Electronic Supplementary Material (ESI) for Analyst.


*Supporting information*

# Highly selective fluorescence 'turn off' sensing of picric acid and efficient cell labelling by water soluble luminescent anthracene-bridged poly(*N*-vinyl pyrrolidone)

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**Figure S1.** $^{1}H$ NMR spectrum of 9,10 bis(azidomethyl)anthracene (in $CDCl_3$ at RT).

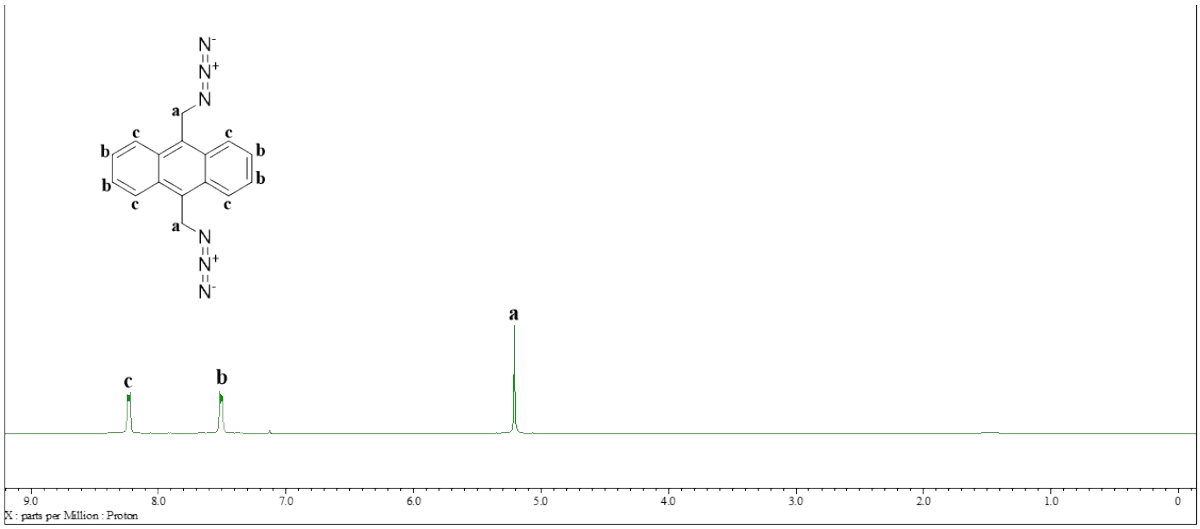



**Figure S2.**$^{13}C$ NMR spectrum of 9,10 bis(azidomethyl)anthracene (in $CDCl_3$, RT).

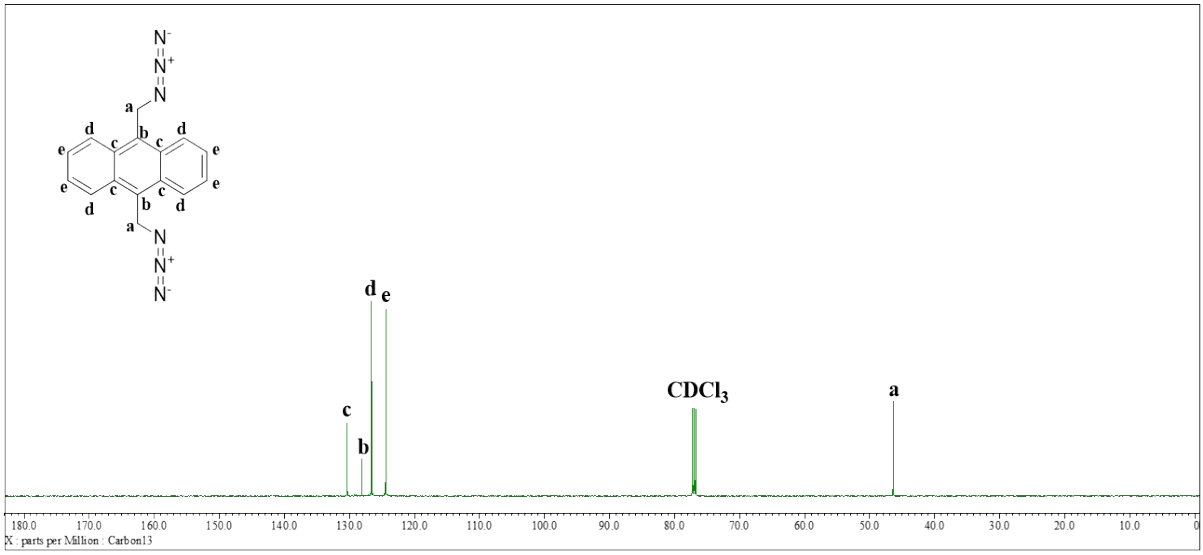


**Figure S3.** FTIR spectra of ATC-PNVP, alkyne terminated PNVP and anthracene azide (using KBr pellet).

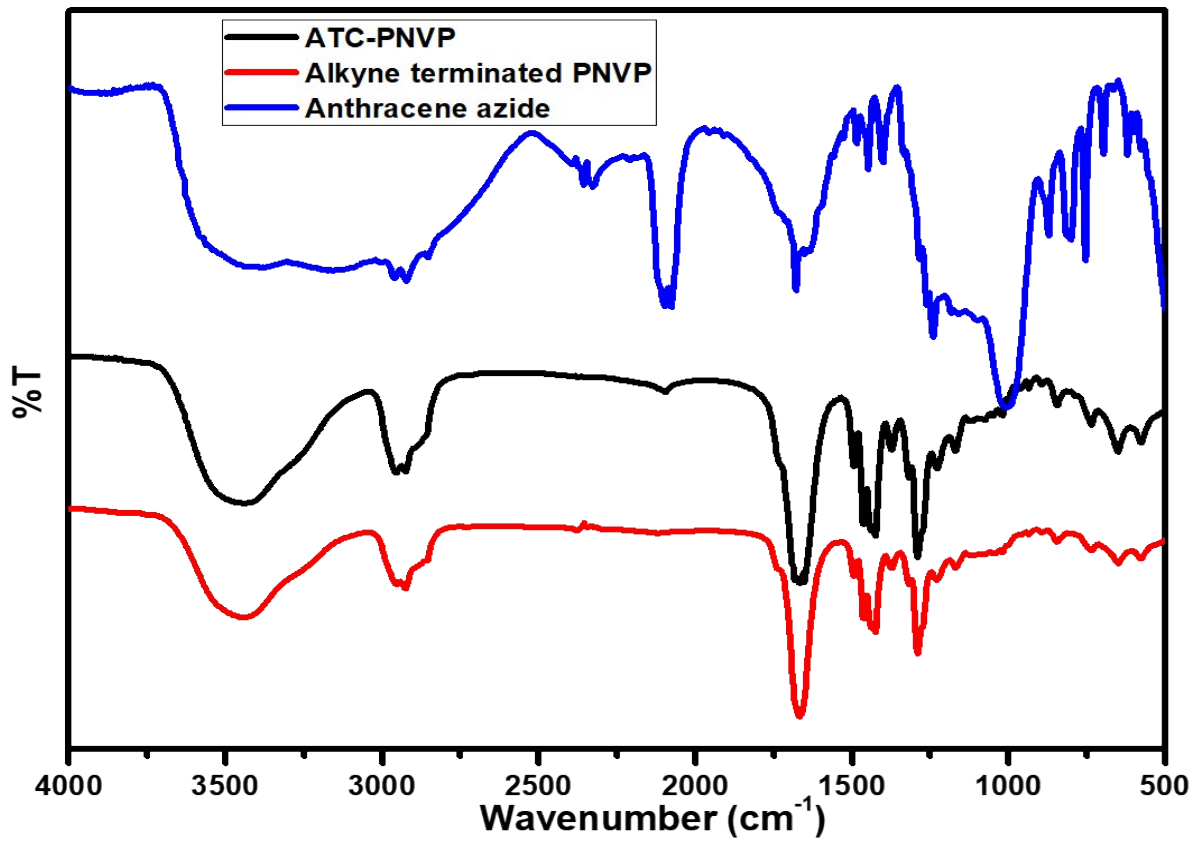



**Figure S4.** UV-Visible spectra of alkyne terminated PNVP, anthracene azide and ATC-PNVP ($1\times10^{-6}$ M in water).

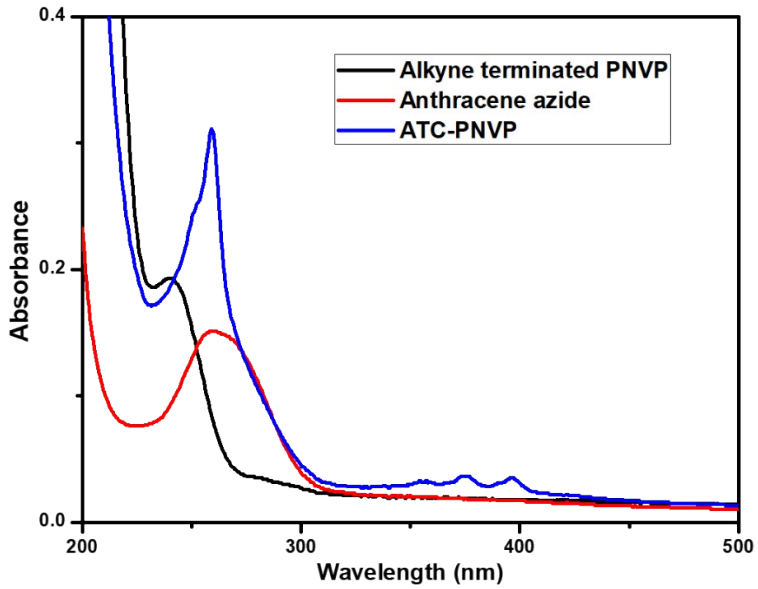


**Figure S5.** Fluorescence spectra of ATC-PNVP (500 µL, 1 x $10^{-5}$ M) in the presence of different aliphatic and aromatic acids and phenolic nitro compounds (5 µL, 1 x $10^{-3}$ M each).

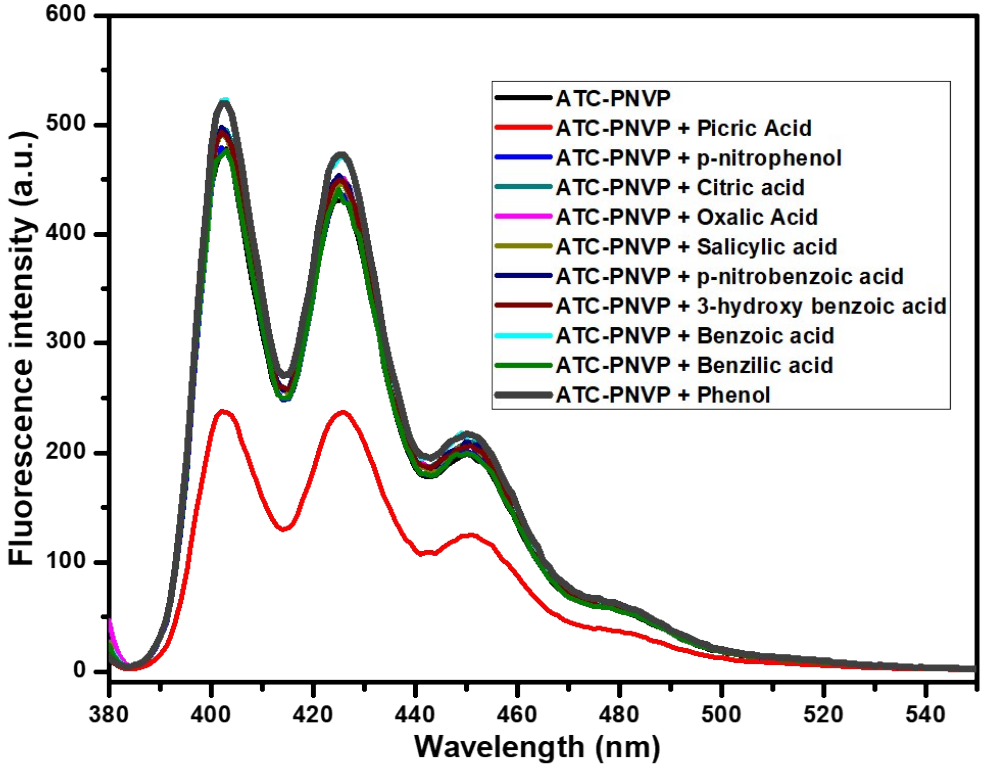



**Figure S6.** Fluorescence spectra of ATC-PNVP (500 µL, 1 x $10^{-5}$ M) in the presence of different (a) metal ions and (b) anions (5 µL, 1 x $10^{-3}$ M each).

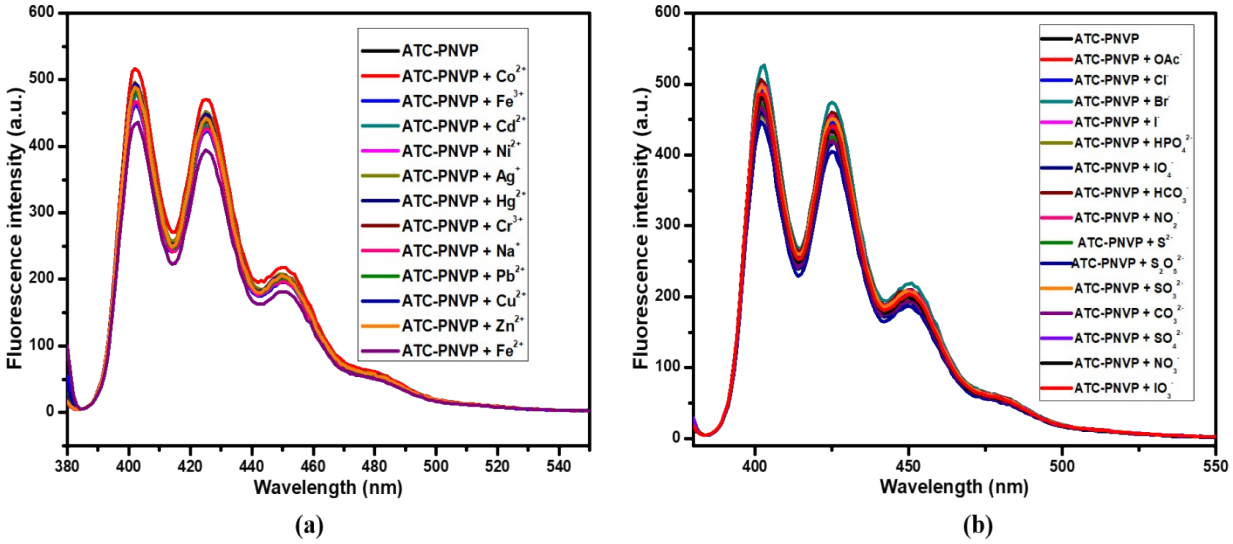


**Figure S7.** Fluorescence responses of ATC-PNVP (500 µL, 1 x $10^{-5}$ M) in the presence of (a) different organic compounds (each 5 µL, 1 x $10^{-3}$ M), (b) different metal ions (each 5 µL, 1 x $10^{-3}$ M), and (c) different anions (each 5 µL, 1 x $10^{-3}$ M) at $\lambda_{ex}$ = 374 nm.

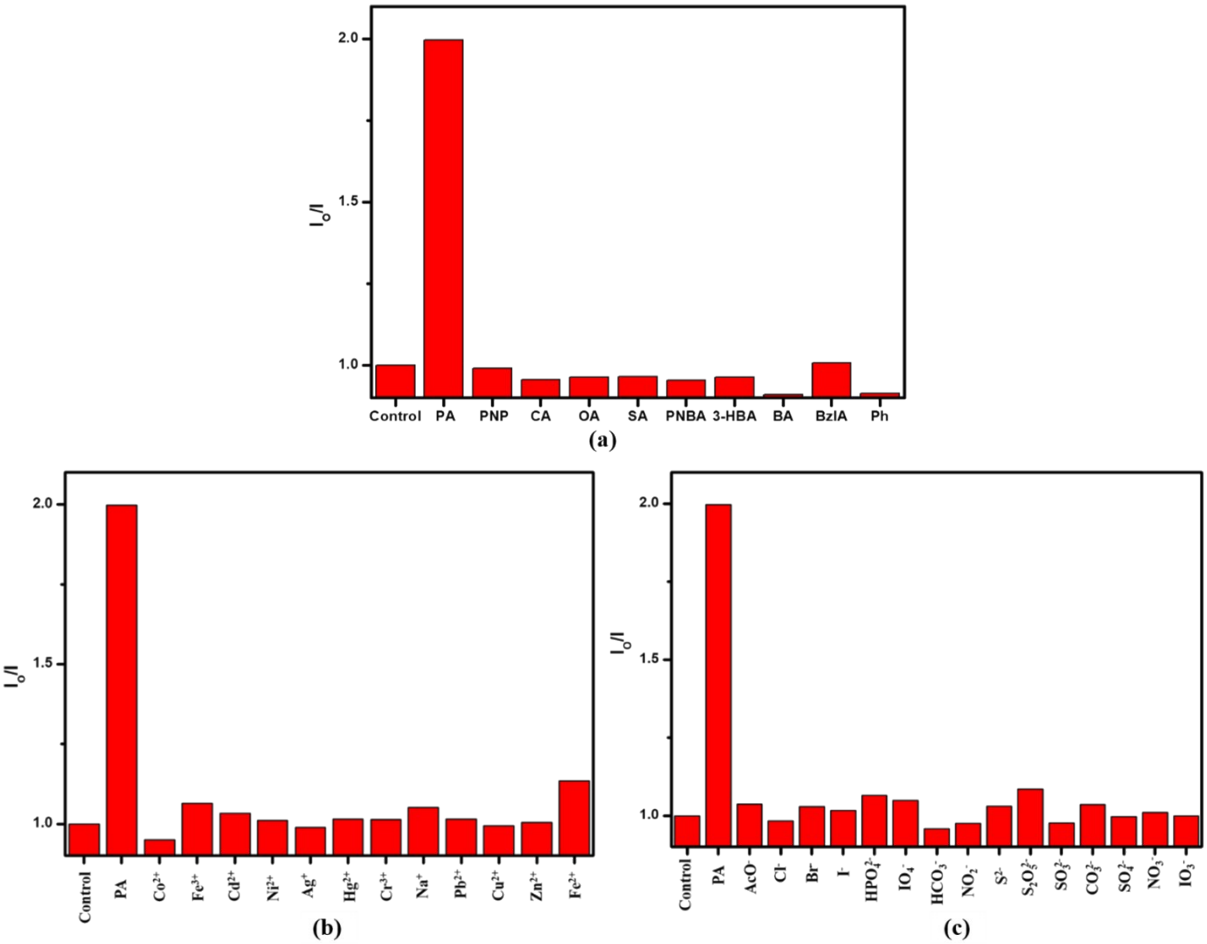


**Figure S8.** Effect of different analytes ( anions + PA, organic compounds + PA, metal ions + PA, interference of all analytes + PA; 1 x $10^{-4}$ M each in mixture, 5 µL added) on the fluorescence quenching of ATC-PNVP (500 µL, 1 x$10^{-5}$ M) by picric acid (PA).

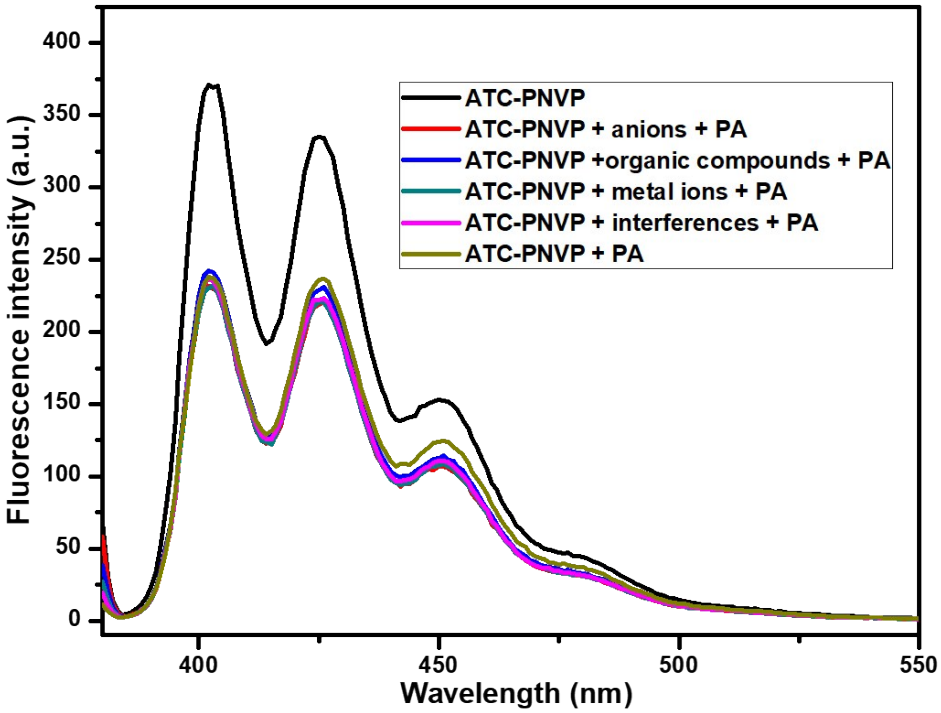


**Figure S9.** Steady state fluorescence titration of ATC-PNVP (500 µL, 1 x $10^{-5}$ M) using picric acid (a) and the corresponding quenching efficiency plot (b) and Stern-Volmer plot (c) at 27 ˚C. Steady state fluorescence titration of ATC-PNVP (500 µL, 1 x $10^{-5}$ M) using picric acid (d) and the corresponding quenching efficiency plot (e) and Stern-Volmer plot (f) at 37 ˚C.

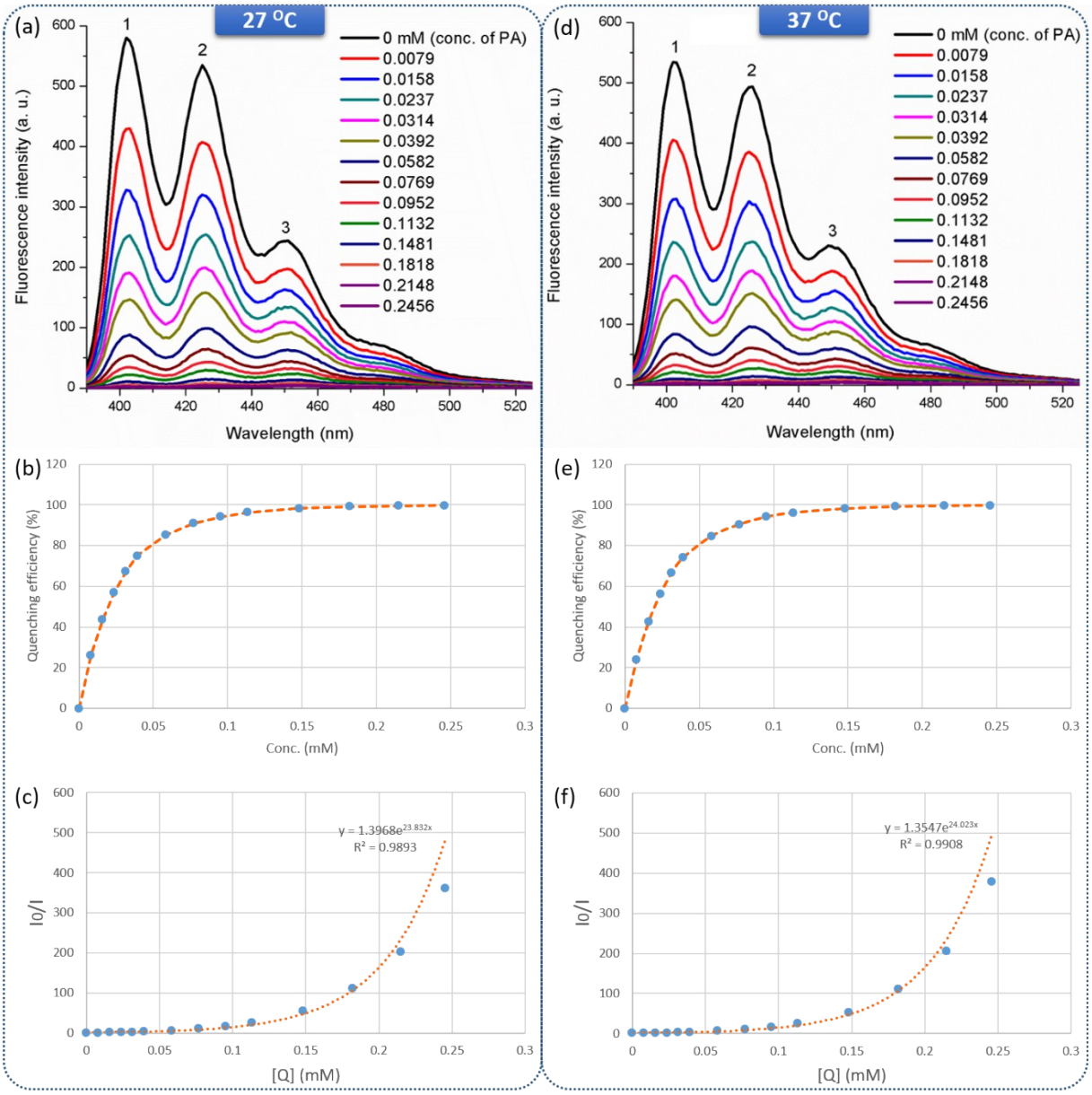
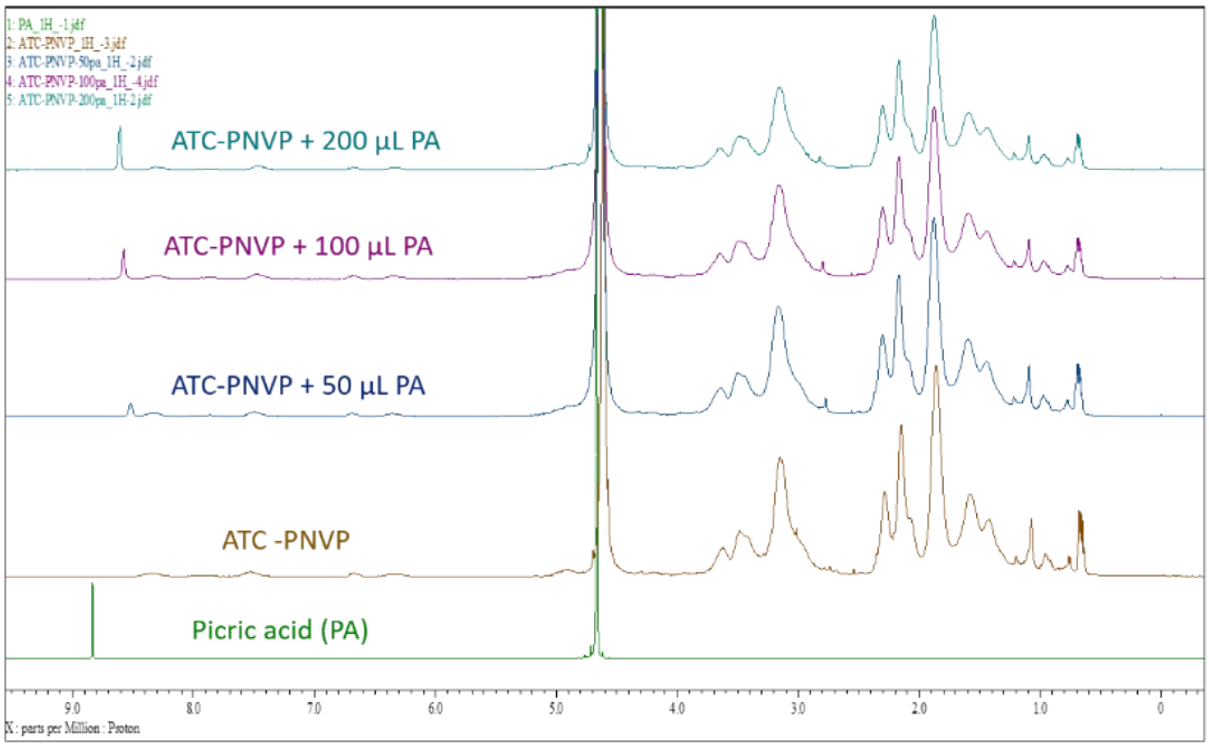
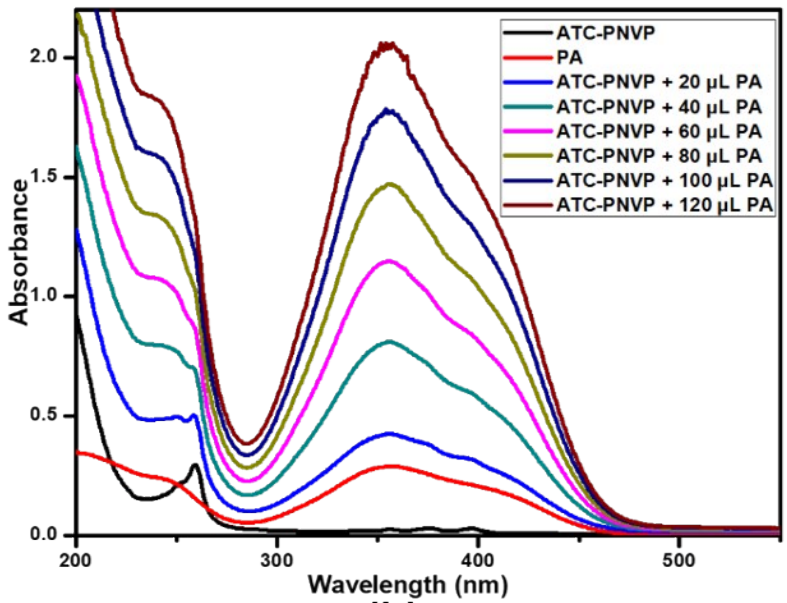


**Figure S10.** (a) $^{1}H$ NMR spectra (in $D_2O$) of picric acid ($5 \times 10^{-2}$ M) alone and ATC-PNVP (500 µL, $10^{-2}$ M) upon addition of 0, 50, 100 and 200 µL picric acid ($5 \times 10^{-2}$ M) and (b) UV-Visible spectra of picric acid ($1 \times 10^{-5}$ M) alone and ATC-PNVP (500 µL, $10^{-5}$ M) with increasing amounts of picric acid (1 x $10^{-3}$ M).




(a)




(b)

**Figure S11.** Fluorescence spectra of ATC- PNVP before and after addition of picric acid (PA) and triethyl amine (TEA).

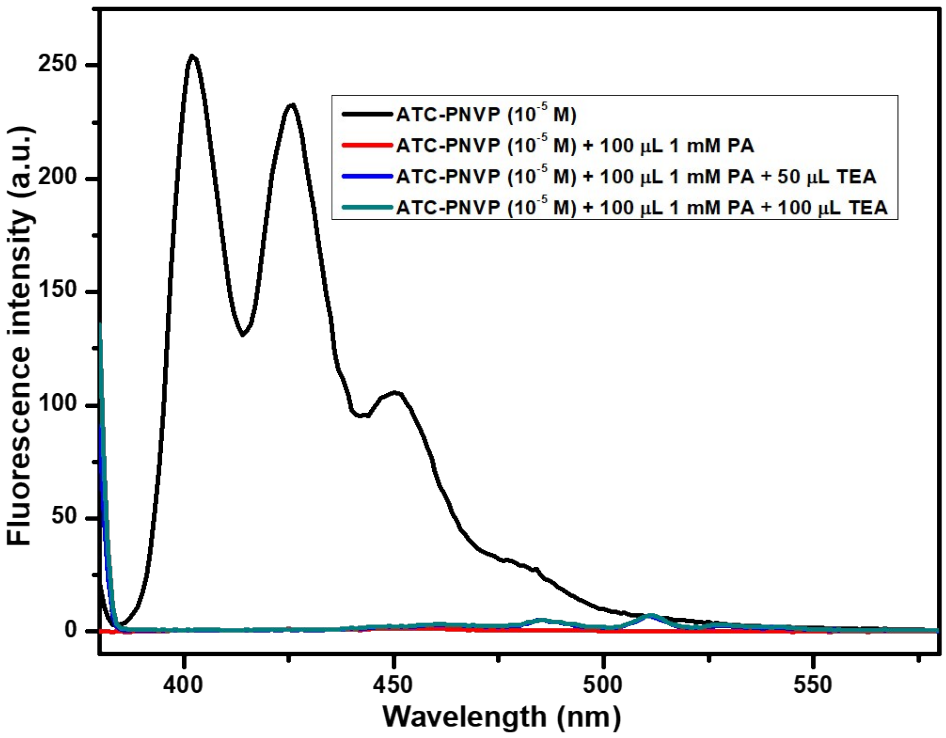



**Figure S12.** Fluorescence spectra of ATC- PNVP in presence and absence of trifluoroacetic acid (TFA) or, picric acid (PA).

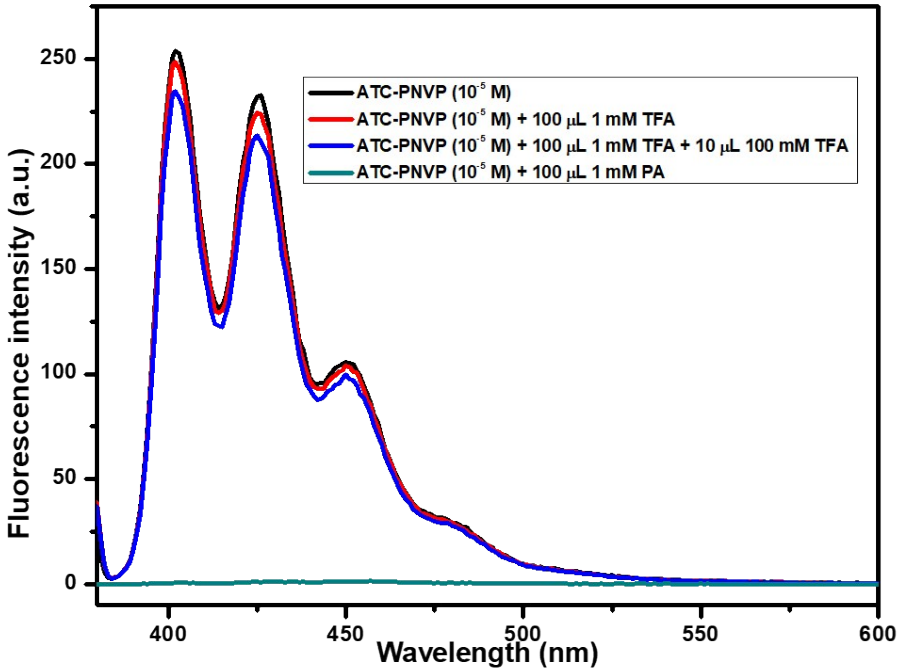


**Figure S13.** Overlap of absorption spectrum of picric acid (1 x $10^{-5}$ M) and fluorescence spectrum of ATC- PNVP (1 x $10^{-5}$ M).

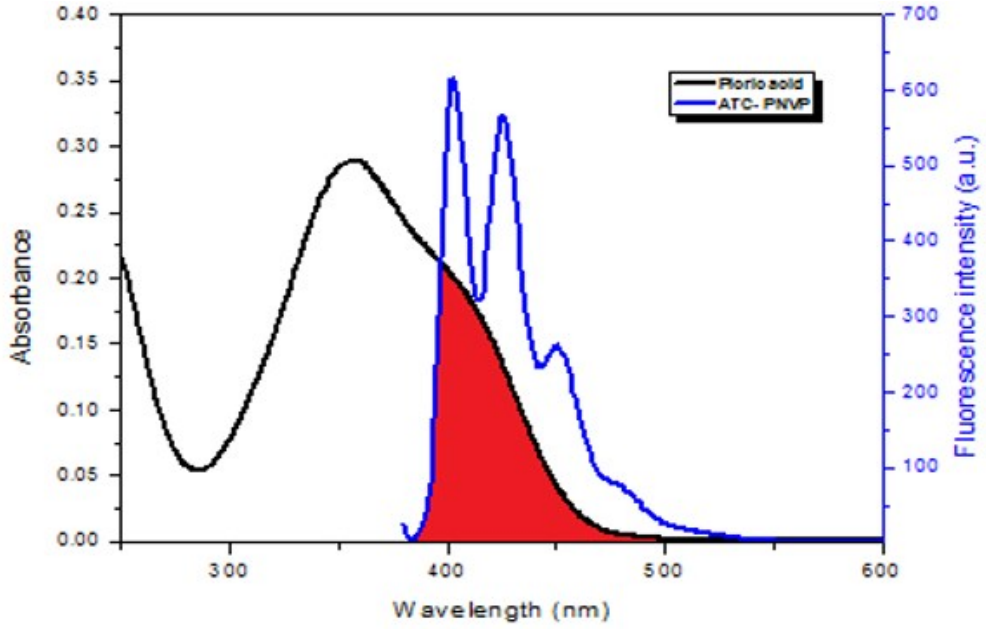



**Figure S14.** Concentration *vs.* $I_0/I$ plot of fluorescence quenching of ATC-PNVP by different concentrations of picric acid (0.002 - 2.0 mM; 50 µL each) for calibration [considering peak at ~402 nm, Fig. 5 (a)].

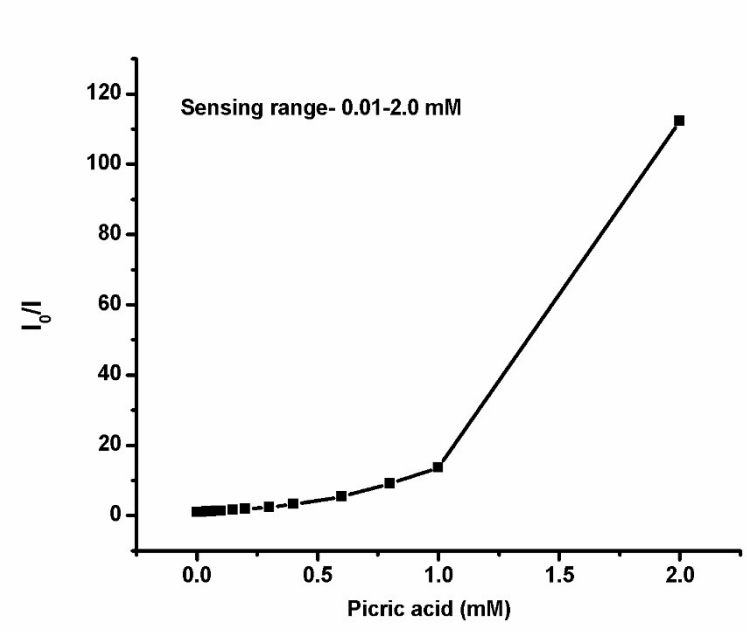


**Table S1.** Standard addition experiment - estimation of picric acid of different concentrations (added 50 μL each) using ATC-PNVP (500 μL, $10^{-5}$ M).

| Sl. No. | Std. solution of PA (mM) | PA measured (mM) | Recovery* (%) | Relative Standard# Deviation (%) |
|---|---|---|---|---|
| **1** | 0.004 | Not detected | NA | NA |
| **2** | 0.114 | 0.1045 | 91.66 | 2.960 |
| **3** | 0.238 | 0.226 | 95.35 | 2.214 |
| **4** | 0.300 | 0.306 | 102.00 | 2.647 |
| **5** | 0.476 | 0.590 | 124.00 | 2.745 |
| **6** | 0.666 | 1.806 | 271.00 | 0.470 |

*Recovery= (Std. concentration/determined concentration) x 100.

#Relative standard deviation = (Standard deviation/ average value) x 100. (n=3).

**Table S2.** Comparison table of some previously reported anthracene based and polymer basedsensors for the detection of picric acid via fluorescence spectroscopy.

| Sl. No. | Sensor material | Linearity/ detec-tion range (μM) | Limitof detection (LOD) (M) | Solvent | Ref. (correspon ding no. in article) |
|---|---|---|---|---|---|
| **1.** | N'-(anthracen-9-ylmethylene) isonicotinohydrazide | 5.0-50 | $4.3 \times 10^{-7}$ | DMF | 1 (23) |
| **2.** | 9-Anthracenecarboxamide | 1-100 | $1.0 \times 10^{-6}$ | Ethanol | 2 (24) |
| **3.** | 2-(anthracen-9-yl methylene ) N-phenylhydrazinecarbo-thioamide | - | $1.0 \times 10^{-7}$ | Acetonitrile-water | 3 (25) |
| **4.** | 6-(10-(naphthalen-2-yl)anthracen-9-yl)-2-phenyl-1H-benzo[de] isoquinoline-1,3(2H)-dione | - | $4.7 \times 10^{-7}$ | THF-water | 4 (26) |
| **5.** | (7E,19E)-N-((anthracen-10-yl)methylene)-N′-((anthracen-9-yl)methylene) propane-1,3-diamine copper complex | - | $1.45 \times 10^{-6}$ | THF-HEPES | 5 (28) |
| **6.** | Lanthanide based coordination polymer | - | $9.8 \times 10^{-5}$ | $CHCl_3$ | 6 (31) |
| **7.** | Microporous polymer based on fluorescein | | $7.22 \times 10^{-7}$ | THF | 7 (32) |
| **8.** | Poly(3,3′-((2-phenyl-9H-fluorene-9,9-diyl) bis(hexane-6,1-diyl))bis (1-methyl-1H-imidazol -3-ium)bromide) nanoparticles | - | $3.09 \times 10^{-11}$ | Water | 8 (33) |
| **9.** | Poly(ethylenimine) dendrimer−D-glucose Schiff base conjugate (PEI-G) polymer nanoparticles | 0.05-1 and 2-70 | $26.0 \times 10^{-11}$ | Britton−Robi nson (BR) buffer-Water | 9 (34) |
| **10.** | Polydiacetylene microtubes | 0.5-20 | $0.48\times 10^{-6}$ | Water | 10 |
| **11.** | Coordination polymer$\{[Zn_2(L)(5\text{-}AIP)_2].3H2O\}_n$ | 0.2-1.2 | $0.70\times 10^{-6}$ | Water | 11 |
| **12.** | Terbium (III) coordination polymer | 0-1000 | $1\times 10^{-8}$ | Water | 12 |
| ***13.*** | ***ATC-PNVP*** | ***10–300*** | ***$6 \times 10^{-6}$*** | ***Water*** | ***This work*** |

**Figure S15.** (a) Typical paper disc prepared for paper based sensor fabrication. (b) Response of paper discs upon adsorption of ATC-PNVP of different concentrations (1 x $10^{-7}$-1x $10^{-4}$ ; 5 µL each). (c) Effect of the mixture of different inorganic salts [$Cu(OAc)_2$, $HgCl_2$, $Na_2HPO_4$, $PbNO_3$, $FeSO_4$; 0.1 mM each in the mixture; 4 µL of mixture added] and the mixture of organic analytes (*p*-nitrophenol, oxalic acid, *p*-nitrobenzoic acid, benzylic acid, and phenol; 0.1 mM each in the mixture; 4 µL of mixture added) on the paper sensors and their interference (inorganic salts + PA and organic analytes + PA, 0.1 mM each in the mixture; 4 µL of mixture added) to the fluorescence quenching by picric acid.

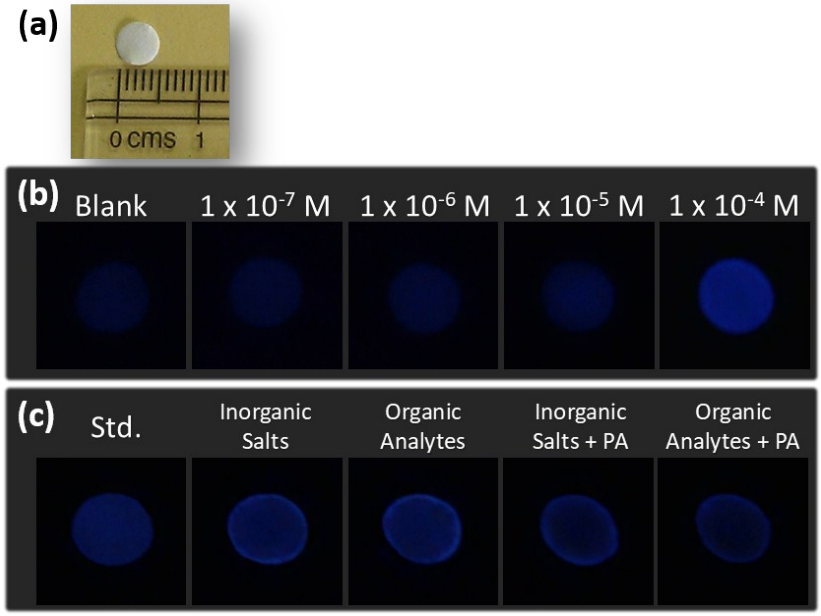



**Figure S16.** (a) Steady state fluorescence spectra of BSA (500 µL, 0.2 mg/mL) with increasing amounts of ATC-PNVP ($\lambda_{ex}$ = 280 nm) at 37 ºC and (b) the corresponding Stern-Volmer plot.

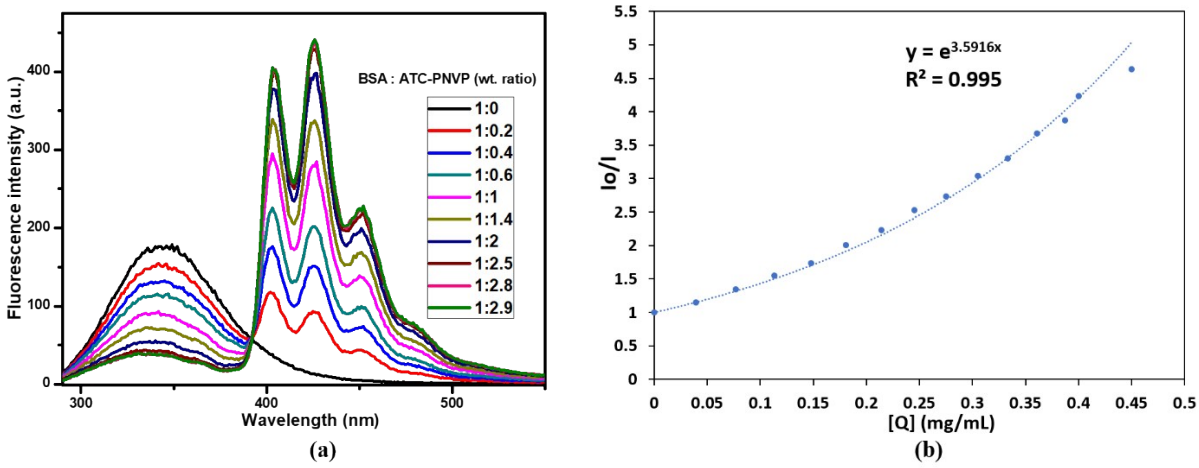


**Figure S17.** Synchronous fluorescence spectra of BSA (0.2 mg/mL) with increasing amounts of anthracene-bridged PNVP at (a) $\Delta\lambda$ = 15 nm and (b) $\Delta\lambda$ = 60 nm.

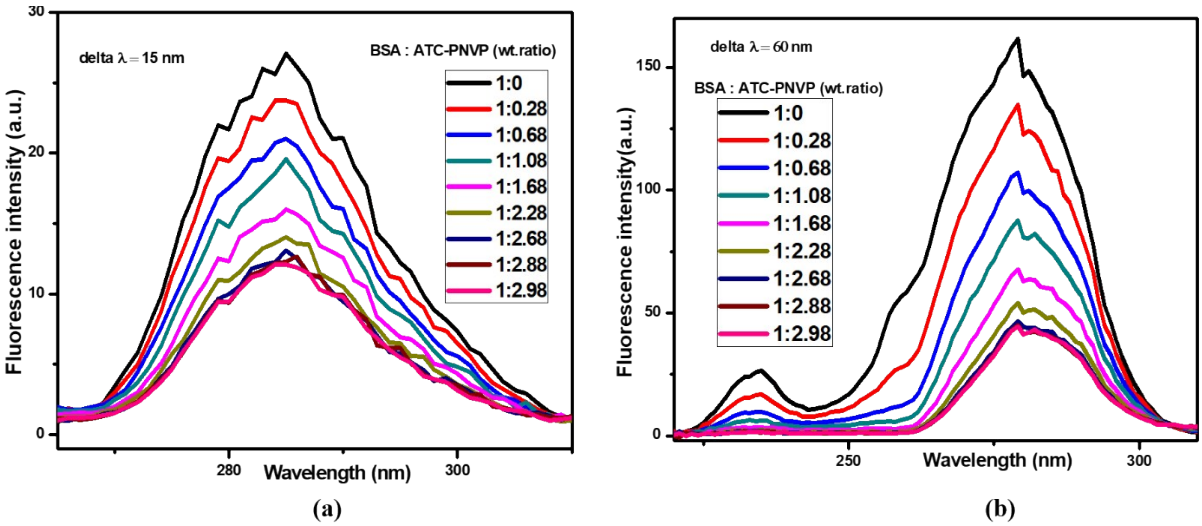


**Figure S18.** (a) 3D fluorescence spectra of BSA (0.2 mg/mL). (b) 3D fluorescence spectra of BSA and ATC-PNVP after saturation (BSA: ATC-PNVP = 1 : 2.98 wt ratio).

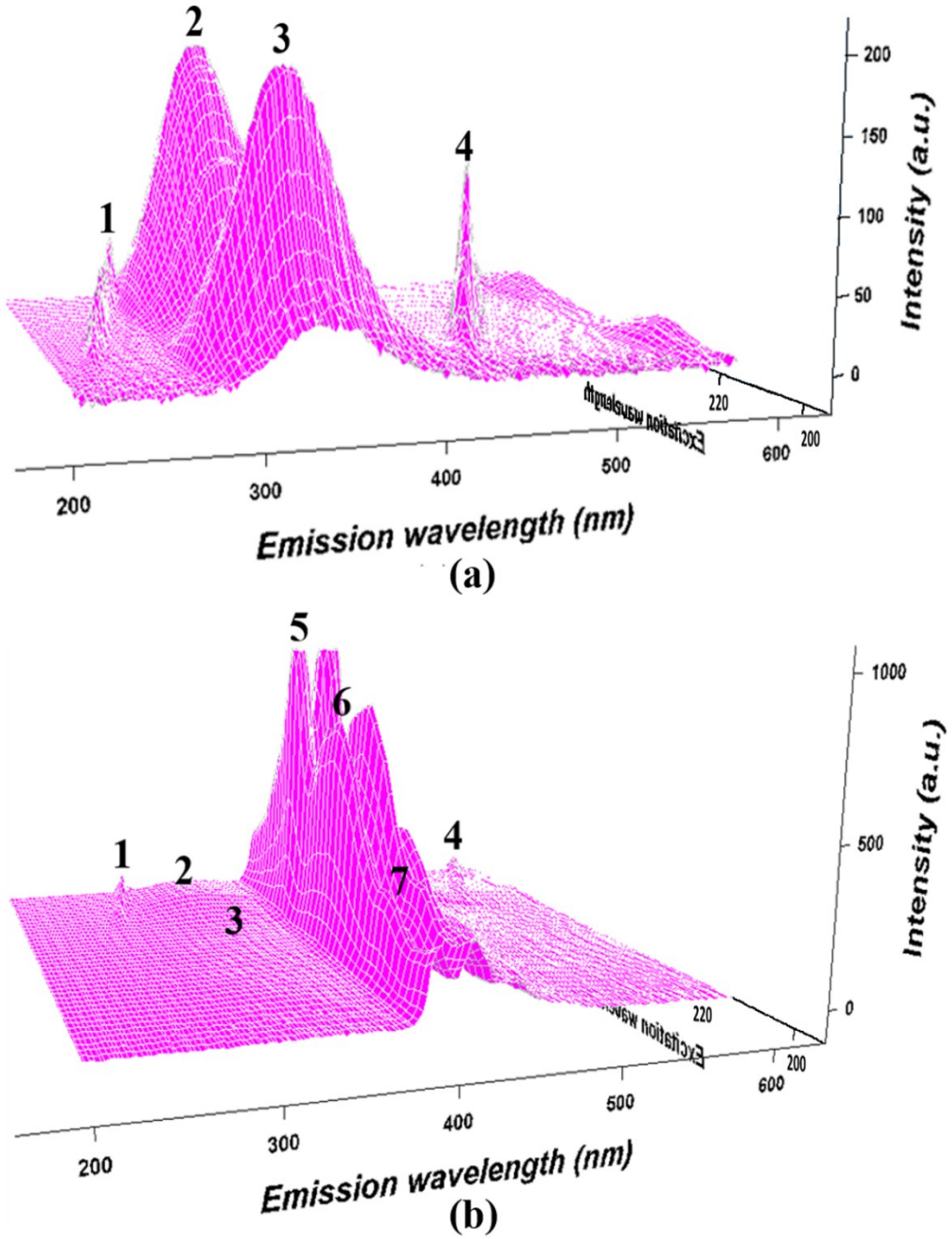


**Figure S19.** Overlap of the absorption spectrum of ATC-PNVP (blue line) (0.2 mg/mL) with the fluorescence emission spectrum of BSA (black line) (0.2 mg/mL).

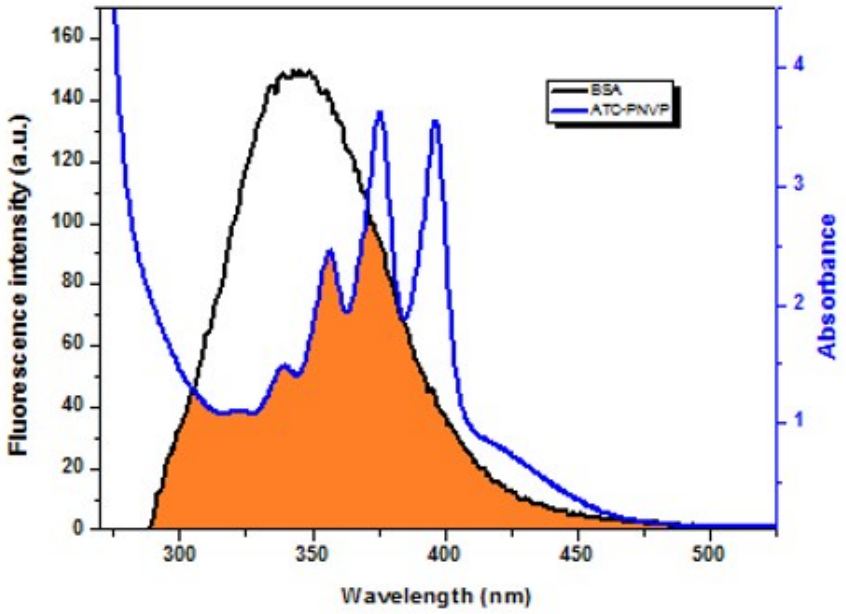
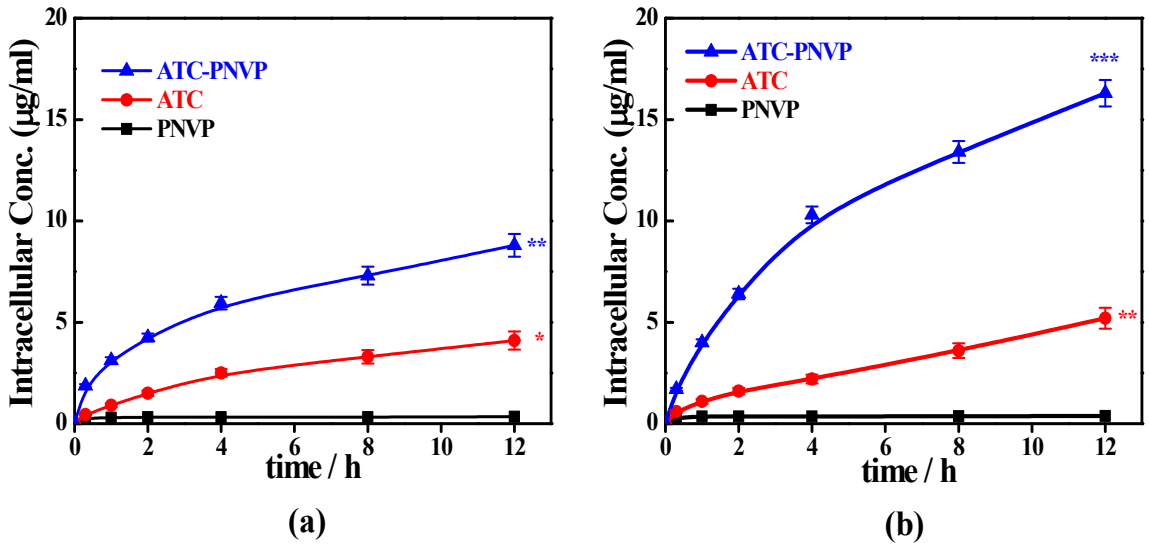



**Figure S20.** Quantitative analysis for the intercellular uptake of the samples in **(a)** NIH-3T3 and **(b)** HeLa cells after treatment with ATC, PNVP and ATC-PNVP (0.2 mg/mL concentration each). Data represent mean ± SD obtained from three different experiments, where *p < 0.05, **p < 0.01, ***p < 0.001.



**Reference:**


(1) Peng, Y.; Zhang, A. J.; Dong, M.; Wang, Y. W. A Colorimetric and Fluorescent Chemosensor for the Detection of an Explosive 2,4,6-Trinitrophenol (TNP). *Chem. Commun*. **2011,** *47*, 4505-4507.

(2) Pandith, A.; Kumar, A.; Lee, J. Y.; Kim, H. S. 9-Anthracenecarboxamide Fluorescent Probes for Selective Discrimination of Picric Acid from Mono- and Di-nitrophenols in Ethanol. *Tetrahedron Lett*. **2015**, *56*, 7094-7099.

(3) Udhayakumari, D.; Velmathi, S.; Venkatesan, P.; Wu, S. P. Anthracene Coupled Thiourea as a Colorimetric Sensor for $F^-$ / $Cu^{2+}$ and Fluorescent Sensor for $Hg^{2+}$ / Picric Acid. *J. Luminescence* **2015**, *161*, 411-416.

(4) Ma, H.; He, C.; Li, X.; Ablikim, O.; Zhang, S.; Zhang, M. A Fluorescent Probe for TNP Detection in Aqueous Solution Based on Joint Properties of Intramolecular Charge Transfer and Aggregation-Induced Enhanced Emission. *Sens. Actuators B***2016**, *230*, 746-752.

(5) Reddy, K. L.; Anabathula, M. K.; Dhir, A.; Krishnan, V. Selective and Sensitive Fluorescent Detection of Picric Acid by New Pyrene and Anthracene Based Copper Complexes. *J. Fluorescence* **2016**, *26*, 2041-2046.

(6) Srivastava, S.; Gupta, B. K.; Gupta, R. Lanthanide-Based Coordination Polymers for the Size-Selective Detection of Nitroaromatics. *Cryst. Growth Des*. **2017**, *17*, 3907-3916.

(7) Geng, T. M.; Ye, S. N.; Wang, Y.; Zhu, H.; Wang, X.; Liu, X. Conjugated Microporous Polymers-Based Fluorescein for Fluorescence Detection of 2,4,6-Trinitrophenol. *Talanta***2017**, *165*, 282-288.

(8) Malik, A. H.; Hussain, S.; Kalita, A.; Iyer, P. K. Conjugated Polymer Nanoparticles for the Amplified Detection of Nitro-explosive Picric Acid on Multiple Platforms. *ACS Appl. Mater. Interfaces* **2015**, *7*, 26968-26976.

(9) Liu, S. G.; Luo, D.; Li, N.; Zhang, W.; Lei, J. L.; Li, N. B.; Luo, H. Q. Water-Soluble Nonconjugated Polymer Nanoparticles with Strong Fluorescence Emission for Selective and Sensitive Detection of Nitro-Explosive Picric Acid in Aqueous Medium. *ACS Appl. Mater. Interfaces* **2016**, *8*, 21700-21709.

(10) Yang, G.; Hu, W.; Xia, H.; Zou, G.; Zhang, Qijin. Highly Selective and Reproducible Detection of Picric Acid in Aqueous Media, Based on a Polydiacetylene Microtube Optical Waveguide. *J. Mater. Chem. A***2014**, 2, 15560-15565.

(11) Das, D.; Biradha, K.Luminescent Coordination Polymers of Naphthalene Based Diamide with Rigid and Flexible Dicarboxylates: Sensing of Nitro Explosives, Fe(III) Ion and Dyes. *Cryst. Growth Des*. **2018**, 18, 3683-3692.

(12) Yang, Y.; Song, X.; Xu, C.; Wang, Y.; Zhang, G.; Liu, W. A Multifunctional and Recyclable Terbium (III) CoordinationPolymer: Displaying Highly Selective and Sensitive Detection of $Fe^{3+}$, $Cr^{VI}$ anions, and Picric Acid in Aqueous Media. *Dalton Trans*. **2018**, 47, 11077-11083.