Conjugated Polymer Nanoparticles for the Amplified Detection of Nitro-explosive Picric Acid on Multiple Platforms

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ABSTRACT: Spontaneously formed conjugated polymer nanoparticles (CPNs) or polymer dots displayed remarkable fluorescence response toward nitroexplosive-picric acid (PA) in multiple environments including 100% aqueous media, solid support using portable paper strips and vapor phase detection via two terminal device. This new cationic conjugated polyelectrolyte (CPE) – poly(3,3′-(2-(phenyl-9H-fluorene-9,9-diyl)bis(hexane-6,1-diyl))bis(1-methyl-1H-imidazol-3-ium)bromide) (PFMI) was synthesized by Suzuki coupling polymerization followed by post functionalization method without employing any hectic purification technique. Highest quenching constant value (Kq) of 1.12 × 10^9 M^−1 and a very low detection limit of 30.9 pM/7.07 ppt were obtained exclusively for PA in 100% aqueous environment which is rare and unique for any CPE/CPNs. Contact mode detection of PA was also performed using simple, cost-effective and portable fluorescent paper strips for achieving on-site detection. Furthermore, the two terminal sensor device fabricated with nanoparticles of PFMI (PFMI-NPs) provides an exceptional and unprecedented platform for the vapor mode detection of PA under ambient conditions. The mechanism for the ultrasensitivity of PFMI-NPs probe to detect PA is attributed to the “molecular-wire effect”, electrostatic interaction, photoinduced electron transfer (PET), and possible resonance energy transfer (RET).

KEYWORDS: conjugated polymer nanoparticles, chemosensors, nitroexplosives, picric acid, current–voltage characteristics

INTRODUCTION

The development of reliable methods for the rapid and selective detection of ultratrace amounts of nitro-explosive are of vital concern for national security as well as catastrophic environmental pollution.1–6 Although, RDX and 2,4,6-trinitrotoluene (TNT) are the most widely used nitroexplosives; picric acid (PA) is another superior explosive material having low safety coefficient, high detonation velocity and extensively used until World War I because of its potent explosive nature than TNT. Owing to the incredible solubility of PA in water and widespread applications in various industries and forensic investigations, it is likely to contaminate soil and groundwater when exposed and is responsible for several health disorders, namely, sycoasis, cancer, anemia, cause strong irritation to eye/skin and potential destruction of liver, kidney and respiratory organs.7–10 Hence, there is an urgent need to develop superior methods for monitoring the traces of PA in multiple environments including aqueous solution, contact mode and vapor phase rapidly, to avert terrorist threats as well as monitoring environmental pollution.

Though, various analytical techniques have been employed for the detection of nitroaromatics, most of them are expensive, complex, less sensitive, time-consuming and suffer from various drawbacks, such as portability and on-site detection capability making them inappropriate for practical applications.8,11–15 Fluorescence signaling is considered as a primary tool for the detection of nitroexplosives due to its simplicity and diverse notable features, namely, remarkable sensitivity, short response time and potential in both solution as well as solid state. Hence, much attention has been paid in designing fluorometric sensors for explosives based on oligomers/conjugated polymers,14,16–25 quantum dots,26 metal–organic frameworks,27–32 micro/nano-aggregates,33–38 etc. However, most of the sensors for PA detection have reported problems of limited selectivity, low sensitivity, on-site detection incapability, and unviability in 100% aqueous medium, as well as incapable vapor phase detection. (Surprisingly there are no efficient methods developed for vapor phase detection of PA.) Thus, development of superior probes for monitoring PA with ultrasensitivity and high selectivity in 100% aqueous medium, solid state on-site as well as in vapor phase is highly desirable and challenging in the present context.

To attain ultrasensitivity, few approaches have been made in designing CP based probes for the detection of PA.14,21,22,39–41 However, low selectivity due to the absence of suitable receptor, interferences by other electron deficient nitro analytes, impracticability in 100% aqueous media and vapor mode detection persists as a challenge for researchers. Recently, conjugated polymer nanoparticles (CPNs) have emerged as a fascinating class of nanomaterials42,43 in the field of chemical and biological sensing, imaging and diagnosis because of their numerous advantages, namely, high quantum efficiency, low...
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Device-based sensors have been proved as promising and excellent candidates for the detection of volatile materials because of their ultralow cost, high sensitivity, good reproducibility, viability under ambient condition, as well as capability to be miniaturized and quantified. However, low volatility of the sensing analyte remains a major obstacle for investigators in developing such detection methods. Although, gas sensors have been designed for monitoring trace investigators in developing such detection methods. Although, gas sensors have been designed for monitoring trace gases. Nevertheless, a highly efficient and reliable protocol for monitoring traces of nitroexplosives-picric acid in multiple media and forms [solution (liquid in various solvents), disposable paper film (solid/powder form), as well as devices (vapor/gas)] using CPNs to gain ultrasensitivity and high/ambiguous signal response.

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**RESULTS AND DISCUSSION**

**Synthesis and Characterization of PFMI and PFMI-NPs.** The cationic conjugated polymer poly(3,3′-(3-(2-phenyl-9H-fluorene-9,9-diyl)bis(hexane-6,1-diyl))bis(1-methyl-1H-imidazol-3-imium) bromide) (PFMI) was synthesized using Suzuki

## Figure 1. (a) Structure of newly synthesized polymer PFMI and its corresponding nanoparticles. (b) FESEM and (c) TEM image showing spherical shaped PFMI-NPs with the average sizes of ~30 nm. (d) SAED pattern of PFMI-NPs exhibited a broad hollow ring confirming the amorphous nature of molecules.

$$\Phi_1 = \Phi_f (A_f / A_d) (n_1^2 / n_2^2)$$

where, $r$ and $s$ represent reference and sample, $\Phi$ denotes the quantum yield, $A$ signifies absorbance, $F$ shows relative integrated fluorescence intensity, and $n$ implies the refractive index of the medium.

**Calculation for Overlap Integral Value and Förster Distance.** The extent of energy transfer was determined by calculating the overlap integral values for all the nitroexplosives using the equation shown below

$$J(\lambda) = \int_0^\infty F_D(\lambda)\varepsilon_A(\lambda)\lambda^4 d\lambda$$

where $J(\lambda)$ denotes the overlap integral value, $F_D(\lambda)$ represents corrected fluorescence intensity of PFMI-NPs from $\lambda$ to $\Delta\lambda$ with total intensity normalized to unity, and $\varepsilon_A$ signifies molar absorptivity of the acceptor at $\lambda$ in M$^{-1}$cm$^{-1}$.

Förster distance $R_0$ was also calculated for the interaction of PFMI-NPs with nitroexplosives using the equation shown below

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

where $J$ represents the extent of spectral overlap between the emission spectrum of donor and absorption spectrum of acceptor, $Q$ denotes the photoluminescence quantum yield of PFMI-NPs (donor), $k^2$ signifies dipole orientation factor (generally consider as 0.667), and $\eta$ is the refractive index of the medium.

**Method Used for Detection Limit Calculation.** For the detection of detection limit, various samples of PFMI-NPs (6.6 × 10$^{-6}$ M) each containing PA (0.16, 0.33, 0.50, 0.66, 0.83, and 1 nM) were prepared separately. The fluorescence spectrum was then recorded for each sample by exciting at 380 nm. A calibration curve was plotted between change in the fluorescence intensity and concentration of picric acid to obtain the regression curve equation.

The detection limit (LOD) was then calculated using the equation $3\sigma / K$, where $\sigma$ is the standard deviation (SD) for PFMI-NPs solution intensity in the absence of PA and $K$ denotes the slope of the curve.

**Cyclic Voltammetry Studies.** Electrochemical measurements were carried out using three-electrode cell with platinum wire as counter electrode, saturated Ag/AgNO$_3$ electrode as reference electrode and a glassy carbon as working electrode. Tetrabutylammoniumhexafluorophosphate (0.1 M) in acetonitrile was used as supporting electrolyte. The Fe$^3$/Fe couple was employed as internal reference and all the measurements were performed at room temperature under inert atmosphere. Single oxidation peak was observed for PFMI-NPs. The HOMO level (~−6.03 eV) was calculated from the onset method [$E_{HOMO} = -(E_{ox(onset vs Fc+/Fc)} + 4.8) \text{ (eV)}$]. Band gap (2.95 eV) of PFMI-NPs were determined from the onset of UV–visible spectrum to calculate its LUMO level (~−3.08 eV).

**Device Fabrication and Electrical Measurements.** For the fabrication of a two-terminal sensor devices, microscopic glass slides were used as substrates. The glass substrates were cleaned in piranha solution (3:1 H$_2$SO$_4$:H$_2$O$_2$) before washing it several times with deionized water. The cleaned substrates were then dried under vacuum at 100 °C. Using masking, 150 nm thick aluminum (Al) electrodes were deposited on to clean glass substrates by thermal evaporation under high vacuum <10$^{-4}$ mbar to make a blank channel with 30 μm length (L) and 1500 μm width (W). From the stock solution of PFMI-NPs (10$^{-3}$ M) in water, a volume of 10 μL was drop-casted over the channel between electrodes. The solvent was fully dried by heating on a hot plate for 10 min at 50 °C to form a thin film (thickness ~60 nm) across the fabricated Al electrodes. The electrical characteristics of the devices were carried out under ambient condition using a Keithley 4200-SCS semiconductor parameter analyzer.

**Vapor Phase Detection.** For vapor phase detection, 50 mg of various nitroaromatics (2,4-DNT, 2,6-DNT, NB, NT, and PA) were kept for 2 days in 20 mL airtight glass vials to ensure complete saturation over the area of headspace. The concentration of vapors in the headspace were calculated using the equation

$$\text{saturation concentration (ppm)} = VP \text{ (mm Hg)} / 760 \text{ mm Hg} \times 10^6$$

where VP denotes vapor pressure of various nitroaromatics. Each nitroaromatics were then diluted to desired concentration by air and injected into the gas chamber using airtight syringe.
NPs was found to be ∼ displayed unprecedented e− to be 15101 g mol−1. Nanoparticles with average sizes of ∼30 nm (Figure 1bc). The SAED pattern of PFMI-NPs exhibited a broad hollow ring, which is attributed to its amorphous nature (Figure 1d). The zeta potential of PFMI-NPs at 25°C in water was found to be 62.8 mV ± 1.2.

**Sensing Studies in Aqueous Medium.** The sensing studies were performed using both free polymer (PFMI), as well as its nanoparticles (PFMI-NPs). The cationic polymer PFMI displayed absorption maximum at 370 nm with an emission maximum (excitation 370 nm) of 418 nm in water. Compared to free polymer PFMI, the PFMI-NPs exhibit a red-shifted absorption peak positioned at 380 nm (Figure S7) and emission at 420 and 444 nm (excitation 380 nm) respectively, indicating an increase in n−π interaction because of the close association of backbone chains.54 The photoluminescence quantum yield (ΦL) of PFMI-NPs was found to be ∼46% in aqueous media. PFMI-NPs displayed unprecedented efficiency during sensing experiments compared to free polymer PFMI, established via the high signal response and low detection limit value obtained for PA with PFMI-NPs. Hence, PFMI-NPs were chosen as probes rather than free polymer PFMI for studying sensing behavior toward various nitroexplosives.

To demonstrate the sensing behavior of PFMI-NPs toward nitroexplosives in solution state, fluorometric titration was performed with various common explosive materials viz. RDX, TNT, PA, NB, NM, 4-NP, 2,4-DNP, 2,4-DNT, 2,6-DNT, 4-NT, 1,3-DNB, and phenol in aqueous media. Interestingly, only PA displayed significant response toward the emission of PFMI-NPs in the presence of PA was obvious under UV light (lamp excitation-325 nm). The quenching efficiency was studied via Stern−Volmer plot (I0/I vs [Q]) where, I0 represents fluorescence intensity in the absence of quencher, I represents fluorescence intensity at various concentrations of PA, and Q implies concentration of quencher) to acquire the Stern−Volmer constant (Ksv). The Ksv obtained from the linear fitting of plot was found to be 1.12 × 106 M−1, signifying very high sensitivity of PFMI-NPs for PA (inset of Figure 2a). The limit of detection (LOD) value calculated for PA on the basis of the standard method reported23 was observed to be 30.99 pM/7.07 ppt (Figure S8). To the best of our knowledge, such high Ksv and incredibly low LOD value is being reported for the first time using CPNs in 100% aqueous media and is superior among all the previous detection methods for PA (Table S1).

Interestingly, other nitroexplosives used in the present study did not cause any significant changes on the photophysical properties of PFMI-NPs (Figures 2b and S9). From the S−V plot of nitroexplosives (Figure 2c), it was clear that at lower PA concentration, linearity in the curve was obtained which

Figure 2. (a) Emission spectra of PFMI-NPs (6.6×10−6 M) with variable concentration of PA in aqueous media. Inset: Stern−Volmer plot at lower PA concentration. (b) Bar diagram showing the effect of various nitroexplosives (5×10−7 M) on the emission of PFMI-NPs (6.6×10−6 M). (c) Stern−Volmer plots obtained for different nitroexplosives used in the study. (d) Percentage quenching of PFMI-NPs (6.6×10−6 M) obtained for various nitroexplosives (5×10−7 M) before and after addition of PA (5×10−7 M) in aqueous media.
indicates static quenching mechanism. However, at higher concentration the curve deviates and increases exponentially suggesting an amplified signal response via the dynamic quenching process. This nonlinear nature of $S-V$ plot may also indicate the possibility of self-absorption or an effective energy transfer process in the quenching mechanism. However, all other nitroexplosives used in the present study did not displayed any deviation in the curve and remained linear even at higher concentration, confirming the absence of energy transfer mechanism. These results confirm that PFMI-NPs displayed an exceptional selectivity and remarkable quenching response for PA in 100% aqueous environment that has remained a challenging problem.

**Demonstrating Selectivity in Competitive Environment.** The specific recognition of PA is an exciting and appealing area of research. However, because of the similar electron deficient nature of all the nitroexplosives, the specific recognition of PA remains a challenging task for researchers. To validate the selectivity of PFMI-NPs system, its fluorescence quenching by PA was performed in the presence of different nitroexplosives. It is noteworthy to mention that PFMI-NPs showed remarkable response toward PA even in the presence of various common interfering nitroanalytes (Figures 2d and S10–S18). Similar experiments were also performed in the presence of various common metal ions (Cr$^{3+}$, Ni$^{2+}$, Zn$^{2+}$, Al$^{3+}$, Co$^{2+}$, Pb$^{2+}$, Cd$^{2+}$, Mn$^{2+}$, Cu$^{2+}$, Ag$^{+}$, Ca$^{2+}$, La$^{2+}$, and Fe$^{3+}$), as well as anions (BH$_4^-$, $\text{NO}_3^-$, $\text{N}_2\text{O}_4^-$, $\text{S}_2\text{O}_5^-$, BF$_4^-$, $\text{H}_2\text{PO}_4^-$, HPO$_4^{2-}$, PO$_4^{3-}$, and AcO$^-$), usually found in natural water. Interestingly, PFMI-NPs showed exceptional response exclusively toward PA even in the presence of these most common interfering analytes (Figures S19 and S20) validating the applicability of this system for the investigation of natural water samples.

To elucidate the effect of ionic strength on PA sensing by PFMI-NPs, fluorescence quenching experiment was performed in the solutions of different salt concentration (0, 0.1, 0.2, 0.4, 0.6, 0.8, and 1 M NaCl). It was observed that increasing the ionic strength reduces the quenching efficiency due to the weak Columbic interaction between the oppositely charged PFMI-NPs and PA molecules (Figure S21). Yet, the quenching efficiency of ~50% was observed in the presence of 1 M NaCl which confirms that PFMI-NPs system can detect PA even at relatively high electrolyte concentrations in the aqueous media.

**Sensing Mechanism.** The origin of the remarkable selectivity and the exceptional quenching efficiency by PA can be explained via the electrostatic interaction between PA and PFMI-NPs. Since PA consists of strong acidic phenolic $-\text{OH}$ group with the ability to deprotonate in aqueous medium, positively charged PFMI-NPs have strong tendency to interact with the resulting picrate ions through Columbic interaction. This interaction may further facilitate the electron and/or energy transfer process. To investigate the possibility of electron transfer process in the quenching mechanism, higher occupied molecular orbital (HOMO) level and lower unoccupied molecular orbital (LUMO) level of PFMI-NPs was obtained via cyclic voltammetry studies (Figure 3a). There is a possibility of excited state electron transfer from LUMO of PFMI-NPs ($-3.08$ eV) to the LUMO of PA ($-3.89$ eV) resulting in the quenching process (Figure 3b). Although, PA ($-3.89$ eV) has lowest LUMO level compared to DNT ($-3.5$ eV), NT ($-3.2$ eV), TNT ($-3.7$ eV) etc.,$^{30}$ the quenching does not follow the order. Thus, it can be concluded that electron transfer process has occurred between PA and PFMI-NPs system.
transfer may not be the only mechanism involved in the quenching process. Nonlinear nature of S–V plot and the outstanding response of PFMI-NPs toward PA suggest that an additional energy transfer process may also be associated with the quenching process. To elucidate this presumption, a plot was obtained between normalized emission spectrum of PFMI-NPs and absorption spectrum of PA unlike other nitroexplosives. Hence, there is a strong possibility of resonance energy transfer (RET) from the fluorophore PFMI-NPs (donor) to the nonemissive PA (acceptor), which can enhance the quenching efficiency as well as sensitivity. The overlap integral value (Jo) was calculated for all the nitroexplosives to ascertain the extent of energy transfer. It was observed that Jo value for PA (1.59 × 10^14 M^−1 cm^−1 nm^4) was significantly higher compared to other explosives by ~100 times (Table S2). The value of Förster distance R0 (33.32 Å) for PFMI-NPs and PA interaction also falls well in the range 10–100 Å that is appropriate for RET.

To confirm the nature of quenching and the occurrence of RET from PFMI-NPs to PA, time correlated single-photon-counting (TCSPC) experiments were performed. The lifetime of PFMI-NPs was measured at 420 nm in the absence and presence of variable concentrations of PA using pulse excitation 375 nm (Figure 3d). Meanwhile, the lifetime of PFMI-NPs was determined to be 0.241 ns that reduces dramatically and shortened to 0.05 ns at 0.5 μM PA. This significant reduction in the lifetime strongly supports the possibility of energy transfer from PFMI-NPs to PA and indicates a dynamic quenching mechanism. To further clarify the interaction between PA and PFMI-NPs, a control experiment was performed using model compounds, that is, 2,4-DNP and 4-NP having properties somewhat similar to PA. The photophysical properties of PFMI-NPs showed similar response to these analytes but with the quenching order as PA > 2,4-DNP > 4-NP (Figure S22). It is notable that the quenching pattern followed the order of acidity by these analytes. Since, PA consists of three electron deficient –NO2 groups that boost its ability to dissociate in aqueous medium, a more favorable electrostatic interaction between PA and PFMI-NPs is expected compared to the 2,4-DNP or 4-NP which subsequently enhanced the quenching efficiency. This interaction may further facilitate the PET or energy transfer process to deliver the remarkable response of PFMI-NPs selectively toward PA. Other nitroexplosives that do not possess any –OH groups were ineffectual toward quenching process even though their LUMO level lies below the LUMO level of PFMI-NPs. Furthermore, triflic acid (TFA), a stronger acid compared to PA did not affect the emission of PFMI-NPs (Figure S23), indicating that acid itself cannot quench the fluorescence of PFMI-NPs and electron and/or energy transfer is the main factor behind the quenching process.

Hence, on the basis of above observations, it can be concluded that extraordinary selectivity and excellent sensitivity of PFMI-NPs for PA in aqueous media is accountable for the favorable excited state electron transfer process, efficient energy transfer process and the well-established46 “molecular-wire effect” employed in these polymers. This simple, yet rare method comprising of conjugated polymer nanoparticles (PFMI-NPs) provides an exceptional and unique platform for transfer. It was observed that Jo value for PA (1.59 × 10^14 M^−1 cm^−1 nm^4) was significantly higher compared to other explosives by ~100 times (Table S2). The value of Förster distance R0 (33.32 Å) for PFMI-NPs and PA interaction also falls well in the range 10–100 Å that is appropriate for RET.

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**Contact Mode Detection.** Lesser volatile explosive materials like PA can contaminate the subjects, containers etc. by leaving trace residues during manufacturing of fireworks, transportation and handling. Hence, detection of such explosives at actual site is highly significant for forensic investigations. To realize portability and low cost on-site detection capability, fluorescent test strips were prepared by dipping the Whatman filter paper (70 mm diameter) in the solution of PFMI-NPs (10^−4 M) in methanol followed by drying the solvent in air. The filter paper coated with PFMI-NPs were then cut into desired number of pieces (1 cm × 1 cm) and used for the instant surface sensing purposes by applying 10 μL of various concentration of PA solution. A solvent spot was also applied as a blank. Noticeable dark spots were observed under UV-light (365 nm excitation) that varies with the concentration of PA (Figure 4). The detection limit of 22.9 fg/cm^2 was obtained for PA which is among the best reported value and confirms the method as simple, portable and most efficient for on-site detection.

**Vapor Phase Detection.** The two terminal sensor devices fabricated with PFMI-NPs were kept in an airtight chamber and connected to Keithley 4200 SCS semiconductor parameter analyzer to perform I–V characterization by sweeping the voltage from −10 to +10 V. The channel and interface between PFMI-NPs film and bare aluminum surface were visualized under optical microscope (Figure S24). The I–V curve thus obtained demonstrated a good conducting nature of PFMI-NPs thin film (Figure 5a). The exposure of device to air did not cause any change in the output current, confirming its stability under ambient condition. The vapors of nitroaromatics were injected into the testing chamber with the help of an airtight syringe (Figure 5b). Four successive on/off cycles were effectively attained that correspond to four different PA concentrations ranging from 0.2 to 1 ppb, respectively (Figure...
confirming the unprecedented sensitivity of PA present even in negligible quantities. Notably, increasing the PA concentration leads to increased output current which subsequently enhances the sensitivity. Although the vapor pressure of PA is much lower than other nitroaromatics, yet it displayed significant increment in the current intensity confirming remarkable sensitivity of PFMI-NPs based device exclusively for PA. Interestingly, the device also displayed high signal response (6 s) and fast recovery (5 s) for PA detection (Figure S25). Furthermore, to check the reproducibility of the device, certain concentrations (0.3 ppb) of PA vapors were exposed repeatedly into the test chamber after certain interval of time (Figure S26). After each exposure, nearly similar increment in current intensity was observed confirming the viability of the device for practical application.

To study the selectivity of the device, similar sensing experiments were performed by introducing various other nitroaromatic vapors. As revealed in Figure 5d, vapors of other nitroexplosives showed negligible responses to the current intensity even at much higher concentration (100 times more) than PA and the current intensity increases rapidly only when PA vapors were delivered into the testing chamber. The robustness and reproducibility of the device response to the PA vapors was tested over several weeks and found consistent.

PA being an electron-withdrawing molecule, could dope the p-channel semiconductors (PFMI-NPs) and induce increase in the output current as the device is exposed to PA vapors. The unprecedented selectivity of PFMI-NPs toward PA is assigned primarily to the specific receptor site for PA present on the side chains of PFMI. Thus, these outcomes established a highly prospective route for the development of a rapid, low cost, reliable and easily processable device for vapor mode sensing of PA which remains an unexplored area of research.

CONCLUSION

In conclusion, a rapid and highly sensitive platform is developed for the selective detection of nitroexplosive picric acid in multiple environments (100% water, disposable film and as devices) using newly synthesized conjugated polymer nanoparticles PFMI-NPs. Ultrasensitivity of PFMI-NPs for PA is attributed to the “molecular-wire effect”, electrostatic interaction, photoinduced electron transfer (PET) and/or possible resonance energy transfer (RET). PFMI-NPs performed PA detection even in the presence of several other interfering nitroexplosives and most common analytes usually found in natural water that makes the protocol reliable and suitable for real sample analysis. Contact mode detection using simple fluorescent strips confirms the technique to be widely applicable for instant on-site detection of PA. Furthermore, vapor mode sensing of PA was achieved for the first time using solution-casted conjugated polymer nanoparticles fabricated as two terminal portable devices on glass substrates that displayed remarkable response exclusively for PA presenting a highly reliable method with rapid on-site detection ability.
Molecules for Sensing Nitroaromatics.

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