Dual-State Emission Triphenylamine-Based Polymer with Donor-Acceptor-Donor Structural Arrangement: Facile Synthesis and Efficient Selective Detection of TNT Based on Fluorescence "Turn-off"

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Experimental Procedure for UV-Visible Absorption Spectroscopy

1 mg of PTPAS solid was added into separate glass vials, and then 20 mL of different polar solvents (HEX, TCM, EA, DCM, THF, DMF, EtOH, and MeOH) were added. After complete dissolution, absorption spectra were measured by using a UV-Visible spectrophotometer .

Experimental Procedure for Fluorescence Testing

1 mg of PTPAS solid was added into separate glass vials, and then 20 mL of different polar solvents (HEX, TCM, EA, DCM, THF, DMF, EtOH, and MeOH) were added. After complete dissolution, fluorescence spectra testing were performed under excitation at the maximum absorption wavelength.

Experimental Procedure for Fluorescence Quantum Yield (φ_F)

A PTPAS solution with an absorbance of less than 0.05 at an absorption wavelength of 360 nm was prepared, and quinine sulfate solution (φ_F = 0.54, solvent: 1.0 N H_2SO_4 aqueous solution) was utilized as a reference sample [1, 2]. The fluorescence spectrum of PTPAS was measured by using a fluorescence spectrometer. The fluorescence quantum yield (φ_F) was calculated by using Equation S1 based on the obtained test data.

$$\varphi_{F,x} = \varphi_{F,st} \times \frac{F_x}{F_{st}} \times \frac{f_{st}}{f_x} \times \frac{n_x^2}{n_{st}^2} \quad (1)$$

st and x represent the standard sample and the test sample, respectively. φ_F denotes the fluorescence quantum yield. F corresponds to the integral area of the fluorescence peak. *f* signifies the absorption factor, and n is the refractive index of the solvent.

Experimental Procedure for Fluorescence Testing of PTPAS in H_2O/THF Solvent

10 mL solutions with varying ratios of H_2O/THF were individually prepared, with ratios of 10:0, 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, 1:9, and 0:10. Subsequently, 100 μL of a 2 mM PTPAS solution was sequentially added to each solution. After thorough shaking and mixing, fluorescence spectra under an excitation wavelength of 365 nm were tested.

Experimental Procedure for the Detection Limit of PTPAS for TNT

A 500 mL solution of PTPAS with a concentration of 0.01 g/L (THF/H_2O = 1:9) was prepared. 10 mL were measured and added to corresponding glass bottles. Subsequently, TNT solutions with concentrations of 1 g/L, including 0, 2.5, 5, 7.5, 10, 17.5, 25, 37.5, 50, 75, and 100 μL, were sequentially added. The fluorescence intensity of the different solutions was tested under an excitation wavelength of 365 nm, and the fitting results were analyzed using equations S2 and S3.

$$\frac{I_0}{I} = 1 + K_{SV}[Q] \quad (2)$$

$$C_L = \frac{3S}{K_{SV}} \quad (3)$$

I_0 and I represent the initial fluorescence intensity of PTPAS before and after adding TNT, respectively.. I denotes the fluorescence intensity after complete response to the added TNT. [Q]

corresponds to the concentration of TNT in the tested sample. K_{sv} signifies the Stern-Volmer constant. C_L is the detection limit of the sensor. S represents the 15-fold standard deviation of the blank sample.

Experimental Procedure for Fluorescence Response Time

10 mL solutions of PTPAS were individually prepared, with the concentrations of 10, 20, 40, 60, 80, and 100 μM (H_2O/THF=9:1), and 3.5 mL of each solution was measured and added to the cuvette. Subsequently, 70 μL of a 2 mM TNT solutions were also added to the corresponding cuvette. The changes in fluorescence intensity of the solutions over time were measured under an excitation wavelength of 365 nm.

Experimental Procedure for the Effect of pH on Fluorescence Performance

50 mL solutions were prepared with pH values ranging from 1 to 13, using a H_2O and THF ratio of 9:1. Subsequently, 10 mL of each solution was measured and added to 100 μL of a 2 mM PTPAS THF solution. After thorough mixing by oscillation, the fluorescence spectra of the solution were measured separately under an excitation wavelength of 365 nm. Subsequently, 100 μL of a 2 mM TNT solution was added to the corresponding solutions, thoroughly mixed by oscillation, and the fluorescence spectra of the solutions at pH=1-13 were measured under an excitation wavelength of 365 nm.

Experimental Procedure for the Selectivity of PTPAS to TNT

Solutions of metal ion nitrates (Ag^{+}, Al^{3+}, Ca^{2+}, Co^{3+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, Mg^{2+}, Mn^{2+}, Ni^{2+}, Zn^{2+}) and nitro-based compounds (CNB, NP, DNB, NT, NB, TNT, DNT, HMX, RDX) were prepared in advance at a concentration of 10 mM. A 500 mL solution of PTPAS with a concentration of 20 μM (THF/water = 1:9) was then prepared, and 10 mL of this solution were measured and added todifferent glass bottles. Subsequently, 20 μL of the pre-prepared metal ion and nitro compound solutions were sequentially added to the corresponding bottles. After equilibration, the fluorescence intensity was measured under an excitation wavelength of 365 nm.

Theoretical Calculation

All theoretical calculations were conducted using the density functional theory (DFT) within the Gaussian 16 program package. The binding energy between the polymer and TNT was calculated at the 6-31G(d,p) level of theory using the B3LYP-GD3(BJ) functional, with the solvent effect of water being considered using the SMD solvent model. The Natural Transition Orbital (NTO) analysis of the polymer was performed at the 6-311G(d,p) level of theory using the B3LYP-GD3(BJ) functional, with the solvent effect of tetrahydrofuran being considered using the SMD solvent model.

Lippert-Mataga equation

$$\Delta f = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \tag{4}$$

Δf represents the orientational polarizability of the solvent. n is the refractive index of the solvent. ε denotes the dielectric constant of the solvent.

Table S1 Elemental analysis for PTPAS

Anal. Calcd for $C_{36}H_{26}N_2O_2S$

	C(%)	H(%)	N(%)	O(%)	S(%)
Expected	78.52	4.76	5.09	5.81	5.82
Found	78.31	4.92	5.26	5.79	5.72

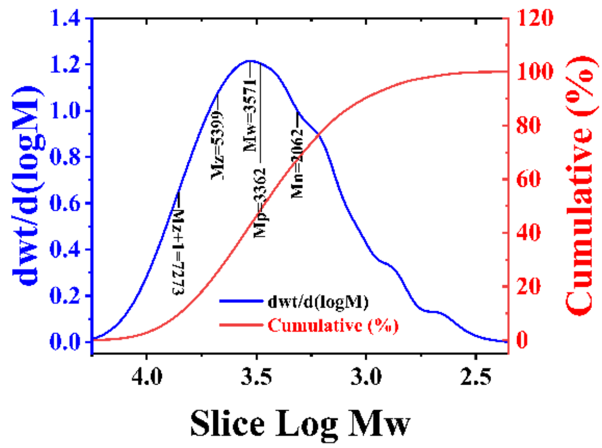


Fig. S1 The molecular weight distribution chart of PTPAS measured by GPC

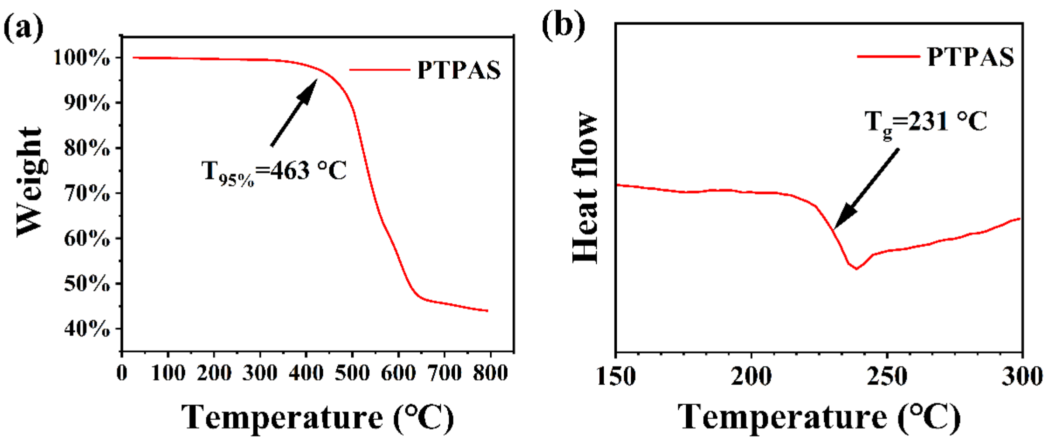


Fig. S2 **(a)** Thermogravimetric Analysis (TGA) of PTPAS under a nitrogen atmosphere; **(b)** Differential Scanning Calorimetry (DSC) of PTPAS under a nitrogen atmosphere.

Table S2. Comparative analysis of thermal properties between PTPAS and D-A-D polymers

Polymers	T_d (°C)	References
P1	310	[3]

P3	480	[4]
PVT-PI	445	[5]
P3	320	[6]
PTPAS	463	This work

T_d was the temperature at which the polymer lost 5% of its weight.

Table S3. Photophysical parameters of PTPAS in solid state

Polymer	λ_{abs}(nm)	λ_{em}(nm)	τ(ns)	φ_F
PTPAS	374	475	1.8	0.09

λ_{abs} is the maximum absorption wavelength. λ_{em} represents the maximum emission wavelength. τ signifies the fluorescence lifetime. φ_F denotes the fluorescence quantum yield.

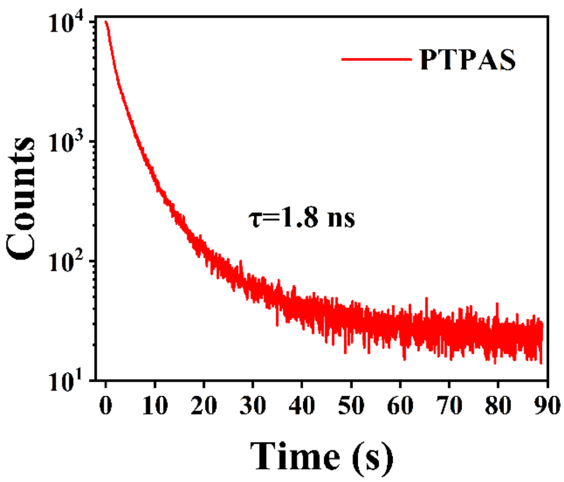


Fig. S3 Fluorescence lifetime of PTPAS in solid state.

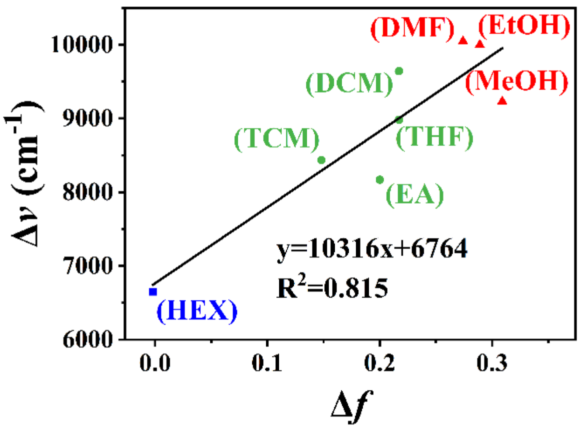


Fig S4. Fitted curve of the relationship between Δ*f* and Δν of PTPAS.

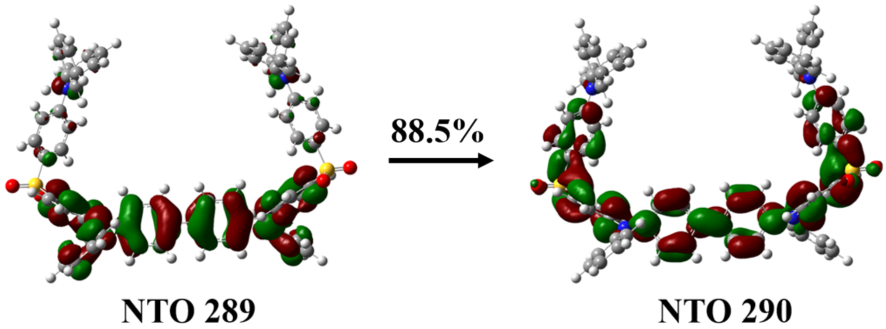
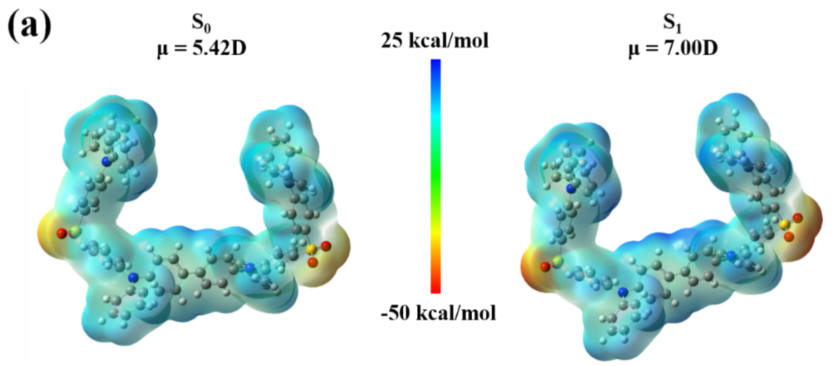


Fig. S5 Natural transition orbital (NTO) analysis of PTPAS



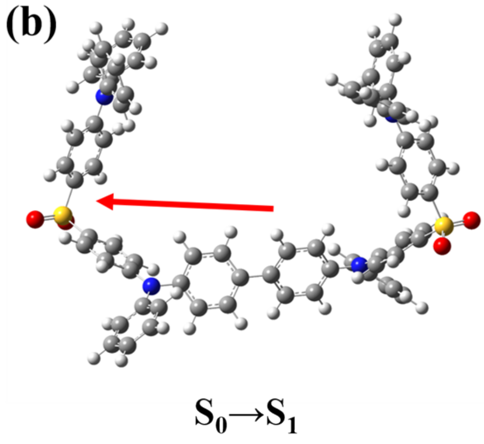


Fig. S6 (a) ESP maps of PTPAS and the resulting molecular dipole; **(b)** The transition dipole moment (red arrow) of PTPAS from the ground state (S_0) to the excited state (S_1).

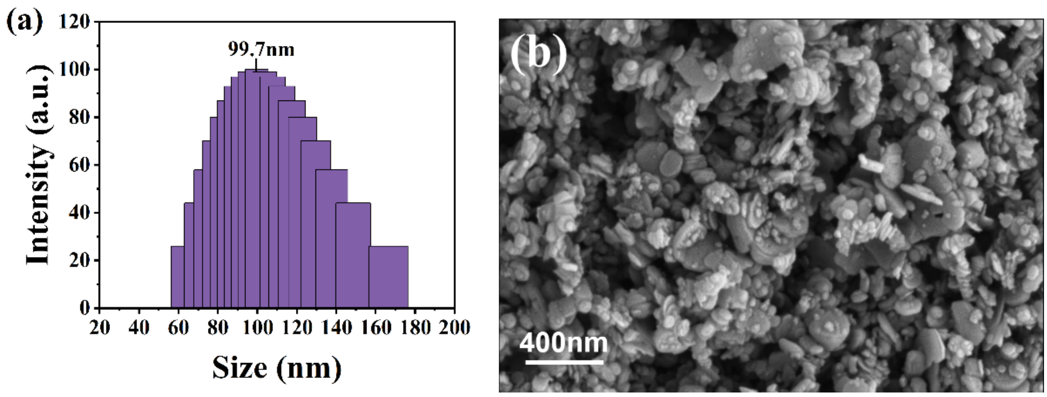


Fig. S7. (a) Particle Size Distribution of PTPAS (20 μM) in a solution with H_2O/THF Ratio of 6:4; **(b)**The SEM image of nanoparticles in PTPAS solution.

Table S4. Performance comparison of PTPAS with reported TNT detectors

Fluorescent probes	linearity range	$K_{SV}(M^{-1})$	LOD	References
PCz-TPE	—	8.5×10^4	—	[7]
PTPA1-TPE	0~41 μM	4.9×10^4	—	[8]
CdTe / CdS（QDs）	3~100 μM	3.2×10^4	375 nM	[9]
ROMP-P2	0.25~10 μM	5.3×10^5	70 nM	[10]
PTPEK	9~440μM	3.29×10^4	4.56 μM	[11]
T3HTP-2	0.2 ~ 60 μM	1.3×10^3	200 μM	[12]

PTPAS	1.1~11 μM	2.98×10^{5}	94 nM	This work

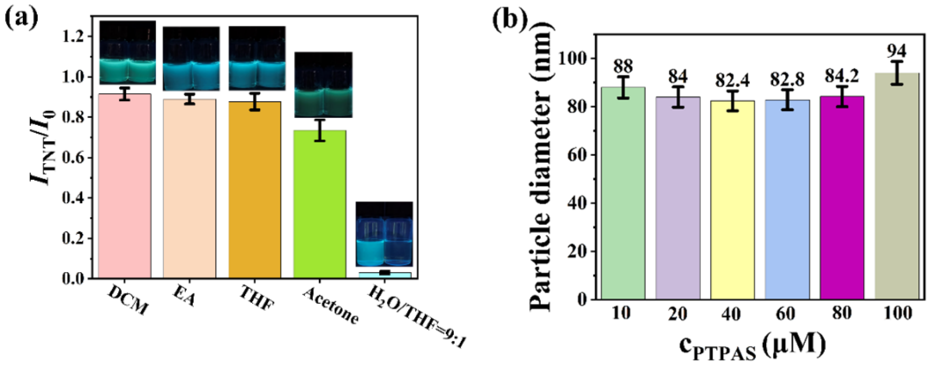


Fig. S8. (a) Fluorescence spectra of PTPAS (20 μM) after adding TNT (40 μM) in different solvents; **(b)** Average particle size of PTPAS solutions (H_2O/THF=9:1) with different concentrations.

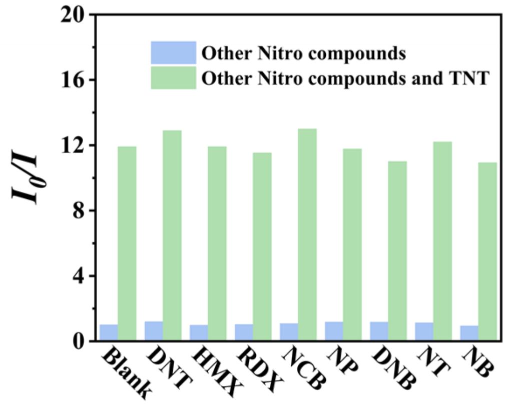


Fig. S9 After adding nitro compounds (20 μM) and TNT (20 μM) to PTPAS (20 Mm, THF/H_2O = 1:9), the ratio of initial fluorescence (I_0) to fluorescence after response (I)

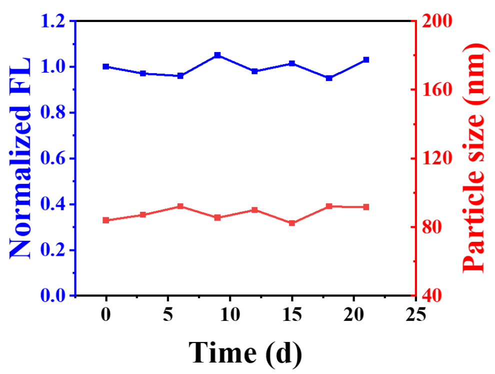


Fig. S10 Variation in average particle size and fluorescence intensity of PTPAS solutions (20μM, H_2O/THF=9:1) over three weeks

References

[1] A. M. Brouwer. Standards for photoluminescence quantum yield measurements in solution (IUPAC technical report). Pure and Applied Chemistry. 2011; 83(12): 2213-2228. DOI: http://doi.org/10.1351/Pac-Rep-10-09-31

[2] C. Würth, M. Grabolle, J. Pauli, et al. Relative and absolute determination of fluorescence quantum yields of transparent samples. Nature Protocols. 2013; 8(8): 1535-1550. DOI: http://doi.org/10.1038/nprot.2013.087

[3] P. C. Raichure, R. Bhatt, V. Kachwal, et al. Multi-stimuli distinct responsive D–A based fluorogen oligomeric tool and efficient detection of TNT vapor. New Journal of Chemistry. 2022; 46(14): 6560-6569. DOI: http://doi.org/10.1039/d1nj05314k

[4] P. Srinivasa Rao, A. Gupta, S. V. Bhosale, et al. Donor–acceptor–acceptor-based non-fullerene acceptors comprising terminal chromen-2-one functionality for efficient bulk-heterojunction devices. Dyes and Pigments. 2017; 146: 502-511. DOI: http://doi.org/10.1016/j.dyepig.2017.07.047

[5] H.-C. Wu, C.-L. Liu, W.-C. Chen. Donor–acceptor conjugated polymers of arylene vinylene with pendent phenanthro[9,10-d]imidazole for high-performance flexible resistor-type memory applications. Polymer Chemistry. 2013; 4(20): 5261. DOI: http://doi.org/10.1039/c3py00107e

[6] E. B. D. Brito, D. C. Santos, T. P. D. Paula, et al. Synthesis and Characterization of Copolymers with Fluorene-di-2-thienyl-2,1,3-benzothiadiazole Units for

Application in Optoelectronic Devices. Polymers. 2024; 17(1): 72. DOI: http://doi.org/10.3390/polym17010072

[7] W. Dong, Z. Ma, P. Chen, et al. Carbazole and tetraphenylethylene based AIE-active conjugated polymer for highly sensitive TNT detection. Materials Letters. 2019; 236: 480-482. DOI: http://doi.org/10.1016/j.matlet.2018.10.162

[8] W. Dong, T. Fei, U. Scherf. Conjugated polymers containing tetraphenylethylene in the backbones and side-chains for highly sensitive TNT detection. RSC Advances. 2018; 8(11): 5760-5767. DOI: http://doi.org/10.1039/c7ra13536j

[9] T. Komikawa, M. Tanaka, A. Tamang, et al. Peptide-functionalized quantum dots for rapid label-free sensing of 2,4,6-trinitrotoluene. Bioconjugate Chemistry. 2020; 31(5): 1400-1407. DOI: http://doi.org/10.1021/acs.bioconjchem.0c00117

[10] B. Ö. Öztürk, S. K. Şehitoğlu. Pyrene substituted amphiphilic ROMP polymers as nano-sized fluorescence sensors for detection of TNT in water. Polymer. 2019; 183: 121868. DOI: http://doi.org/10.1016/j.polymer.2019.121868

[11] Y. W. Xu, C. Zhong, B. Y. Zhang, et al. Facile preparation of tetraphenylethylene-based porous polymer with dual role of adsorption and detection for trinitrotoluene. Polymer. 2023; 288: 126454. DOI: http://doi.org/10.1016/j.polymer.2023.126454

[12] B. K. Doan, T. V. T. Tran, T. H. Nguyen, et al. One-pot synthesis of star-shaped conjugated oligomers based on 3-hexylthiophene, pyrene and triphenylamine as

TNT chemosensors. Journal of Photochemistry and Photobiology A: Chemistry. 2020; 394: 112496. DOI: http://doi.org/10.1016/j.jphotochem.2020.112496