# Electronic Supplementary Information

# Selective Recognition of Biologically Important Anions Using a Diblock Polyfluorene-Polythiophene Conjugated Polyelectrolyte

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## 1. Supporting Experimental Data

### 1.1 Photoluminescence (PL) spectra

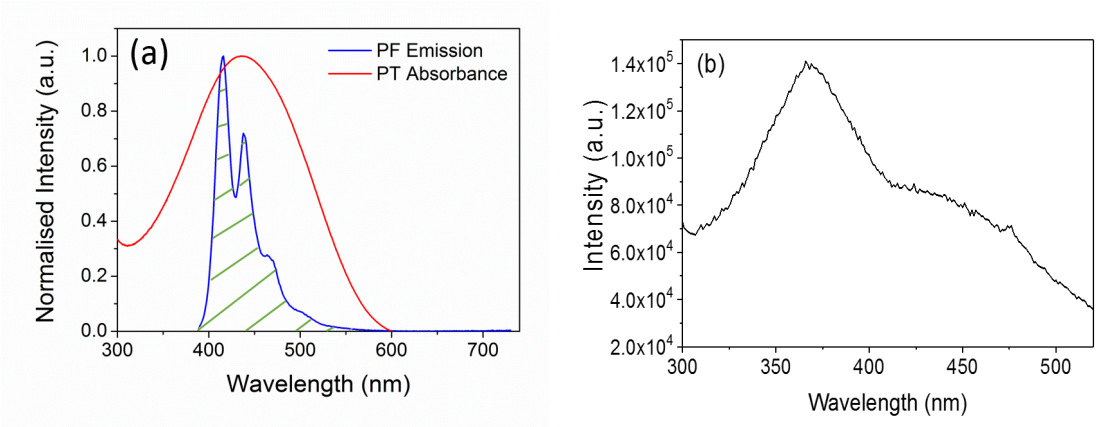


**Figure S1.** (**a**) Spectral overlap between the emission spectrum of **PF2/6** (blue line, $\lambda_{ex}$ = 370 nm in THF) and UV/Vis absorption spectrum of **P3TMAHT** (red line $\lambda_{ex}$ = 430 nm in aqueous solution). The green shaded regions highlight the spectral overlap. (**b**) PL excitation ($\lambda_{em}$ = 570 nm) spectrum for **PF2/6-*b*-P3TMAHT** in aqueous solution ($1.06 \times 10^{-6}$ M).

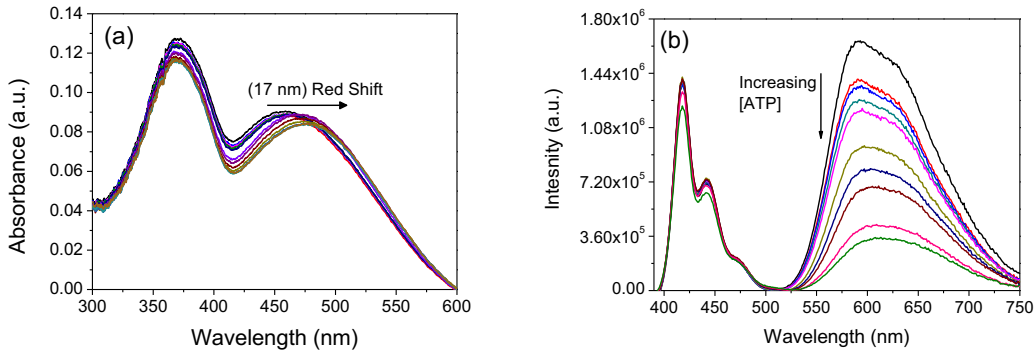


**Figure S2.** (**a**) UV/Vis absorption and (**b**) PL spectra ($\lambda_{ex}$ = 380 nm) for **PF2/6-*b*-P3TMAHT** in aqueous solution in the presence of increasing concentration of **ATP** (0 – 38 μM).

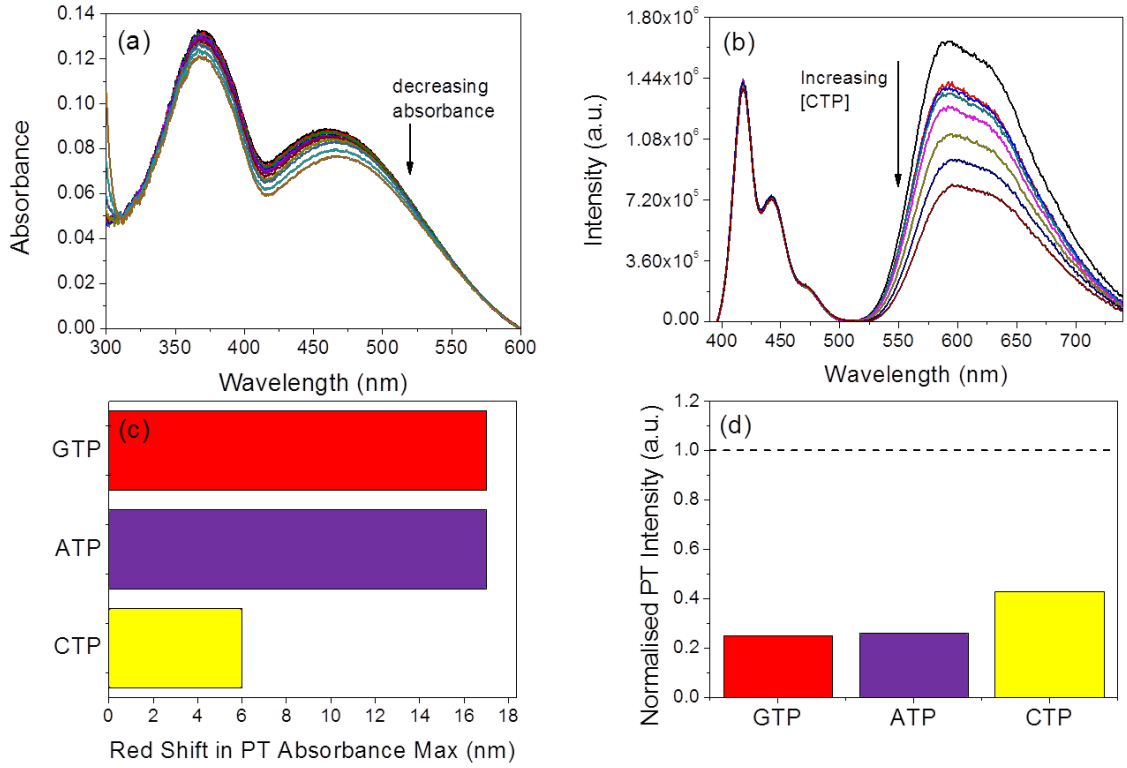


**Figure S3.** (**a**) UV/Vis absorption and (**b**) PL spectra ($\lambda_{ex}$ = 380 nm) for **PF2/6-*b*-P3TMAHT** in aqueous solution in the presence of increasing concentration of **CTP** (0 – 38 μM). (**c**) Magnitude of the shift in the PT absorption maximum and (**d**) intensity of the PT emission on addition of an excess of **GTP**, **ATP** and **CTP** normalised relative to the initial PT emission intensity. The black dashed line serves only to guide the eye, indicating the relative intensity of the initial PT emission.

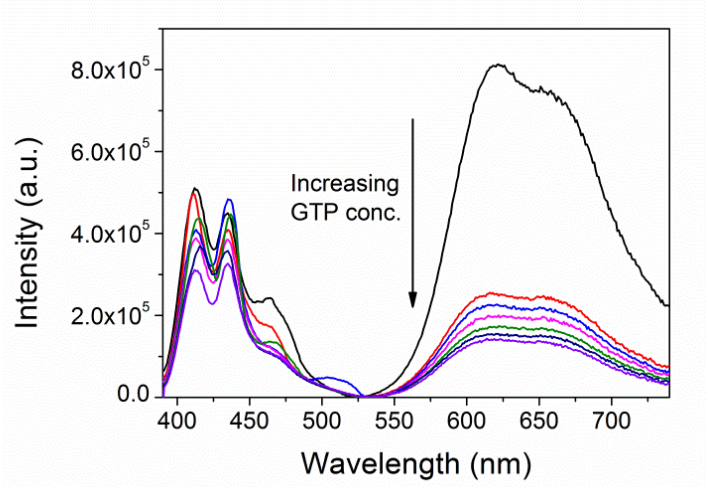


**Figure S4.** PL spectra ($\lambda_{ex}$ = 380 nm) for **PF2/6-*b*-P3TMAHT** in Tris buffer solution (100 mM, pH = 7.4) in the presence of increasing concentration of **GTP**.

## 1.2 Isothermal calorimetry

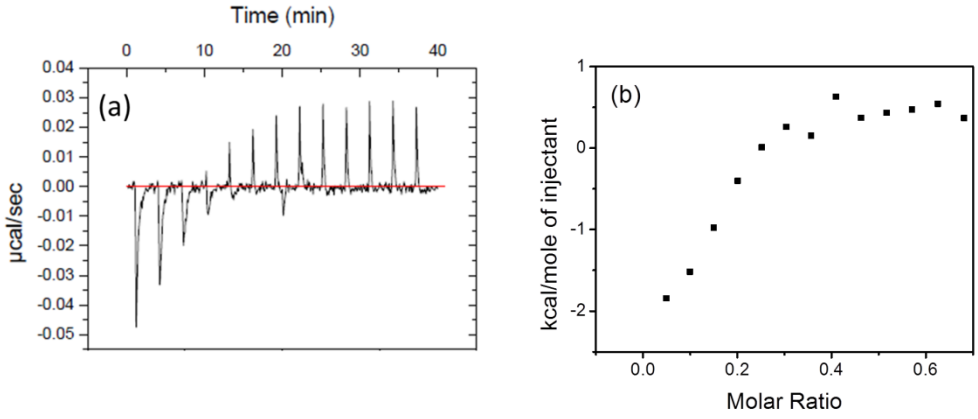


**Figure S5.** (**a**) Thermogram and (**b**) differential enthalpy curve for the titration of **GTP** (300 µM) into **P3TMAHT** (60 µM) at 20 °C. This plot represents heat evolved vs. molar ratio for injecting GTP into a **P3TMAH**T solution which has been corrected for the contribution of the heat of dilution of the **GTP**. Molar ratio refers to the ratio of the **GTP** concentration to the concentration of **P3TMAHT** repeat units.

Isothermal titrations allow direct observation of the binding enthalpy ($\Delta H^0$) and derivation of entropy and $K_a$ (association constant) from curve fitting and the free energy relationship, $\Delta G^0=\Delta H^0-T\Delta S^0= -RTlnK_a$.[1] The resulting thermodynamic parameters were calculated assuming a single set of equivalent binding sites and are displayed in **Table S1**. For each titration, the heat released or absorbed, $q$, is given by:[2]

$$q = V\Delta H\Delta[L_B] \qquad (1)$$

where $\Delta[L_B]$ is the change in the bound nucleotide concentration, $\Delta H$ is the change in enthalpy and $V$ is the volume of the reaction. The total cumulative heat released or absorbed, $Q$, is directly proportional to the total amount of the bound ligand:

$$Q = V\Delta H\sum\Delta[L_B] = V\Delta H[L_B] \qquad (2)$$

where $[L_B]$ is the concentration of bound nucleotide. For a system exhibiting a single set of equivalent, independent binding sites the concentration of bound nucleotide is given by:

$$[L_B] = [M]\frac{nK_a[L]}{1+K_a[L]} \qquad (3)$$

where [$M$] is the concentration of CPE capable of binding the nucleotide, $K_a$ is the CPE-nucleotide association constant, $n$ is the number of binding sites and [$L$] is the concentration of the free nucleotide. Thus, by substituting **Eqn. 3** into **Eqn. 2,** the cumulative heat released can be expressed as:

$$Q = V[M]\sum \frac{n\Delta H K_a[L]}{1 + K_a[L]} \qquad (4)$$

which can be related to the total ligand concentration by way of the mass conservation expression $[L_T]=[L_B]+[L]$, where $[L_T]$ is the total nucleotide concentration. Fitting to the calorimetric data provides values for $n$, $K_a$ and $\Delta H$.

**Table S1** Thermodynamic parameters of the interaction between **GTP** and **P3TMAHT**.

| **Anion** | **Number of binding sites, *n*** | **Binding constant, $K_a$ ($M^{-1}$)** | **$\Delta H^0$ (kJ mol$^{-1}$)** | ***T*** **(K)** | **$\Delta S^0$ (kJ mol$^{-1}$ K$^{-1}$ )** | **$\Delta G^0$ (kJ mol$^{-1}$)** |
|---|---|---|---|---|---|---|
| GTP | 0.152 ±0.009 | $1.2\times10^6\pm5\times10^5$ | -10.3±0.9 | 293 | 0.082±0.002 | -34.3±0.9 |

## 1.3 Stern-Volmer analysis

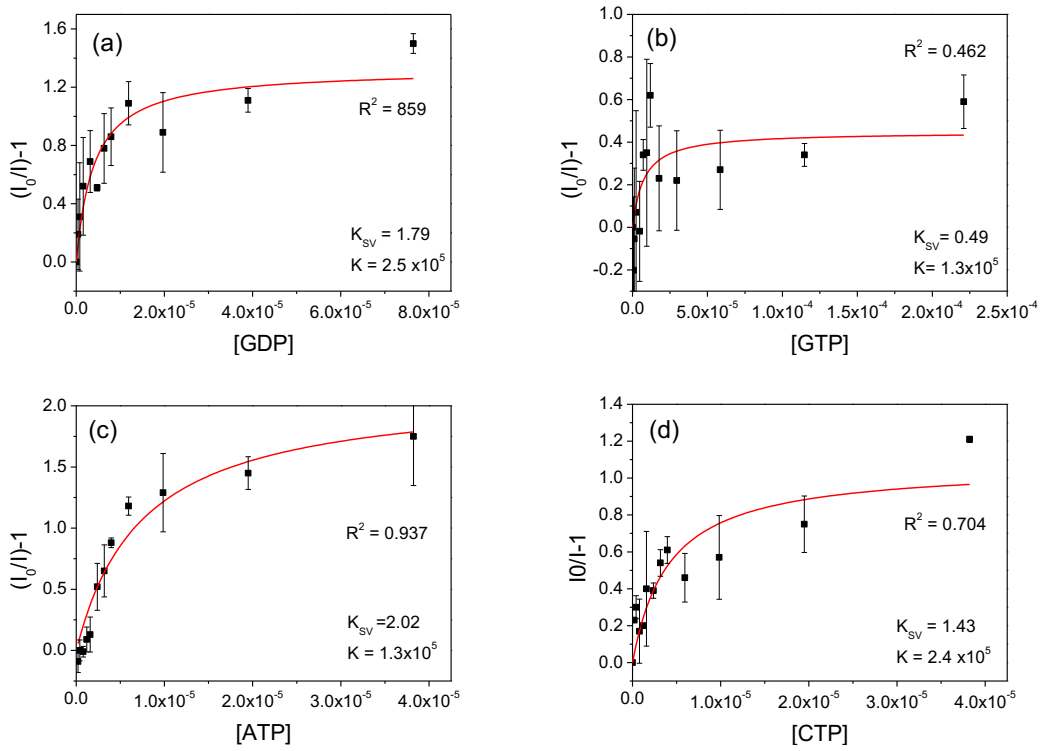


**Figure S6.** Fit to a multi-equilibrium model (**Eqn. 6**) of modified Stern-Volmer plot for fluorescence quenching of **PF2/6-*b*-P3TMAHT** ($\lambda_{ex}$ = 380 nm) by (**a**) **GDP** (**b**) **GMP** (**c**) **ATP** and (**d**) **CTP**.

## 1.4 Electrochemical measurements

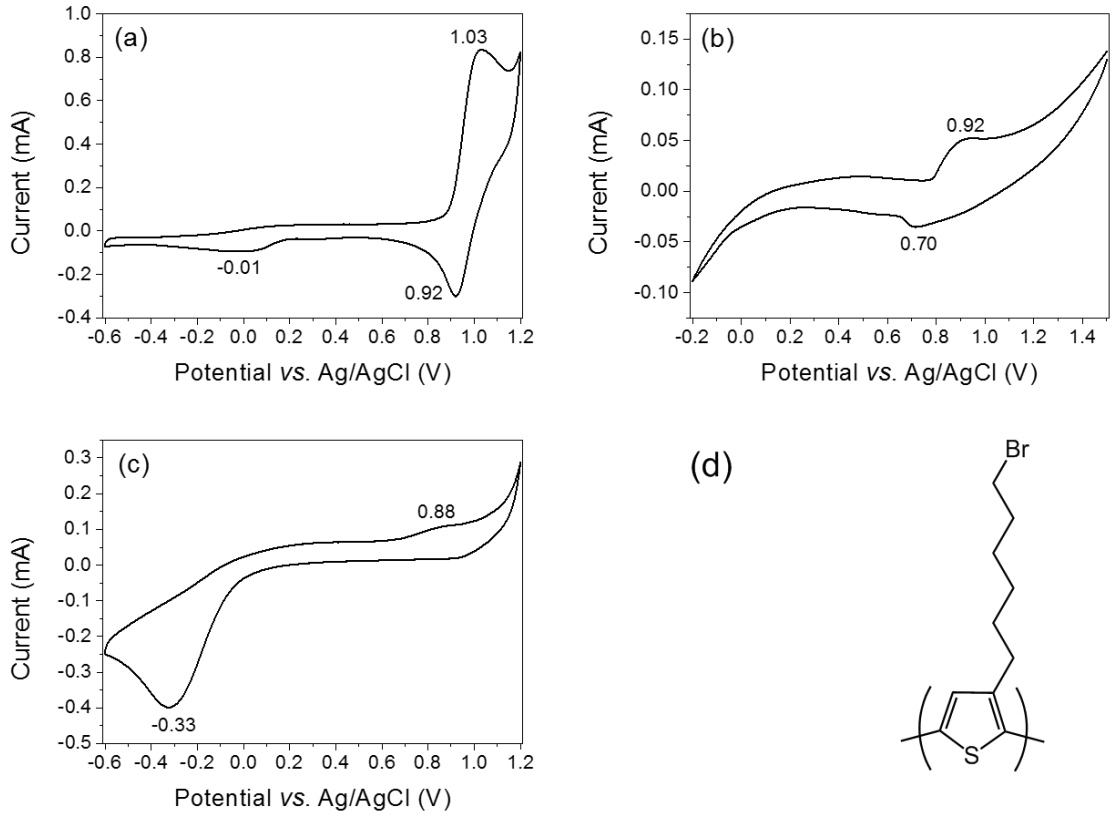


**Figure S7.** Cyclic voltammograms for (**a**) **P3TMAHT** in $H_2O$,(**b**) homopolymer precursor with bromohexyl side chains, **P3BrHT**, in THF (**c**) **PF2/6-*b*-P3TMAHT** in THF/$H_2O$ 20:80 (*v/v*) and at 50 mV $s^{-1}$ scan rate using Pt as the working and counter electrode, Ag/AgCl as reference electrode and KCl (0.1 M) as the supporting electrolyte for the aqueous solutions and tetrabutylammonium hexafluorophosphate (0.1 M) as the supporting electrolyte for the THF solution. (**d**) Chemical structure of the polythiophene precursor with bromohexyl side chains, **P3BrHT**.

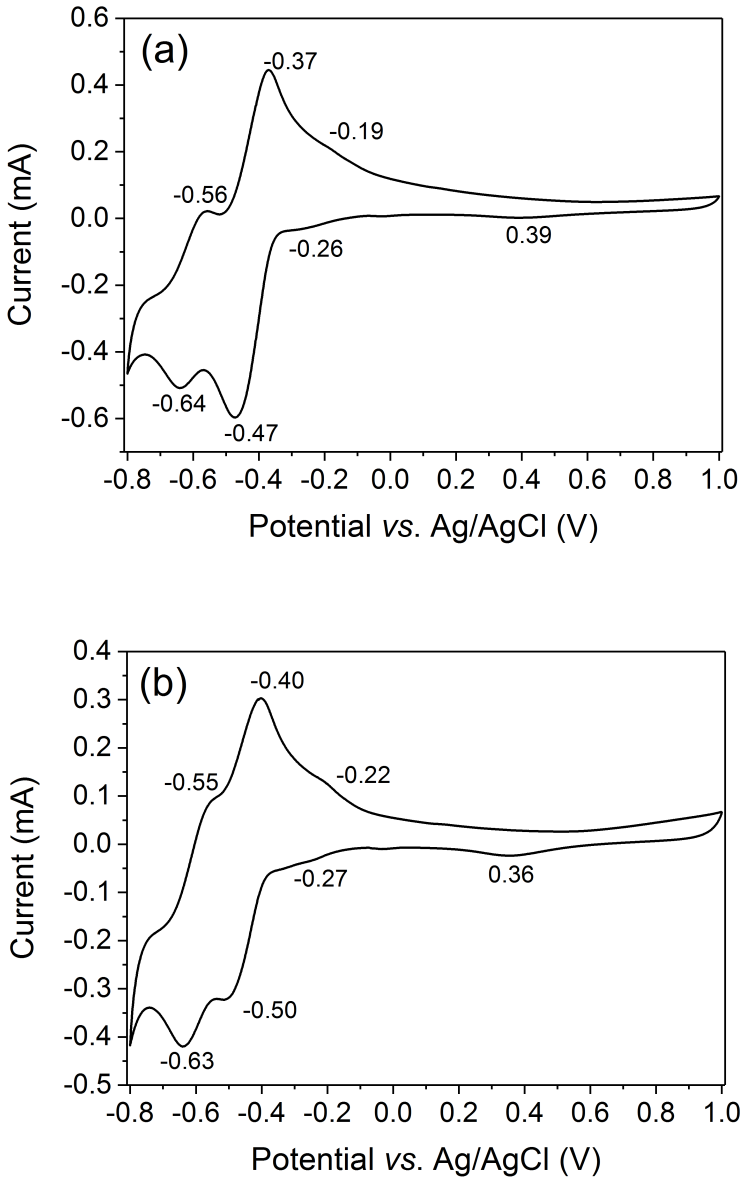


**Figure S8.** Cyclic voltammogram in $H_2O$ at 50 mV $s^{-1}$ using Pt as the working and counter electrode, Ag/AgCl as reference electrode and KCl (0.1 M) as the supporting electrolyte for (**a**) **ATP** and (**b**) **CTP**.

## References

1. P. S. Nagle, S. J. Quinn, J. M. Kelly, D. H. O'Donovan, A. R. Khan, F. Rodriguez, B. Nguyen, W. D. Wilson and I. Rozas, *Org. Biomol. Chem.*, 2010, **8**, 5558–5567.

2. E. Freire, O. L. Mayorga and M. Straume, *Anal. Chem.*, 1990, **62**, 950-959.