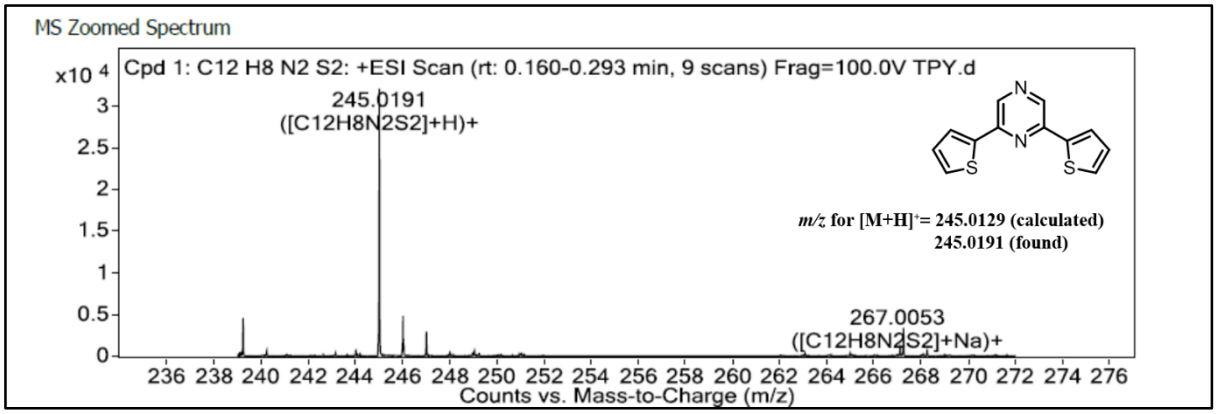

Fig. S3 HRMS of **TPyz**

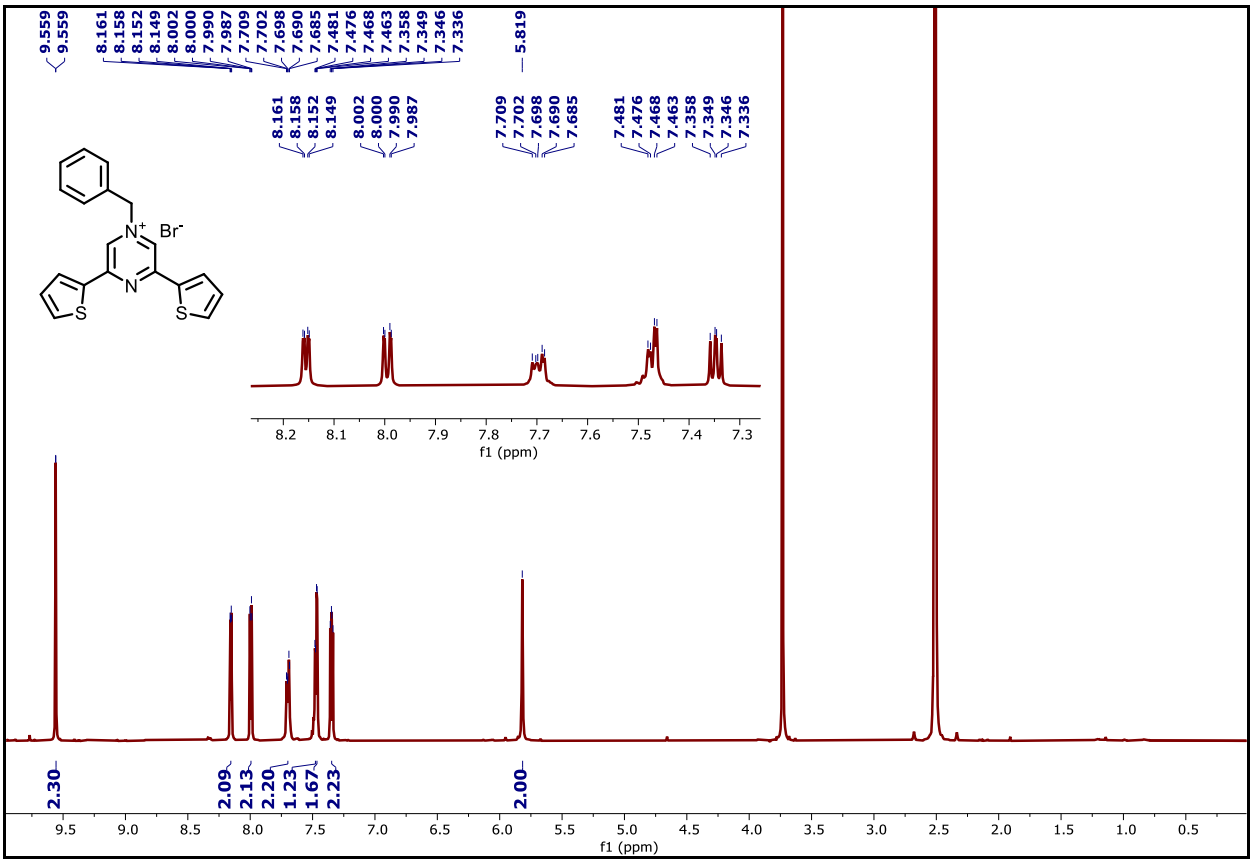

Fig. S4 ^{1}H NMR of **BTPyz**

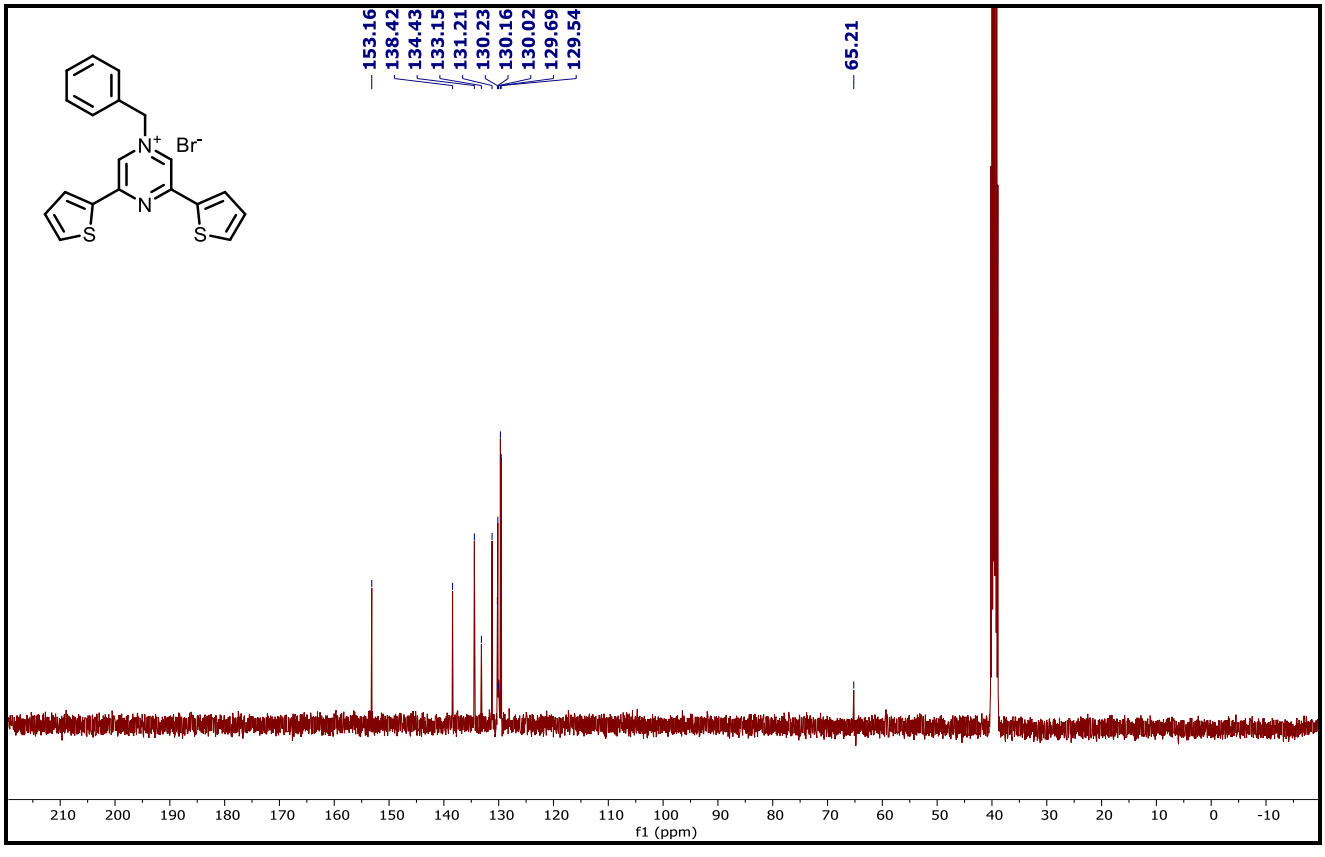

Fig. S5 ^{13}C NMR of **BTPyz**

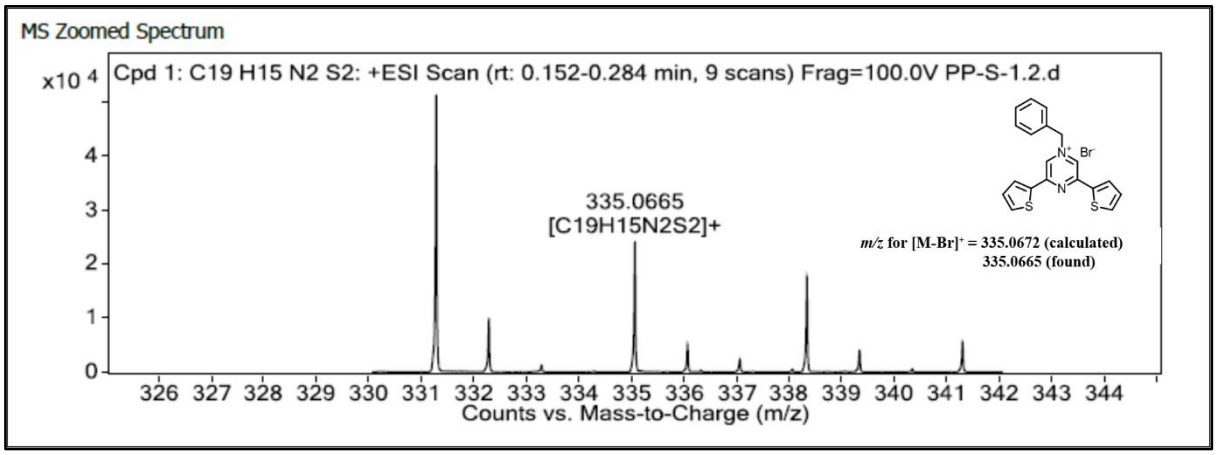

Fig. S6 HRMS of **BTPyz**

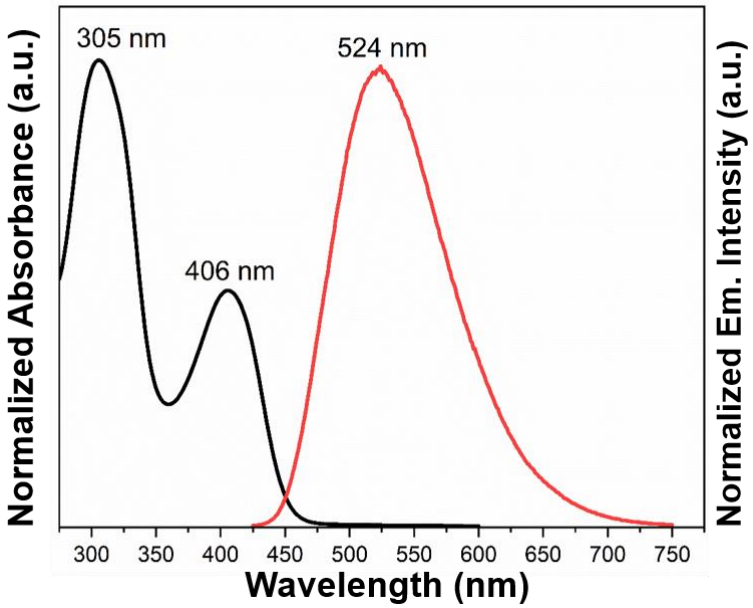

Fig. S7 UV-vis and fluorescence spectra of **BTPyz**

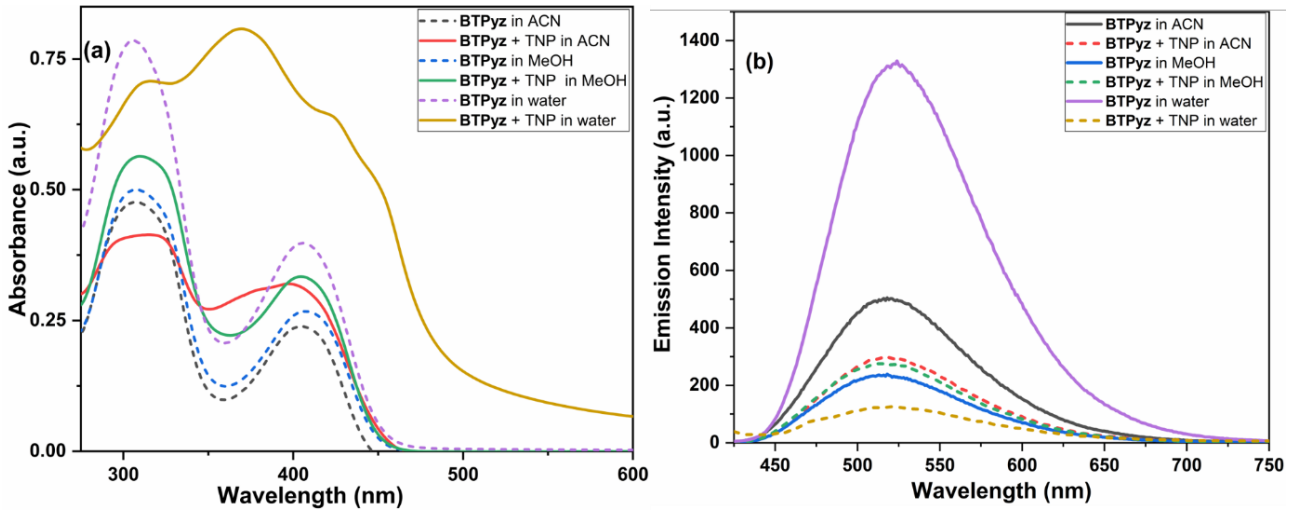

Fig. S8 (a) Absorbance (b) Fluorescence response of **BTPyz** towards TNP in different solvents

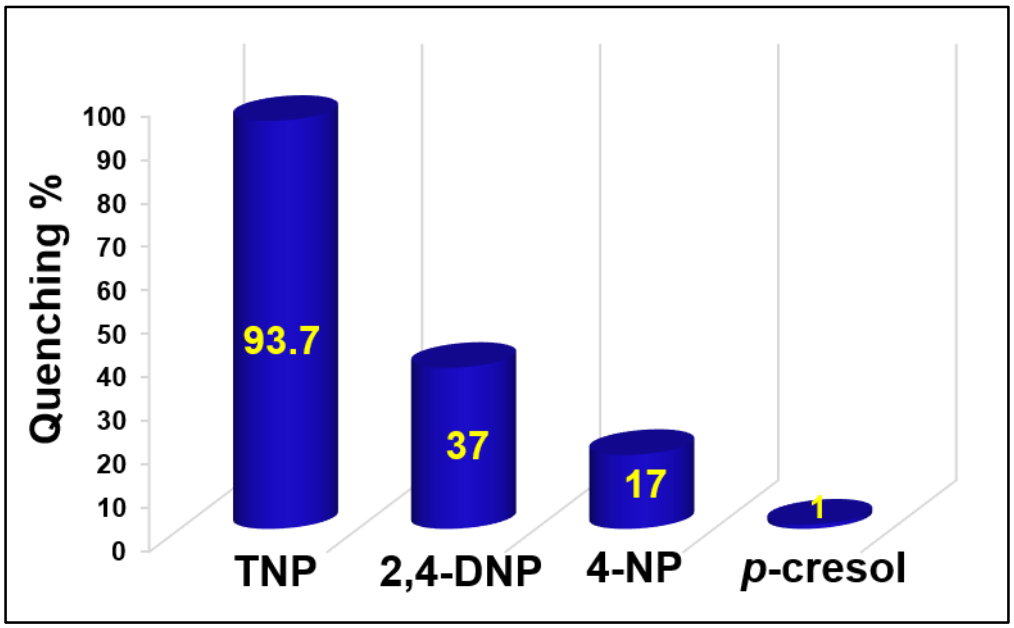

Fig. S9 Fluorescence quenching percentage of *p*-cresol, 4-NP, 2,4-DNP and TNP

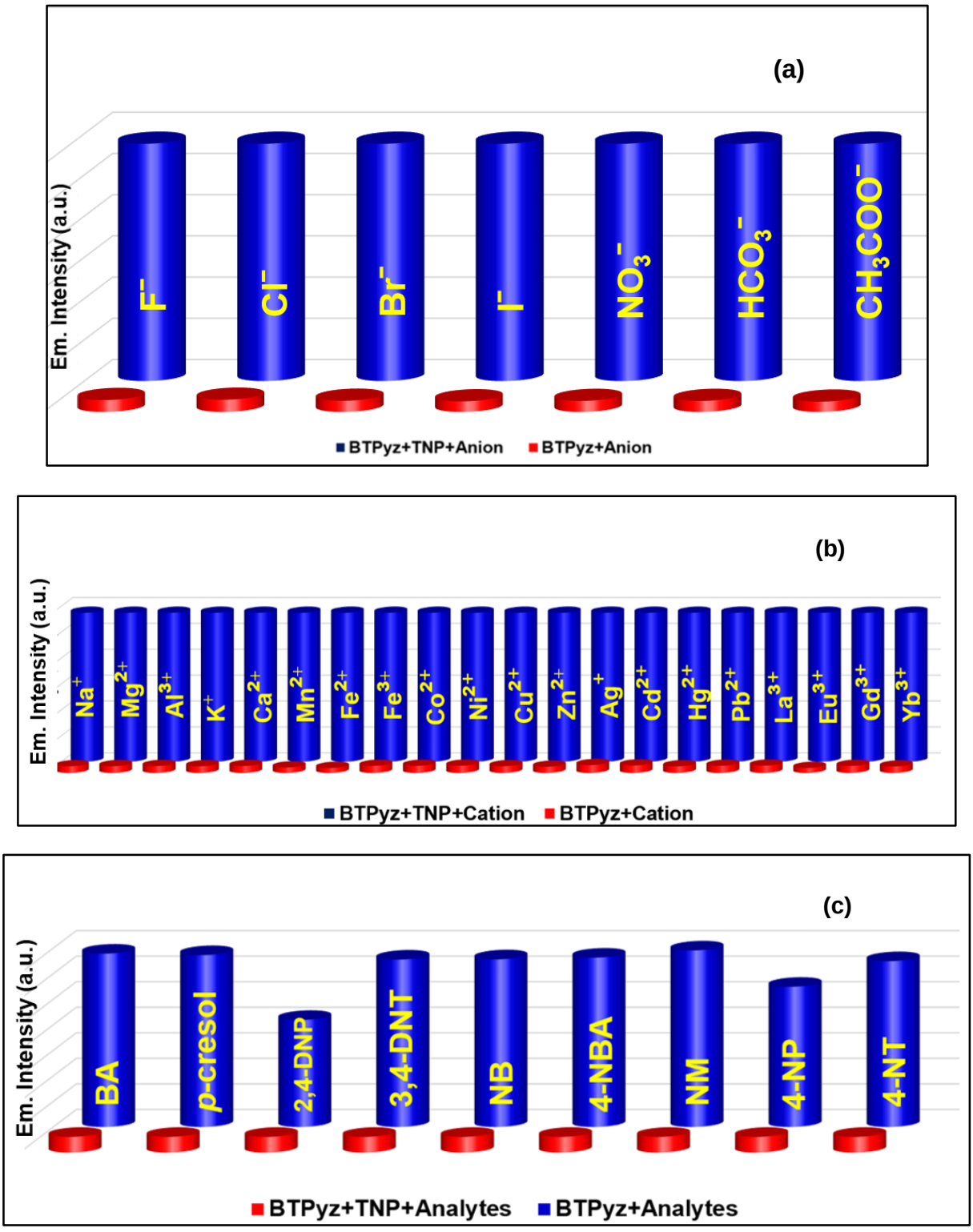

Fig. S10 Selectivity of **BTPyz** towards TNP in the presence of (a) anions, (b) cations, and (c) organic analytes

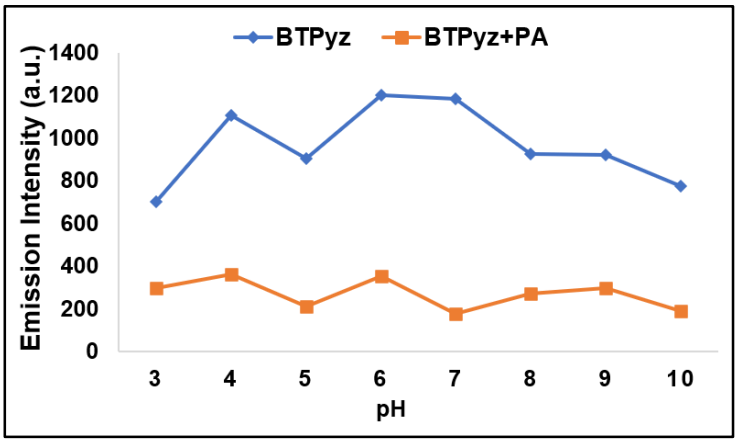

Fig. S11 Effect of pH on fluorescence intensity

Methods

Photophysical studies

For photophysical studies, 10 mM stock solutions of **BTPyz** and different analytes (cations, anions and organic analytes) were prepared in Milli-Q water. The stock solutions of 4-nitrotoluene (NT), 3,4-dinitrotoluene (3,4-DNT), and 4-nitrobenzoic acid (NBA) were prepared in UV grade THF.

Quantum yield calculation[1]

The fluorescence quantum yield was executed using quinine sulfate as a reference in 0.1 M H_2SO_4 (Φ_R = 0.54) and calculated using the following equation

$$\Phi_S = \Phi_R \frac{I_S}{I_R} \times \frac{A_R}{A_S} \times \frac{\eta_S^2}{\eta_R^2}$$

Where I = integrated area under the fluorescence curve, A = absorbance at the excitation wavelength, η = refractive index of the medium and Φ = fluorescence quantum yield. Subscripts S and R refer to the sample and the reference standard, respectively.

Fluorescence quenching percentage calculation[2]

The fluorescence quenching percentage was calculated using the equation

$$Fluorescence\ quenching\ \% = \left(1 - \frac{I}{I_0}\right) \times 100\%$$

Where I_0 = initial fluorescence intensity in the absence of analyte, I = fluorescence intensity in the presence of analyte.

Overlap Integral Calculations[3]

Analytes Overlap integral values were calculated using the equation

$$J(\lambda) = F_D(\lambda)\varepsilon_A(\lambda)\lambda^4 d\lambda$$

Where $F_D(\lambda)$ represents the corrected fluorescence intensity of donor in the range of λ to $\lambda + \Delta\lambda$ with the total intensity normalized to unity. ε_A is the molar absorptivity of the acceptor at λ in M^{-1} cm^{-1}.

The Förster distance R_0 was calculated for **BTPyz**-TNP interaction using the equation

$$R_0 = 0.211\ [(J)Q\ (\eta^{-4})(\kappa^2)]^{1/6}$$

Where J is the degree of spectral overlap between the donor fluorescence spectrum and the acceptor absorption spectrum. Q = 0.30; fluorescence quantum yield of the donor (without acceptor). η is the refractive index of the medium, κ^2 (dipole orientation factor) = 0.667.

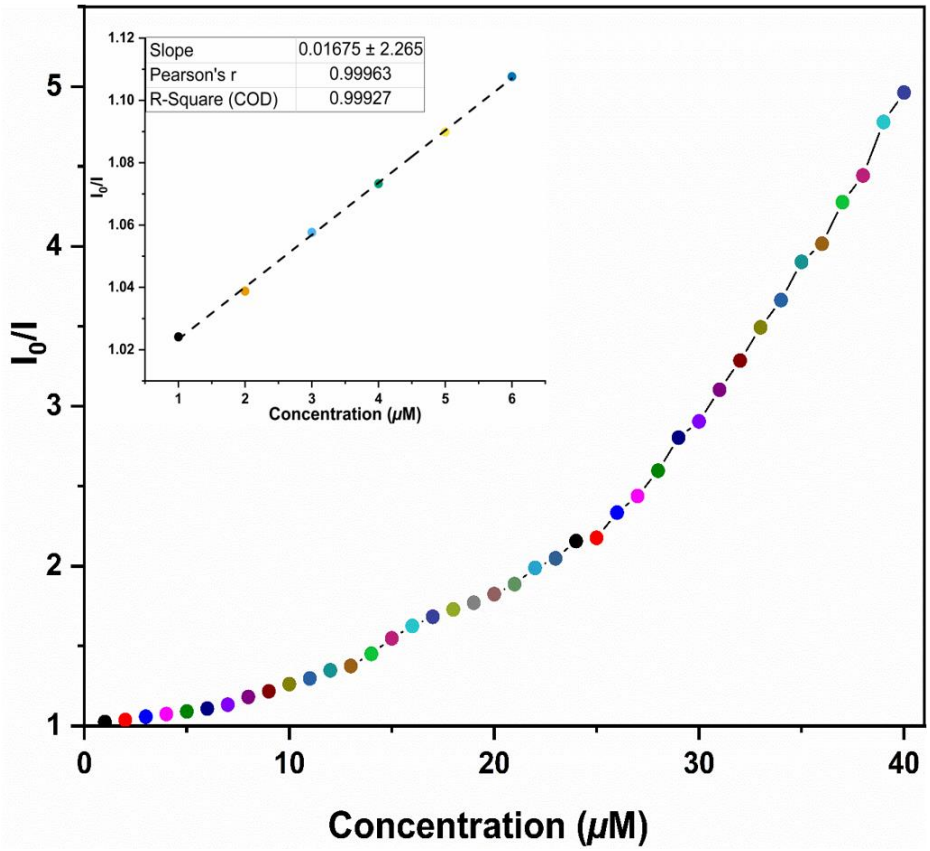

Fig. S12 Stern−Volmer plot of **BTPyz** using TNP as a quencher

Table S1: A comparison of literature reported Chemosensors for TNP detection

S. No.	Publication	Material used	Detection Limit	Stern-Volmer constant	Medium used
1	Present Study	Pyrazinium-based	11.6 nM	3.8×10^4 M^{-1}	Aqueous medium
2	H. M. Junaid, M. T. Waseem, Z. A. Khan, H. Gul, C. Yu, A. J. Shaikh and S. A. Shahzad, *J. Photochem. Photobiol. A: Chem.*, 2022, **428**, 113865	Fluorene-based	0.5 nM	–	Aqueous medium
3	H. Muniyasamy, C. Chinnadurai, M. Nelson, A. Veeramanoharan, M. Sepperumal and S. Ayyanar, *Ind. Eng. Chem. Res.*, 2021, **60**, 7987–7997	Triazine derivative	209 nM	1.02 mM,	Aqueous medium
4	C. Gogoi, H. Reinsch and S. Biswas, *CrystEngComm*, 2019, **21**, 6252–6260.	Organic framework	13.08 ppb	4.56×10^5 M^{-1}	Aqueous medium
5	N. Tripathi, P. Singh and S. Kumar, *New J. Chem.*, 2017, **41**, 8739–8747	Pyridinium-based	10^{-13} M	6.73×10^8 M^{-1}	Aqueous media
6	A. S. Tanwar and P. K. Iyer, *ACS Omega*, 2017, **2**, 4424–4430	Pyridinium-based	295 nM	–	HEPES Buffer (pH-7)
7	S. Kumari, S. Joshi, T. C. Cordova-Sintjago, D. D. Pant and R. Sakhuja, *Sens. Actuators B Chem.*, 2016, **229**, 599–608	Imidazolium-based	107 nM and 87 nM	5×10^4 M^{-1} and 2.2×10^4 M^{-1}	Aqueous media
8	A. Kumar, A. Pandith and H. S. Kim, *Sens. Actuators B Chem.*, 2016, **231**, 293–301	Imidazolium-based	10 nM	1.01×10^6 M^{-1}	Aqueous medium

9	A. H. Malik, S. Hussain, A. Kalita and P. K. Iyer, *ACS Appl. Mater. Interfaces*, 2015, **7**, 26968–26976.	Imidazolium-based	7.07 ppt	1.12×10^{8} M^{-1}	Aqueous media
10	S. Hussain, A. H. Malik, M. A. Afroz and P. K. Iyer, *Chem. Commun.*, 2015, **51**, 7207–7210	Imidazolium-based	128 ppt	0.1×10^{8} M^{-1}	Aqueous media
11	S. Sandhu, R. Kumar, P. Singh, A. Mahajan, M. Kaur and S. Kumar, *ACS Appl. Mater. Interfaces*, 2015, **7**, 10491–10500	Benzimidazolium-based	5×10^{-13} M	4.8×10^{5} M^{-1}	H_2O: DMSO
12	S. Pramanik, V. Bhalla and M. Kumar, *Anal. Chim. Acta*, 2013, **793**, 99–106	Hexaphenylbenzene derivative	6.87 ppb	1.92×10^{5} M^{-1}	Aqueous medium

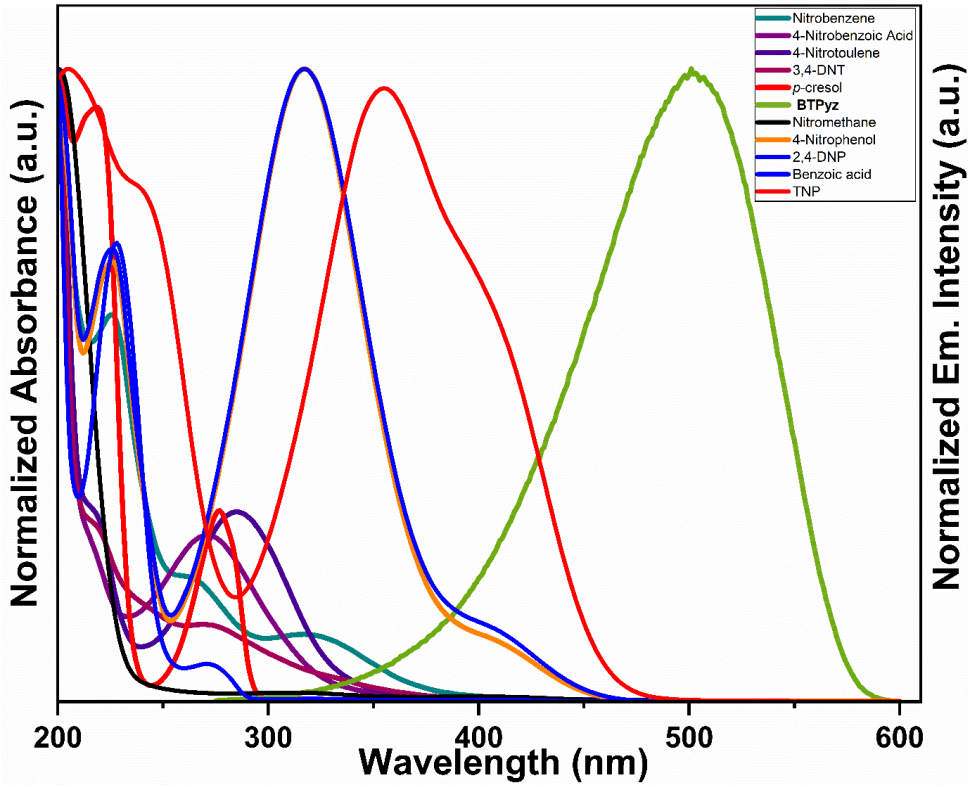

Fig. S13 Spectral overlap between the normalized emission spectrum of **BTPyz** and normalized absorption spectra of different analytes

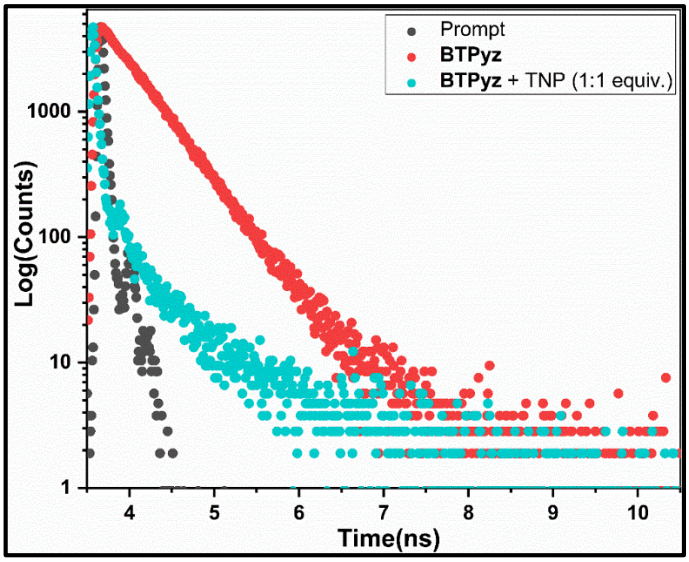

Fig. S14 Fluorescence lifetime decay curves of **BTPy**z and **BTPyz-**TNP

Table S4 Calculations of inner filter effect corrections for quenching of **BTPyz** by TNP

TNP [μM]	A_{em}	A_{ex}	I_{obs}	I_{corr}	I_{corr}/I_{obs}	$I_{corr}/I_{obs,0}$
0	0.000152	0.01867	1080000	1104967	1.021906	0
5	0.000426	0.02137	1000000	1028167	1.024959	0.93049
10	0.000211	0.02499	884830	910878.6	1.029439	0.82434
15	0.00157	0.02871	742340	768675.2	1.035476	0.69565
20	0.00252	0.03054	608020	631608.4	1.038795	0.57160
25	0.00395	0.03063	499450	519735.1	1.040615	0.47036
30	0.00573	0.03168	384120	401025.4	1.044011	0.36292
35	0.00688	0.03224	293830	307366.2	1.046068	0.27816
40	0.00755	0.03474	225310	236551.4	1.049893	0.21407
45	0.00786	0.03685	169340	178284.9	1.052822	0.16134
50	0.00761	0.0395	128660	135830.9	1.055735	0.12292

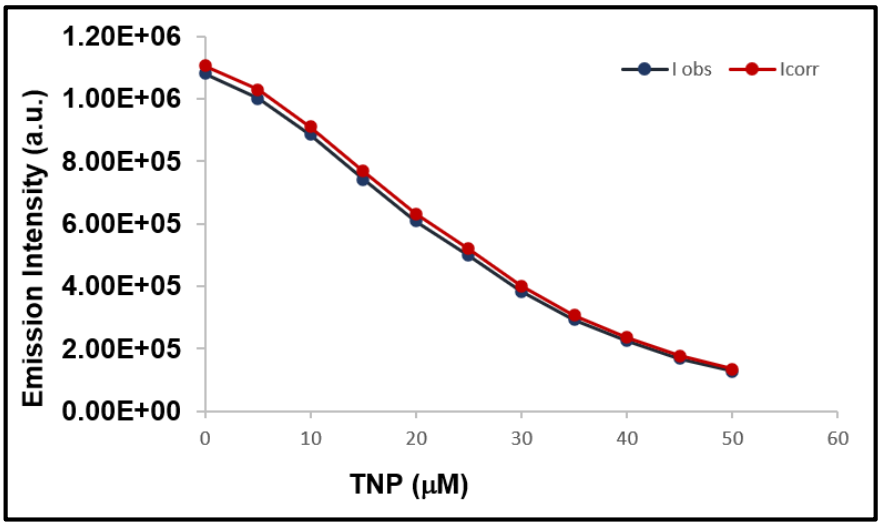

Fig. S15 Emission intensity of **BTPyz** observed and after inner filter effect corrections

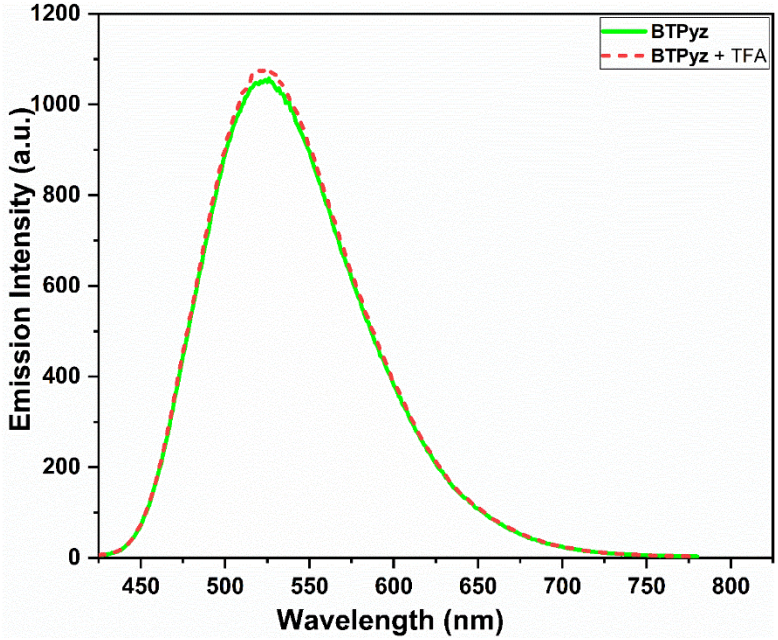

Fig. S16 Fluorescence spectra of **BTPyz** and **BTPyz** with TFA

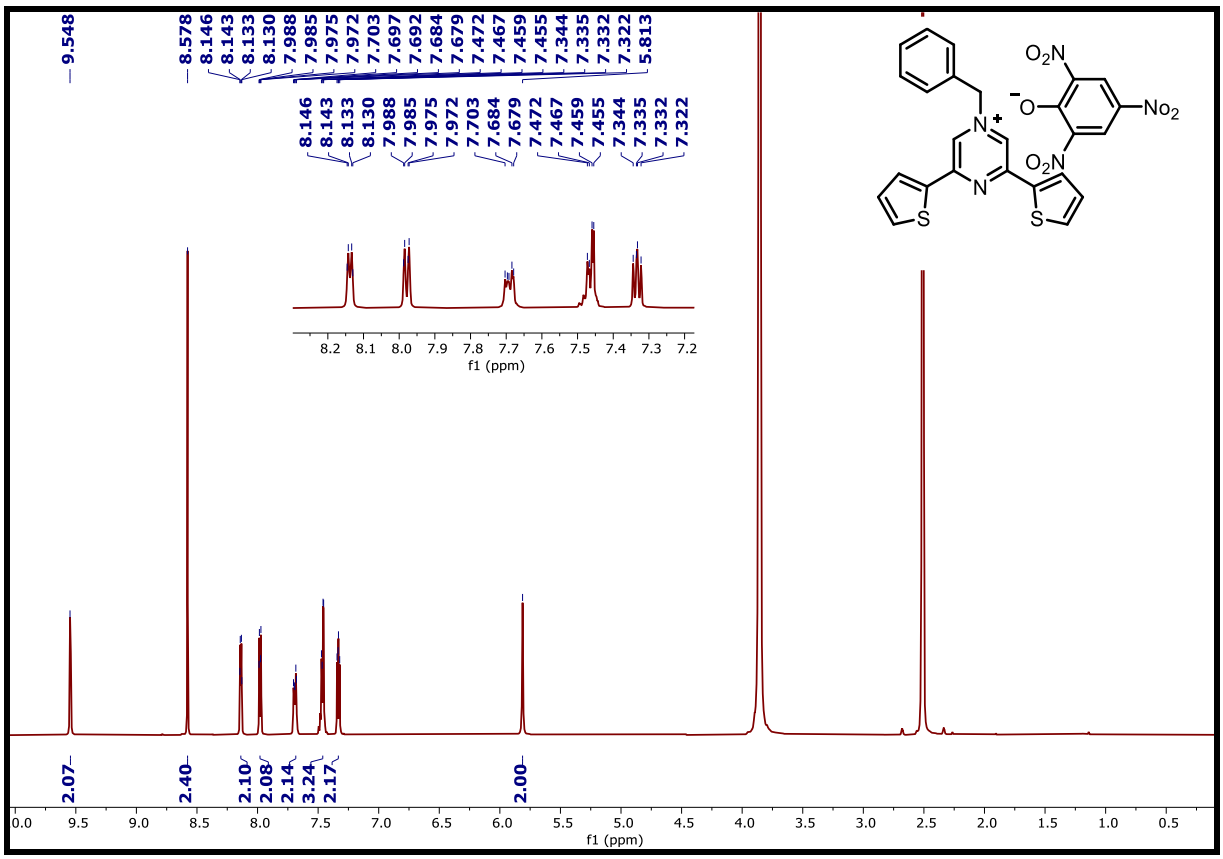

Fig. S17 ^{1}H NMR of **BTPyz**-TNP complex

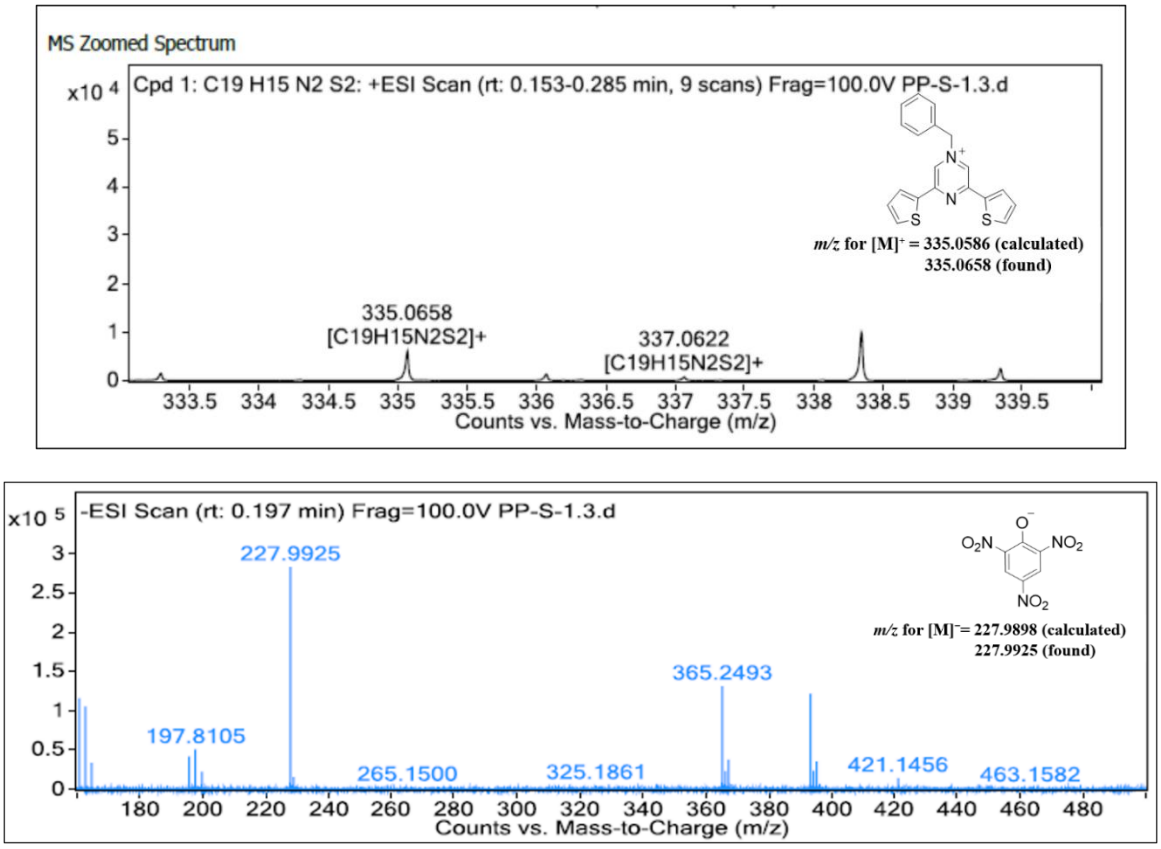

Fig. S18 HRMS of **BTPyz**-TNP complex

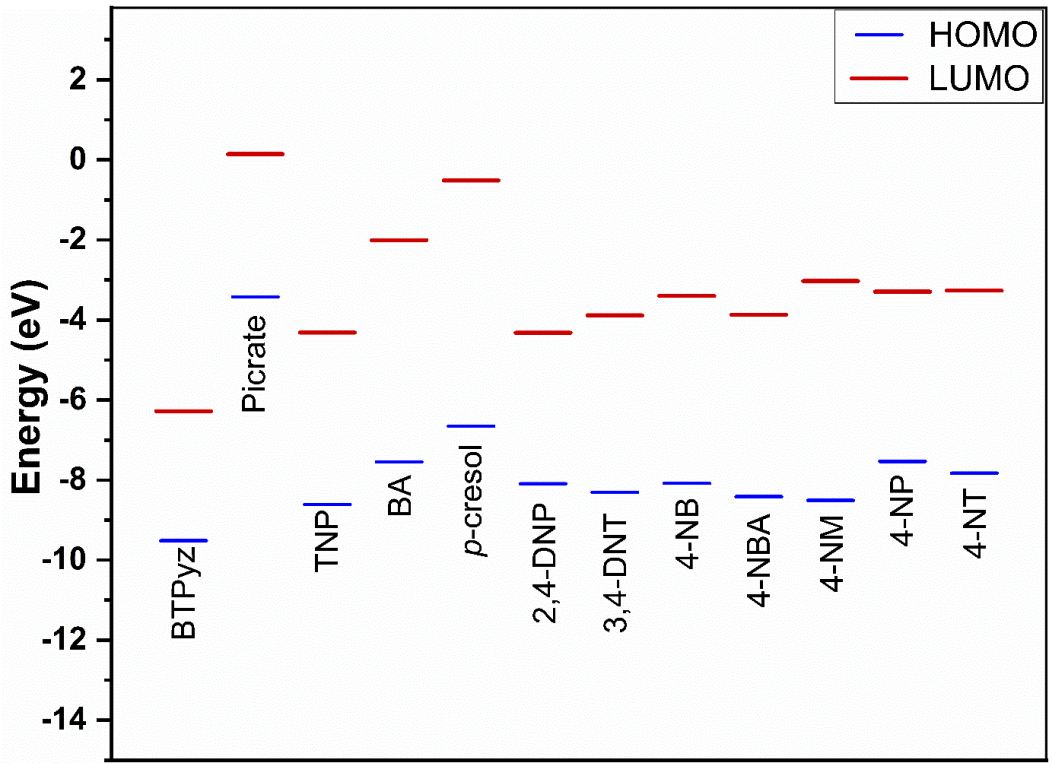

Fig. S19 HOMO-LUMO energy levels of **BTPyz** and organic analytes

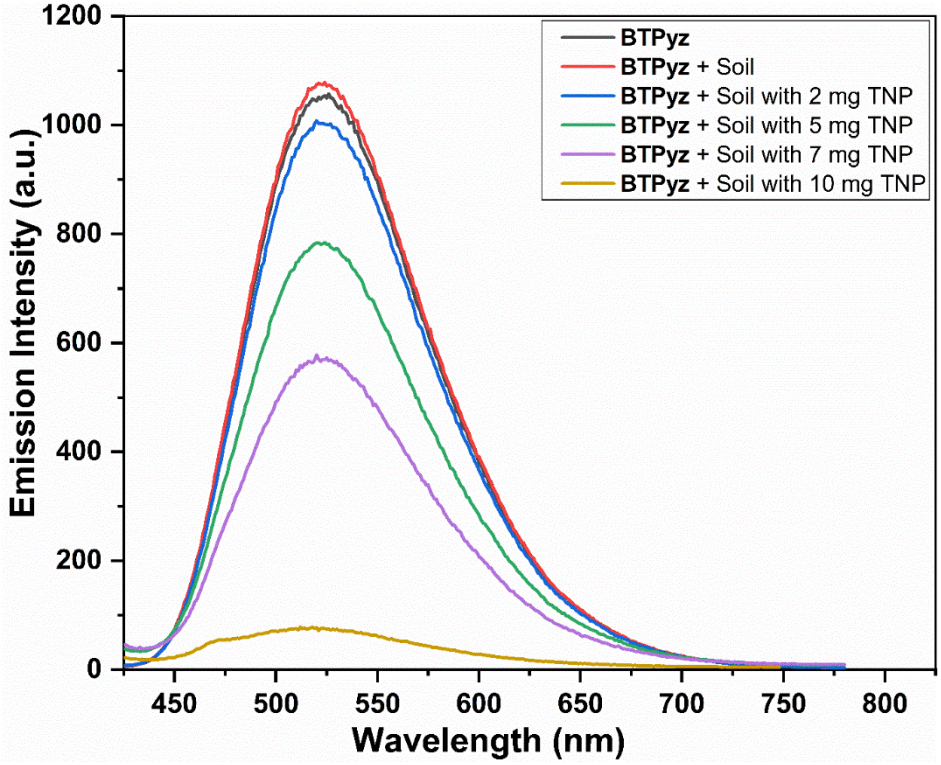

Fig. S20. Fluorescence quenching of TNP in soil samples

Table S3 Single-crystal XRD data and structure refinement of **BTPyz** and **BTPyz**-TNP complex

Compound	**BTPyz**	**BTPyz**-TNP complex
Empirical formula	$C_{19.5}H_{17}BrN_2O_{0.5}S_2$	$C_{25}H_{17}N_5O_7S_2$
Formula weight	431.38	563.55
Temperature/K	293(2)	93(2)
Crystal system	Monoclinic	monoclinic
Space group	$P2_1/n$	C2/c
a/Å	13.6130(2)	18.0779(3)
b/Å	18.6032(2)	20.0433(3)
c/Å	15.0166(2)	14.3377(3)
α/°	90	90
β/°	90.2640(10)	111.423(2)

γ/°	90	90
Volume/Å^3	3802.84(9)	4836.20(16)
Z	8	8
ρ_{calc}g/cm^3	1.507	1.548
μ/mm^{-1}	5.049	2.513
F(000)	1752.0	2320.0
Crystal size/mm^3	0.1 × 0.1 × 0.08	0.15 × 0.1 × 0.04
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.566 to 159.874	8.094 to 159.676
Index ranges	-14 ≤ h ≤ 17, -23 ≤ k ≤ 22, -16 ≤ l ≤ 19	-21 ≤ h ≤ 23, -25 ≤ k ≤ 24, -17 ≤ l ≤ 18
Reflections collected	15315	14206
Independent reflections	7340 [R_{int} = 0.0249, R_{sigma} = 0.0296]	5121 [R_{int} = 0.0327, R_{sigma} = 0.0347]
Data/restraints/parameters	7340/0/453	5121/0/352
Goodness-of-fit on F^2	1.104	1.093
Final R indexes [I>=2σ (I)]	R_1 = 0.0487, wR_2 = 0.1321	R_1 = 0.0473, wR_2 = 0.1418
Final R indexes [all data]	R_1 = 0.0504, wR_2 = 0.1333	R_1 = 0.0504, wR_2 = 0.1451
Largest diff. peak/hole / e Å^{-3}	1.48/-0.93	0.44/-0.34
CCDC No.	2110747	2168277

Table S4 Bond Lengths of **BTPyz**

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
S1	C5	1.726(3)	C14	C15	1.390(5)
S1	C8	1.707(4)	C14	C13	1.504(5)
S101	C105	1.727(4)	C14	C19	1.388(5)

S101	C108	1.706(4)	C104	C103	1.395(5)
S2	C9	1.721(3)	C104	C109	1.453(5)
S2	C12	1.705(4)	C15	C16	1.394(5)
S102	C109	1.720(3)	C114	C113	1.512(5)
S102	C112	1.701(4)	C114	C00X	1.392(5)
N1	C1	1.344(4)	C114	C115	1.389(5)
N1	C4	1.342(4)	C105	C106	1.386(5)
N2	C2	1.340(4)	C6	C7	1.425(5)
N2	C3	1.338(4)	C16	C17	1.381(6)
N2	C13	1.492(4)	C109	C110	1.391(5)
N101	C101	1.343(5)	C106	C107	1.428(5)
N101	C104	1.341(5)	C110	C111	1.421(5)
N102	C102	1.337(5)	C00X	C118	1.397(5)
N102	C113	1.501(4)	C11	C12	1.355(5)
N102	C103	1.338(4)	C19	C18	1.389(6)
C1	C5	1.453(5)	C116	C115	1.405(6)
C1	C2	1.392(4)	C116	C117	1.376(6)
C101	C102	1.404(4)	O1	C20	1.463(9)
C101	C105	1.450(5)	C17	C18	1.390(6)
C4	C3	1.394(4)	C7	C8	1.358(6)
C4	C9	1.443(5)	C111	C112	1.358(5)
C5	C6	1.390(5)	C108	C107	1.360(6)
C10	C9	1.395(5)	C117	C118	1.381(6)
C10	C11	1.417(5)			

Table S5 Bond Angles of **BTPyz**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C8	S1	C5	91.48(17)	C103	C104	C109	121.1(3)
C108	S101	C105	91.34(18)	N102	C102	C101	118.4(3)
C12	S2	C9	91.70(17)	C14	C15	C16	120.2(4)
C112	S102	C109	91.72(18)	C00X	C114	C113	120.1(3)
C4	N1	C1	117.9(3)	C115	C114	C113	120.1(3)
C2	N2	C13	119.9(3)	C115	C114	C00X	119.8(3)
C3	N2	C2	121.6(3)	C101	C105	S101	119.4(3)
C3	N2	C13	118.5(3)	C106	C105	S101	111.8(3)
C104	N101	C101	118.7(3)	C106	C105	C101	128.8(3)
C102	N102	C113	119.4(3)	N102	C113	C114	110.9(3)
C102	N102	C103	121.8(3)	C5	C6	C7	111.1(3)
C103	N102	C113	118.8(3)	C17	C16	C15	119.5(4)
N1	C1	C5	117.6(3)	N2	C13	C14	110.4(3)
N1	C1	C2	122.2(3)	N102	C103	C104	118.7(3)
C2	C1	C5	120.2(3)	C104	C109	S102	119.9(3)
N101	C101	C102	121.1(3)	C110	C109	S102	111.4(3)
N101	C101	C105	118.2(3)	C110	C109	C104	128.5(3)
C102	C101	C105	120.7(3)	C105	C106	C107	111.4(3)
N1	C4	C3	121.4(3)	C109	C110	C111	111.4(3)
N1	C4	C9	118.7(3)	C114	C00X	C118	120.4(4)
C3	C4	C9	119.9(3)	C12	C11	C10	113.1(3)
C1	C5	S1	119.8(3)	C14	C19	C18	120.2(4)
C6	C5	S1	111.8(2)	C117	C116	C115	119.5(4)

C6	C5	C1	128.4(3)	C114	C115	C116	119.8(4)
N2	C2	C1	118.0(3)	C16	C17	C18	120.8(4)
C9	C10	C11	111.4(3)	C8	C7	C6	113.2(3)
C15	C14	C13	119.9(3)	C112	C111	C110	112.8(4)
C19	C14	C15	119.9(3)	C11	C12	S2	112.5(3)
C19	C14	C13	120.2(3)	C7	C8	S1	112.5(3)
N2	C3	C4	118.9(3)	C107	C108	S101	112.9(3)
C4	C9	S2	120.9(2)	C116	C117	C118	121.5(4)
C10	C9	S2	111.2(3)	C117	C118	C00X	119.0(4)
C10	C9	C4	127.8(3)	C108	C107	C106	112.6(4)
N101	C104	C103	121.3(3)	C111	C112	S102	112.7(3)
N101	C104	C109	117.6(3)	C19	C18	C17	119.4(4)

Table S6 Bond Lengths of **BTPyz**-TNP complex

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
S2	C9	1.7221(18)	C1	C2	1.405(2)
S2	C12	1.707(2)	C1	C5	1.449(3)
S1	C5	1.7240(19)	C24	C23	1.398(3)
S1	C8	1.696(2)	C24	C25	1.363(2)
O1	C20	1.241(2)	C6	C5	1.409(3)
O5	N4	1.238(2)	C6	C7	1.416(3)
O4	N4	1.229(2)	C23	C22	1.385(2)
N2	C2	1.339(2)	C10	C9	1.381(3)
N2	C3	1.343(2)	C10	C11	1.415(2)
N2	C13	1.502(2)	C22	C21	1.379(2)

N1	C4	1.343(3)	C14	C19	1.388(3)
N1	C1	1.337(2)	C14	C13	1.504(2)
N4	C23	1.437(2)	C14	C15	1.397(2)
O6	N5	1.220(2)	C20	C25	1.453(2)
N3	O3	1.206(2)	C20	C21	1.448(3)
N3	O2	1.220(2)	C19	C18	1.388(3)
N3	C21	1.463(2)	C15	C16	1.388(3)
N5	O7	1.204(2)	C18	C17	1.385(3)
N5	C25	1.467(3)	C11	C12	1.359(3)
C4	C3	1.397(2)	C7	C8	1.364(3)
C4	C9	1.453(2)	C16	C17	1.392(3)

Table S7 Bond Angles of **BTPyz**-TNP complex

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
C12	S2	C9	91.42(9)	C21	C22	C23	120.01(17)
C8	S1	C5	91.27(10)	C4	C9	S2	120.14(14)
C2	N2	C3	121.56(15)	C10	C9	S2	111.62(13)
C2	N2	C13	119.88(15)	C10	C9	C4	128.24(17)
C3	N2	C13	118.56(16)	C19	C14	C13	120.43(16)
C1	N1	C4	118.97(15)	C19	C14	C15	119.58(17)
O5	N4	C23	118.13(16)	C15	C14	C13	119.96(17)
O4	N4	O5	122.57(16)	O1	C20	C25	121.06(18)
O4	N4	C23	119.28(16)	O1	C20	C21	127.49(18)
O3	N3	O2	122.32(18)	C21	C20	C25	111.43(15)

O3	N3	C21	118.95(17)	C1	C5	S1	118.97(14)
O2	N3	C21	118.73(18)	C6	C5	S1	111.91(14)
O6	N5	C25	117.60(17)	C6	C5	C1	129.10(17)
O7	N5	O6	123.81(19)	C24	C25	N5	117.89(17)
O7	N5	C25	118.58(18)	C24	C25	C20	126.22(18)
N1	C4	C3	121.16(16)	C20	C25	N5	115.86(16)
N1	C4	C9	118.20(16)	C22	C21	N3	116.34(17)
C3	C4	C9	120.64(17)	C22	C21	C20	123.34(16)
N1	C1	C2	121.17(17)	C20	C21	N3	120.32(16)
N1	C1	C5	117.97(16)	C18	C19	C14	120.51(17)
C2	C1	C5	120.85(16)	N2	C13	C14	110.28(14)
C25	C24	C23	117.35(17)	C16	C15	C14	119.84(18)
C5	C6	C7	110.43(17)	C17	C18	C19	119.90(19)
C24	C23	N4	118.75(16)	C12	C11	C10	112.92(18)
C22	C23	N4	119.72(16)	C8	C7	C6	113.16(18)
C22	C23	C24	121.36(16)	C15	C16	C17	120.16(18)
C9	C10	C11	111.70(17)	C11	C12	S2	112.34(14)
N2	C2	C1	118.47(16)	C18	C17	C16	120.00(18)
N2	C3	C4	118.64(17)	C7	C8	S1	113.23(17)

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