



Highly emissive triphenylamine based fluorophores for detection of picric acid



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ABSTRACT

Triphenylamine based, dumbbell shaped, highly fluorescent compound **1** was designed and synthesized. Compound **1** showed blue emission with quantum efficiency as high as 0.78 in benzene solution. Compound **1** showed turn-off sensitivity to picric acid, which is a common constituent of many powerful explosives and unavoidable environmental threats. The turn-off sensitivity to picric acid is attributed to the excited state charge transfer from compound **1** to picric acid. Compound **1** selectively senses picric acid with a detection limit of ~400 ppb.

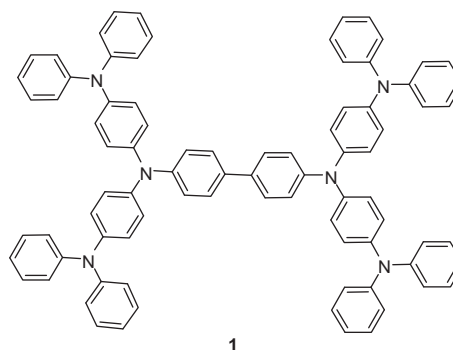
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Picric acid (PA) is a strong organic acid,¹ and like other nitroaromatics (NACs) it is used as a powerful explosive. It is even more explosive in nature than trinitrotoluene (TNT). PA can cause acute health effects such as skin and eye irritation and even liver damage, gastritis, aplastic anaemia and cyanosis.² However, its use is unavoidable as it has importance in dye industries, pharmaceuticals and chemical laboratories.³ PA is also an environmental threat because of its high solubility in water.⁴ Hence, the development of efficient sensors to detect PA at very low concentrations is highly desirable for both health and security.

Current detection methods for nitroaromatic explosives rely on the use of canines or sophisticated instruments, which are not easily accessible.⁵ Fluorescence quenching based sensing is much simpler and a very sensitive technique. Design and synthesis of new organic fluorophores for the detection of nitroaromatic explosives with high emission efficiency have attracted considerable interest.⁶ Electron rich conjugated polymers have proven to be excellent candidates for the detection of nitroaromatic explosives.⁷ Several metal-organic architectures have been employed to detect the presence of electron-deficient nitro-aromatics.⁸ Polycyclic aromatic hydrocarbons (PAHs) such as anthracene^{6b} and pyrene⁹ have been proved to be another important class of fluorophores sensitive to NACs.¹⁰ Compared to conjugated polymers, highly emissive

small conjugated molecules are more interesting because of their simple synthesis and purification, well-defined structures and better batch-to-batch reproducibility.

Triphenylamine is established as a good hole-transporting moiety. It is very much useful for organic electronic materials as it has a tendency to locate the cationic charge. Here we report the synthesis of a triphenylamine based dumbbell shaped new organic fluorophore with blue emission, its photophysical properties and sensitivity towards nitroaromatics. Compound **1** showed high sensitivity towards picric acid in ppb level.

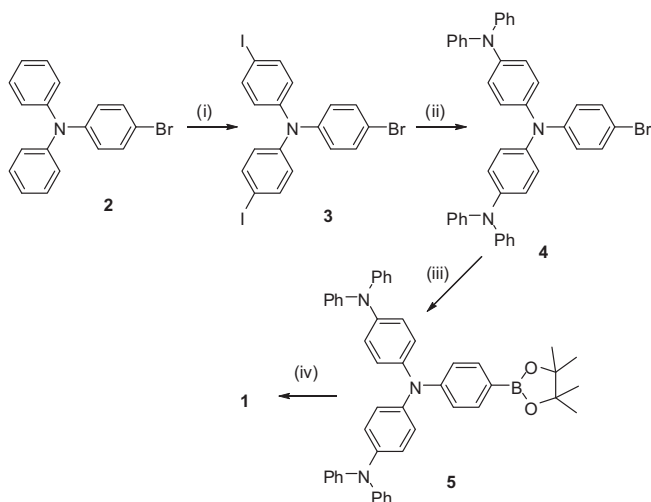


Compound **1** was synthesized by following the synthetic path shown in Scheme 1. Iodination of compound **2** by periodic acid and iodine gave compound **3**. Compound **4** was synthesized by

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Scheme 1. Synthetic route of **1**; (i) I_2 , periodic acid, ethanol, reflux, 2 h, 92%; (ii) diphenylamine, CuI, KOH flakes, 1,10-phenanthroline, reflux, 24 h, 74%; (iii) bis(pinacolato)diboron, Pd(dppf)Cl₂, KOAc, DMF, 80 °C, 12 h, 52%; (iv) **4**, Pd(PPh₃)₄, K₂CO₃, THF/Water, 80 °C, 12 h, 56%.

Cu-catalysed C–N coupling of diphenylamine and compound **3** in 52% yield. Pd-catalysed coupling of compound **4** with bis(pinacolato)diboron afforded compound **5**. Pd(0) catalysed Suzuki cross coupling between compounds **4** and **5** afforded **1** in 56% yield.

The absorption spectra of **1** in benzene solution exhibited two major bands with absorption maxima at 312 and 347 nm which arise from $\pi \rightarrow \pi^*$ transitions (Fig. 1). Compound **1** exhibited intense blue emission in the region of 400–550 nm with an emission maximum at 446 nm when it was excited at 347 nm. Blue emission is very much important as it is one of the primary colours of the R–G–B colour spectrum. Designing molecules with pure blue emission is difficult due to their characteristic properties like wide band gap and low lying HOMO level. Compound **1** showed as high quantum yields (Φ_F) as ~ 0.78 in benzene solution. The Φ_F in solution was measured with respect to quinine sulfate which has absolute Φ_F value of 0.58 in 0.1 M sulfuric acid solution.

To get a clear idea about excited state phenomenon, the absorption (Fig. S1 in SI) and emission (Fig. S2 in SI) spectra of compound **1** were recorded in solvents of increasing dielectric constants (such as benzene (2.3), toluene (2.4), chloroform (4.8), tetrahydrofuran (THF, 7.5) and dichloromethane (DCM, 9.1)) (Table 1). Absorption spectra of **1** showed negligible solvatochromic changes. However, a considerable red-shift in emission maxima was observed by

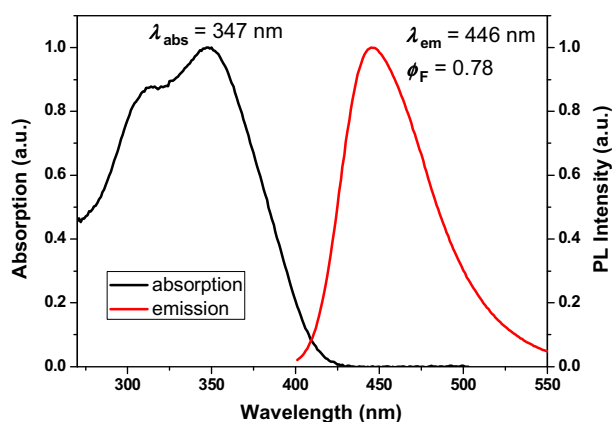


Figure 1. Absorption and emission spectra of **1** in benzene solution.

Table 1
Absorption and fluorescence data of **1** in various solvents

Solvent	$\lambda_{\max,ab}$ (nm)	$\lambda_{\max,em}$ (nm)	Stokes shift (nm)
Toluene	350	446	95
Benzene	348	445	97
Chloroform	348	466	118
THF	349	468	119
DCM	351	490	139

changing the solvent from benzene to DCM. It indicates more polar excited state of **1** compared to the ground state. Polarity of excited state was also supported by the DFT generated frontier molecular orbitals (vide infra).

The cyclic voltammetry (CV) of compound **1** was studied in dry THF using tetrabutyl ammonium perchlorate (TBAPC) as electrolyte and non-aqueous Ag/AgCl as reference electrode (Fig. S3 in SI). Compound **1** showed two quasi reversible oxidation peaks and a reduction peak. The first oxidation potential at 0.66 V corresponds to the removal of electron from the first half of the molecule, whereas the second oxidation at 0.84 V can be assigned to the removal of electron from the second half. The HOMO level of **1** calculated from the onset oxidation potential was found to be -4.88 eV.¹¹ The LUMO energy of **1** was calculated to be -1.88 eV from CV data.

The fluorescence titration was carried out with compound **1** (3.3 μ M) in an aqueous THF (THF/water; 7:3) by adding 30 equiv of various nitroaromatics such as picric acid (PA), 2,4-dinitrophenol (2,4-DNP), *para*-nitrophenol (*p*-NP), nitrobenzene (NB) and nitromethane (NM) and other compounds such as benzoic acid (BA), benzophenone (BP) and catechol. All nitroaromatics act as fluorescence quenchers for compound **1**. Among them, the most effective quencher is picric acid and benzophenone is the least effective (Fig. 2a). Quenching efficiency was calculated by using the formula $(I_0 - I)/I_0 \times 100\%$, where I_0 and I are the fluorescence intensities of **1** before and after the exposure to the analyte, respectively. Figure 2b shows quenching efficiency of nitroaromatics and related compounds. Considerably high quenching efficiency was observed for picric acid (98%). Quenching of emission intensity of an electron rich fluorophore and electron poor nitroaromatics is associated with an intermolecular photoinduced donor–acceptor electron transfer mechanism.¹² Due to the delocalized π^* excited state, compound **1** has strong donor ability, which facilitates interaction between **1** and electron-deficient nitroaromatic analytes.¹³ Figure 3 shows the probable molecular arrangement due to $\pi \dots \pi$ stacking interactions between the π -electron rich compound **1** and π -electron poor picric acid. To get more information about the interaction between compound **1** and picric acid, we have done the UV–vis titration (Fig. S4 in SI). However, picric acid and compound **1** absorb in the same region of UV–vis spectrum. Therefore, we could not abstract any useful information from the UV–vis titration.

To get an idea about the electronic distribution in the frontier orbitals of compound **1**, density functional theory (DFT) calculation was carried out at B3LYP/6-31G(d) level using Gaussian 09.¹⁴ The HOMO of **1** is delocalized over the whole molecule, whereas LUMO electron density is concentrated on the two central phenyl rings (Fig. 4). The electron density distribution on LUMO corroborates the proposed $\pi \dots \pi$ stacking interactions with PA which facilitates the charge transfer from the excited state of **1** to PA. Cyclic voltammetry study of compound **1** (Fig. S3 in SI) supports the excited state electron-transfer from LUMO of **1** (at -1.88 eV) to the lower energy LUMO of PA (-3.89 eV).¹⁵

After confirming the sensitivity of **1** towards picric acid, the fluorescence titration was carried out by adding different equiv (0–30 equiv) of picric acid to the solution of **1**. With a gradual

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