Supporting Information

Switching the recognition ability of a photoswitchable receptor towards phosphorylated anions

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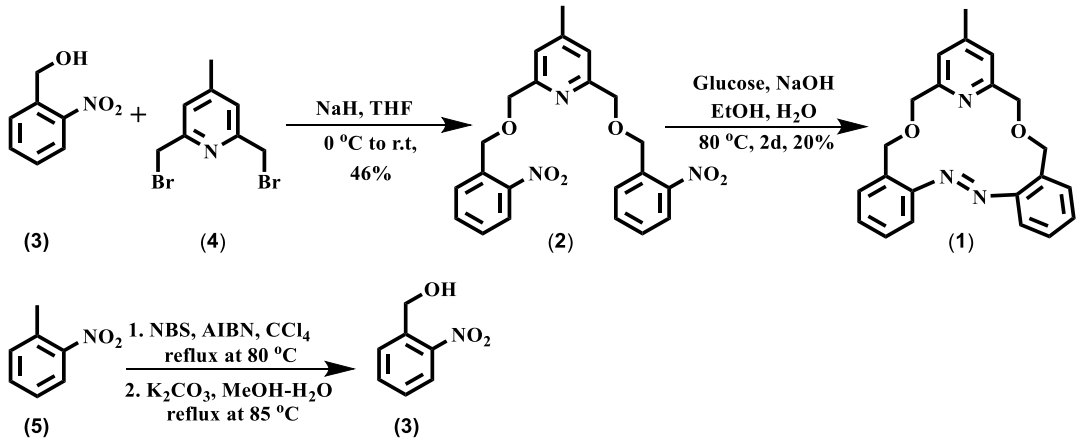
General methods:

All reagents and solvents for synthesis were purchased commercially and used without further purification. Tetrahydrofuran (THF) was pre-dried over sodium metal in presence of benzophenone and then distilled. Column chromatography was performed on Merck silica gel (100 – 200 mesh). Thin layer chromatographies (TLCs) were carried out with E. Merck silica gel 60-F254 plates. Tris buffer, metal salts and all the phosphate derivatives were purchased of molecular biology grade from Sigma. Double distilled water was used for all the spectroscopic experiments. Yields are indicates to the chromatographically and spectroscopically pure compounds, except as otherwise indicated.

Physical measurements:

The ^{1}H NMR spectra were recorded on 400 MHz JEOL or 500 MHz Bruker spectrometer instruments. Similarly, ^{13}C NMR experiments were performed with 100 MHz Jeol and 125 MHz Bruker instruments using either residual solvent signals as an internal reference or from internal tetramethylsilane on the δ scale. The chemical shifts (δ) were reported in ppm and coupling constants (*J*) in Hz. The following abbreviations were used: m (multiplet), s (singlet), d (doublet), t (triplet) dd (doublet of doublet). The solvents used for the spectroscopy experiments were of the spectroscopic grades and were free from any fluorescent impurities. UV spectra were recorded with an Agilent cary 60 UV-vis spectrophotometer. Fluorescence spectra were recorded from Fluoromax 3 from Horiba Jobin Yvon. All spectroscopic data were processed either by Origin 8.0 and Origin 18 program. ChemBio Draw 15 Ultra software was used for drawing structures and processing figures. HRMS data were obtained from an Acquity ultraperformance Bruker MaXis Impact liquid chromatography instrument by positive mode electrospray ionization (Q-TOF). The LRMS spectrometric data were obtained from an AcquityTM Ultra Performance LC-ESI/quadrupole-TOF MS. X-ray data were collected with Mo Kα radiation by a Bruker APEX-2 CCD diffractometer. The data were processed using Bruker SAINT Package. The structure solution and refinement were performed by SHELX97. FT-IR spectroscopy in the solid state was performed with a Perkin Elmer Spectrum RX1 spectrophotometer using KBr disk method and Melting point was measured with a Secor, India digital melting point apparatus in melting point tube. Optimized geometries were obtained from DFT calculation by using Gaussian 09 software.

Synthetic scheme:



Synthesis:

Synthesis of the cyclic azobenzene compound 1*E* ($C_{22}H_{21}N_3O_2$):

To a solution of glucose (800 mg, 4.49 mmol; in 5 mL water), compound **2** (190 mg, 0.449 mmol) in ethanol (20 mL) and NaOH (290 mg, 7.26 mmol) was added and the reaction mixture was then stirred for 48 h at 80 °C.[1] After completion of the reaction, ethanol was evaporated under reduced pressure and the reaction mixture was extracted with ethyl acetate, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by preparative TLC over silica gel G (eluent: ethyl acetate : hexane = 1:3 v/v) to furnish compound **1,** m.p.: 124-127 °C**, ^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.79 (d, *J* = 7.6 Hz, 4H), 7.66 (d, *J* = 7.6 Hz, 4H), 7.47 (t, *J* = 8.0 Hz, 4H), 7.38 (t, *J* = 8.0 Hz, 4H), 7.06 (s, 2H), 5.0 (s, 4H), 4.75 (s, 4H), 2.25 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 156.42, 150.86, 149.97, 134.69, 130.73, 128.52, 127.83, 123.67, 121.79, 73.65, 67.37, 29.61; **IR:** ν/cm^{-1} 2917, 2841, 1583, 1414, 1123, 1023, 686 **HRMS (ESI):** Calc. for $C_{22}H_{21}N_3O_2H^+$ (M+ H)$^+$: 360.1712; Found: 360.1715.

Synthesis of 2, 6-bis ((2-nitrobenzyloxy) methyl)-4-methylpyridine 2 ($C_{22}H_{21}N_3O_2$):

To the solution of (2-Nitrophenyl) methanol **3** (630 mg, 4.12 mmol) in dry THF (5 mL), sodium hydride (86 mg, 3.58 mmol) in dry THF (2 mL) was added drop wise under inert condition at 0 °C and the mixture was stirred for 20 min. To the reaction mixture, 2, 6-Bis (bromomethyl) -4-methylpyridine **4** (500 mg, 1.79 mmol) in dry THF (5 mL) was added drop wise at 0 °C. The reaction mixture was then stirred for 12 h at room temperature. After completion of the reaction, THF was

evaporated under reduced pressure and the reaction mixture was extracted with ethyl acetate, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography over silica gel (Eluent: 25% ethyl acetate in hexane) to furnish compound **2**, m.p.: 90-93 ^oC. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.03 (d, *J* = 8.4 Hz, 4H), 7.86 (d, *J* = 8.4 Hz, 4H), 7.63 (t, *J* = 7.6 Hz, 4H), 7.42 (t, *J* = 8.4 Hz, 4H), 7.21 (s, 2H), 5.0 (s, 4H), 4.71 (s, 4H), 2.38 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 157.00, 148.77, 147.18, 134.65, 133.57, 128.69, 127.95, 124.56, 121.12, 73.70, 69.36, 21.16; **IR:** ν/cm^{-1} 2928, 1617, 1522, 1330, 1123, 717 **LRMS (m/z):** Calc. for $C_{22}H_{21}N_3O_6Na^+$ $(M+ Na)^+$: 446.1328; Found: 446.9550.

Synthesis of (2-nitrophenyl) methanol ($C_7H_7NO_3$):

To the solution of *o*-nitro toluene (4 mL, 33.54 mmol) in CCl_4 (50 mL), NBS (11.9 g, 67.08 mmol) and AIBN (1.1 g, 6.7 mmol) were added at room temperature. The reaction mixture was then refluxed for 3 h at 80 ^oC. After completion of the reaction, the reaction mixture was filtered with Whatman 40. Filtrate was then evaporated under reduced pressure. Finally, the crude product was dissolved in MeOH-H_2O (40 ml, v/v= 1:1) with the subsequent addition of K_2CO_3 (9.6 g, 69.78 mmol) and refluxed under 80 ^oC. The crude product was purified by column chromatography over silica gel (Eluent: 10% ethyl acetate in hexane) to furnish compound **3** as yellow solid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.03 (d, 1H), 7.71 (d, 1H), 7.61 (t, 1H), 7.41 (t, 1H), 4.91 (s, 2H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 147.22, 136.82, 133.96, 129.38, 128.20, 124.75, 62.05; **LRMS (m/z):** Calc. for $C_7H_7NO_3H^+$ $(M+ H)^+$: 154.05; Found: 154.03. (Matching with the literature value).[2]

Synthesis of 2, 6-Bis (bromomethyl)-4-methylpyridine 4 ($C_8H_9Br_2N$):

To the solution of 2, 4, 6-trimethylpyridine (0.7 mL, 5.37 mmol) in CCl_4 (20 mL), NBS (3.8 g, 21.48 mmol) and AIBN (88 mg, 0.537 mmol) were added at room temperature. The reaction mixture was then refluxed for 3 h at 80 ^oC. After completion of the reaction, the reaction mixture was filtered with Whatman 40. Filtrate was then evaporated under reduced pressure. The crude product was purified by column chromatography over silica gel (Eluent: 2% ethyl acetate in hexane) to furnish compound **4** as white solid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.19 (s, 2H), 4.50 (s, 4H), 2.36 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 155.05, 148.16, 122.25, 32.09, 19.51; **LRMS (m/z):** Calc. for $C_8H_9Br_2NH^+$ $(M+ H)^+$: 277.91; Found: 277.90.

Photo isomerisation Study:

The photophysical properties, particularly the switching behavior of the receptor **1** was determined in acetonitrile solvent. UV–Vis spectra and the photostationary states were measured upon irradiation with 366 nm and 466 nm light. The thermally stable *trans* form (**1*E***) of the receptor showed strong distinctive absorption band at 319 nm ($\varepsilon = 8.96 \times 10^3\ M^{-1}cm^{-1}$) corresponding to the π–π* transition, and the weak absorbance band at 450 nm ($\varepsilon = 4.16 \times 10^2\ M^{-1}cm^{-1}$) attributed to the symmetry forbidden n–π* transition.

Upon irradiation with UV light (λ = 366 nm, 2.3 $mW.cm^{-2}$), the thermally stable **1*E*** (30 μM) form progressively isomerized to **1*Z*** and consequently the strong π–π* band gradually decreased with the spectral shift to the shorter wavelength (300 nm). At the same time, the evolution of the n–π* band was also observed, indicating the ***Z***-rich photostationary state (PSS). On the other hand, conversion of the **1*Z*** to the **1*E*** isomer was accomplished by irradiating the **1*Z*** solution with blue light (λ = 466 nm, 0.5 $mW.cm^{-2}$). Photo-irradiation with 466 nm light, converted the ***Z***-rich PSS to corresponding thermally stable **1*E*** isomer (Fig. S1).

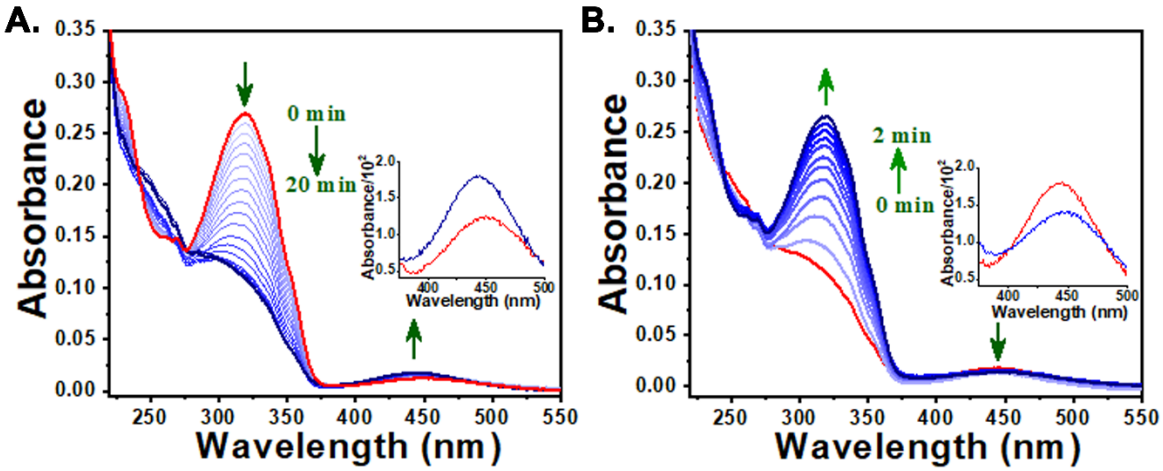


Figure S1. Photoisomerization of receptor **1** (30 μM) (A) ***E*** to ***Z*** isomerization (inset: n–π* transition for ***E*** to ***Z*** isomerization) and (B) ***Z*** to ***E*** isomerization (inset: n–π* transition for ***Z*** to ***E*** isomerization) in acetonitrile solvent.

The photoswitching behavior of the receptor **1** was also studied by the ^1H NMR spectroscopy in CD_3CN solvent. Receptor **1** showed strong NMR signals at □ 7.79, 7.66, 7.47, 7.38, 7.06 corresponding to the aromatic protons of the azobenzene along with some less intense signals, slightly in the upfield region at □ 7.38, 7.15, 7.13, 7.11 and 6.63, which showed receptor **1** preferentially exist

in thermally stable ***E***-form along with a small amount of ***Z***-isomer (Fig. S2). Upon irradiation at 366 nm, gradual evolution of the less intense signals attributed to the ***Z***-isomer was observed with the course of time and thereby the system reached to the ***Z***-rich PSS.[3] Again, exposure of the solution containing ***Z***-rich PSS to 466 nm light, led to change the spectral intensity to the initial state indicating back isomerization (Fig. S2–S3).

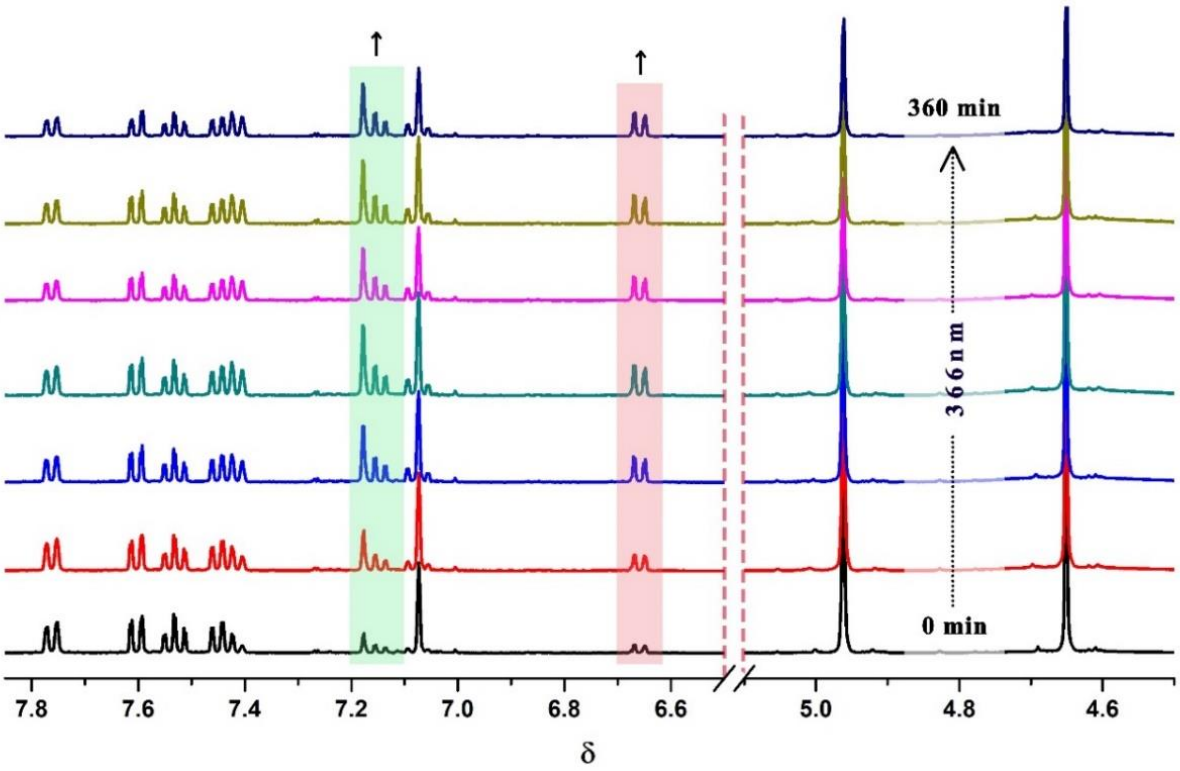


Figure S2. NMR spectra (in 400 MHz) of receptor **1*E*** in CD_3CN (5 mM) displaying a clear changes in the aromatic protons upon irradiation with 366 nm light for 360 min (green and pink region corresponds to the ***Z***-isomer.

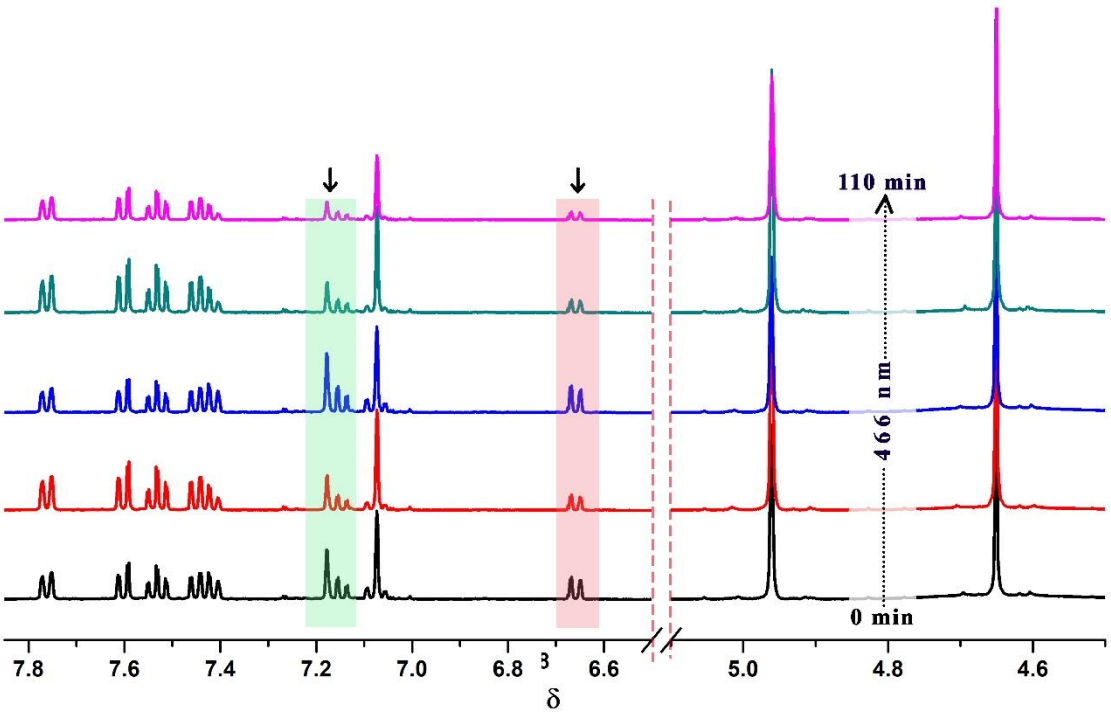


Figure S3. NMR spectra (in 400 MHz) displaying decrease in the intensity of the aromatic protons corresponding to ***Z***-isomer, upon irradiation with 466 nm light on the **1*Z***-rich (5 mM) PSS in CD_3CN for 110 min.

The response upon addition of the phosphate derivatives (sodium salts) on the absorption spectrum of receptor **1*E*** (10 μM) was examined in an aqueous solution of Tris (1 mM, buffered at pH 6.8) at 25 ^{o}C. In the absence of an anion guests, the absorption spectrum of the receptor **1*E*** was characterized by the intense π–π* band and less intense n–π* band centered at 319 nm and 450 nm respectively. Upon addition of the ATP in increasing amounts (up to 10 equivalents), the peak at 319 nm was found to be decreased with the evolution of a new peak at 266 nm (Fig. S4).

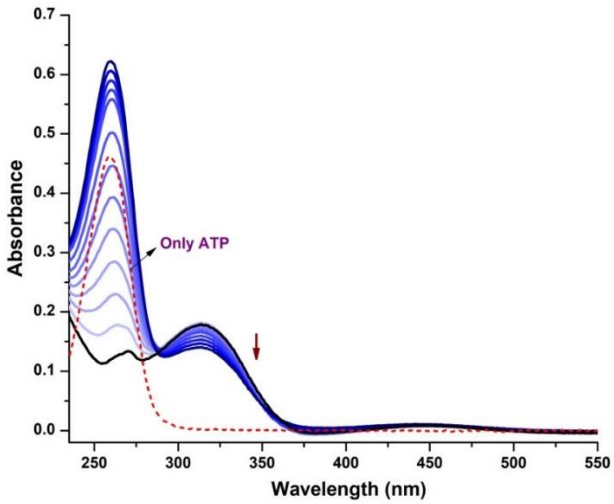


Figure S4. The changes in the UV-Vis absorption spectra of receptor **1*E*** (10 μM) upon titration with ATP (50 μM) in aqueous solvent of Tris (1 mM, buffered at pH 6.8) at 25 ^{o}C.

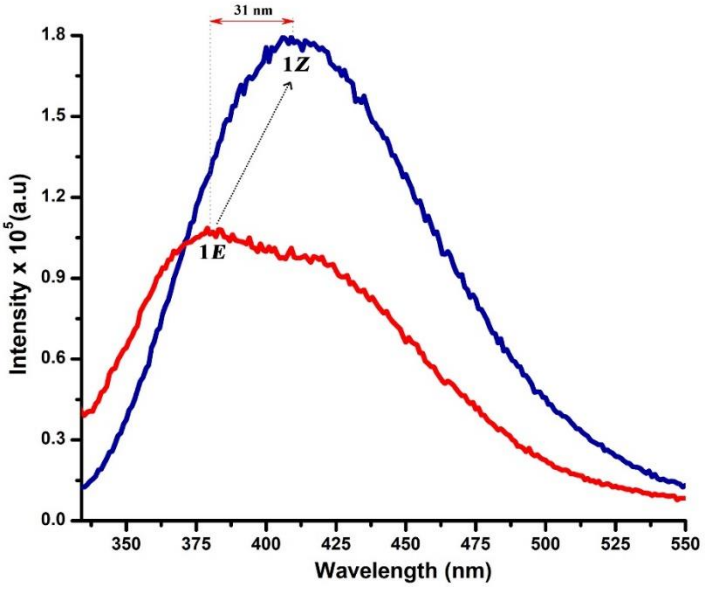


Figure S5.The changes in fluorescence emission spectrum (λ_{ex}= 292 nm, slit width = 5/5) for ***E*** to ***Z*** isomerization of receptor **1** in aqueous solvent of Tris (1 mM, buffered at pH 6.8) at 25 ^{o}C. Quantum yield calculated as φ_{trans}= 0.05 and $\varphi_{cis\ (PSS)}$ = 0.09 taking quinine sulphate as a reference.

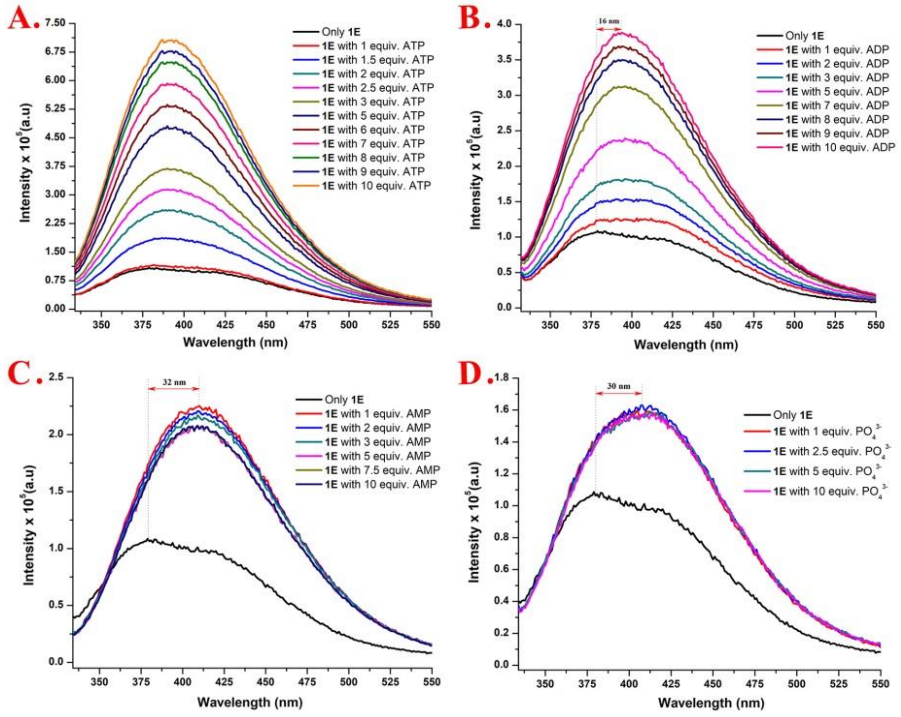


Figure S6. The changes in the fluorescence emission spectra of receptor **1*E*** (10 μM) upon titration with (A) ATP (0 to 100 μM), (B) ADP (0 to 100 μM), (C) AMP (0 to 100 μM) (D) PO_4^{3-} (0 to 100 μM) in Tris buffer (1 mM, pH 6.8) at 25 ^{o}C.

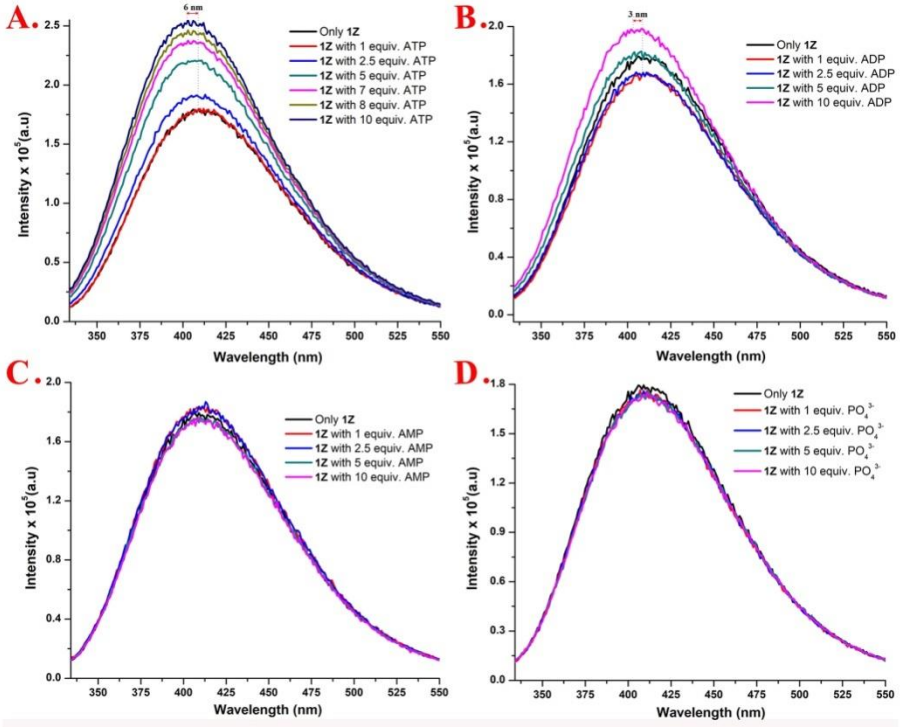


Figure S7. The changes in the fluorescence emission spectra of receptor **1*Z*** (10 μM) upon titration with (A) ATP (0 to 100 μM), (B) ADP (0 to 100 μM), (C) AMP (0 to 100 μM) (D) PO_4^{3-} (0 to 100 μM) in Tris buffer (1 mM, pH 6.8) at 25 ^oC.

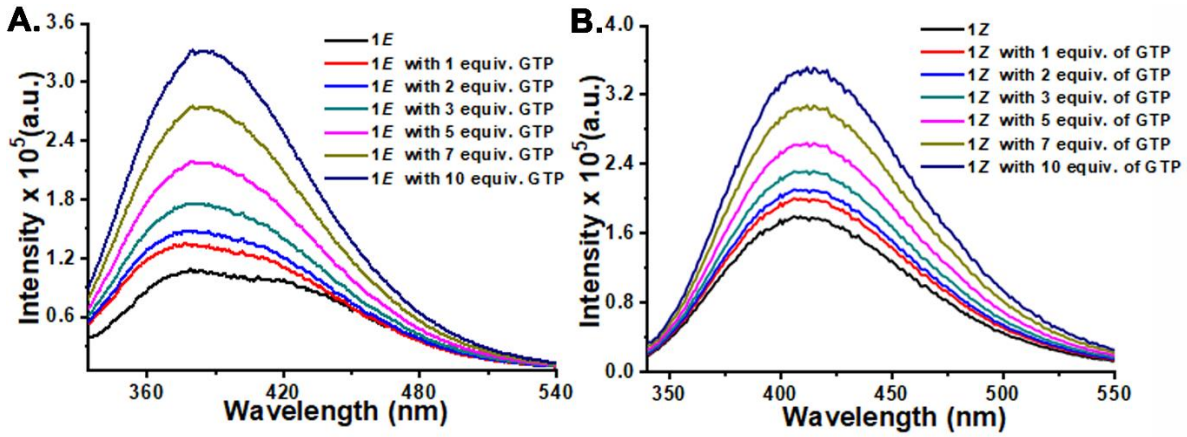


Figure S8. The changes in the fluorescence emission spectra of the receptor (A) **1*E*** and (B) **1*Z*** (10 μM each) upon titration with GTP (0 to 100 μM) in Tris buffer (1 mM, pH 6.8) at 25 ^oC.

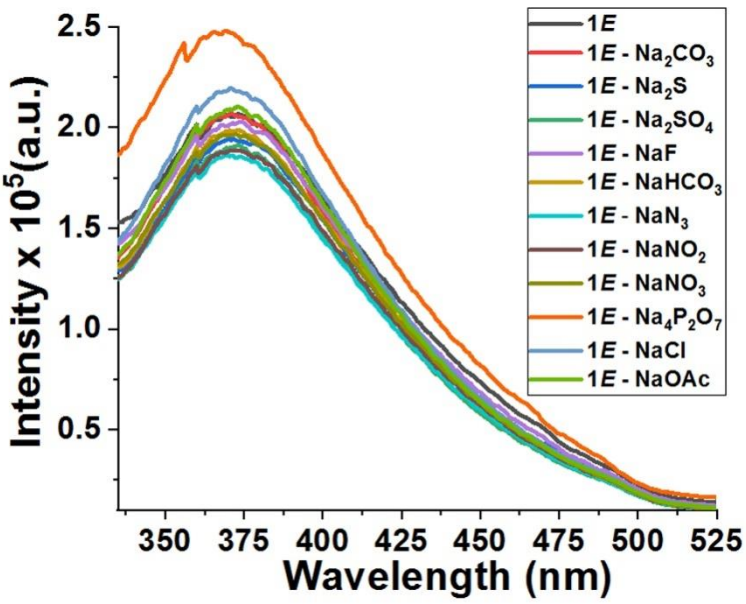


Figure S9. The changes in the fluorescence emission spectra of receptor **1*E*** (20 μM) upon titration with sodium salt of various anions in Tris buffer (1 mM, pH 6.8) at 25 ^{o}C. Here we used 20 μM (instead of 10 μM) to see the clear changes in the fluorescence spectra upon addition of analytes.

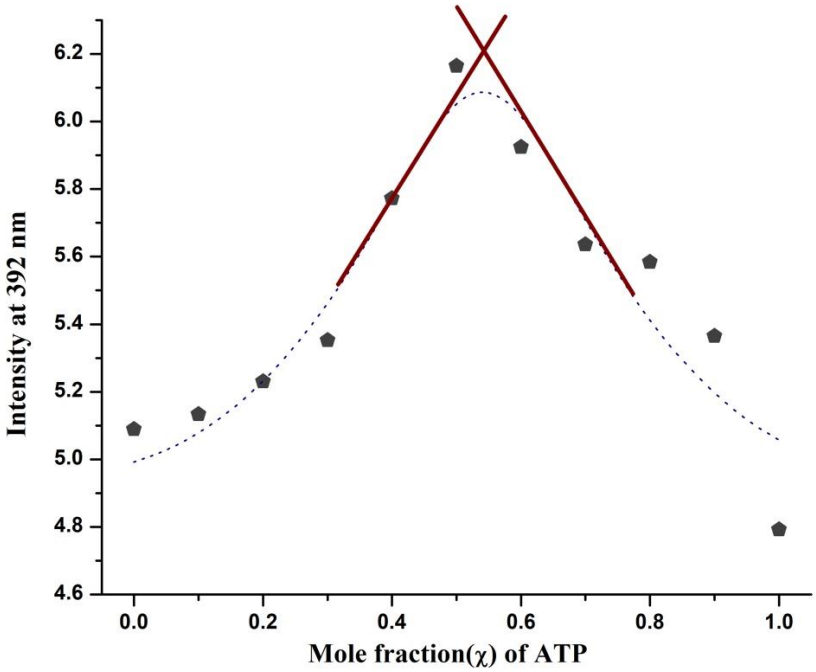


Figure S10. Job's plot of receptor **1*E*** with ATP shows (1:1) stoichiometry

Definition of distribution coefficient (K_d)

The distribution coefficient is defined in the equation below,

$$K_d = \frac{\Delta[ATP]}{[ATP]_{final}} \bullet \frac{Volume\ of\ the\ treated\ solution\ (mL)}{Mass\ of\ compound\ \mathbf{1}E\ (g)}$$

Where, Δ[ATP] is the reduction in concentration of the anion and $[ATP]_{final}$ is the final equilibrium concentration of the anion. The concentrations of the residual ATP were measured by the fluorimetric method described below. The standard solution of the compound **1*E*** was prepared from the pure crystalline samples and the mass of **1*E*** was calculated from the known volume of the standard solution. Again, the standard solution of the compound **1*Z*** was prepared from **1*E*** by shining 366 nm light.

The binding constants of the phosphorylated anions with both **1*Z*** and **1*E*** are presented below.

Table S1: Binding constants of the phosphorylated anions with **1*Z*** and **1*E***

Analytes	Binding constant (M^{-1})	
	1*E*	1*Z*
ATP	5.36×10^3	1.1×10^3
ADP	2.80×10^3	Too low to assign
GTP	8.92×10^2	1.9×10^3
AMP	Too low to assign	Too low to assign
P_i	Too low to assign	Too low to assign

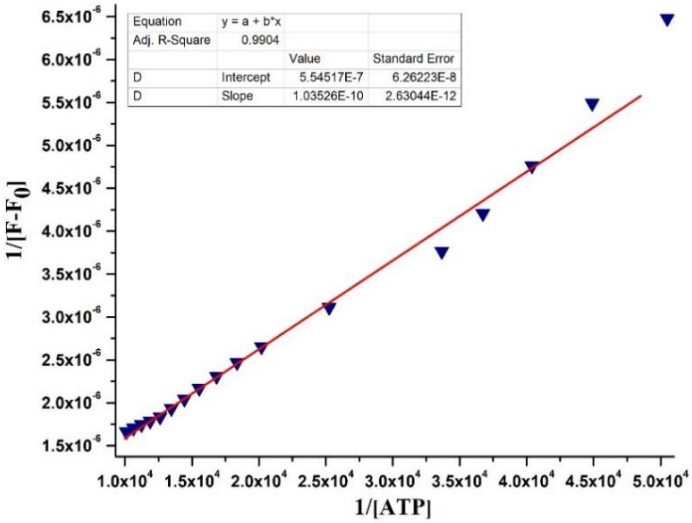


Figure S11. Binding constant (in Tris buffer 1 mM, pH 6.8) between **1*E*** and ATP was determined from the plot of 1/ [F-F_0] against 1/ [ATP]; the stoichiometry of **1*E***-ATP association, obtained from the slope/intercept, is 1.87×10^{-4}. Following the equation, binding constant is $5.36 \times 10^3\ M^{-1}$.

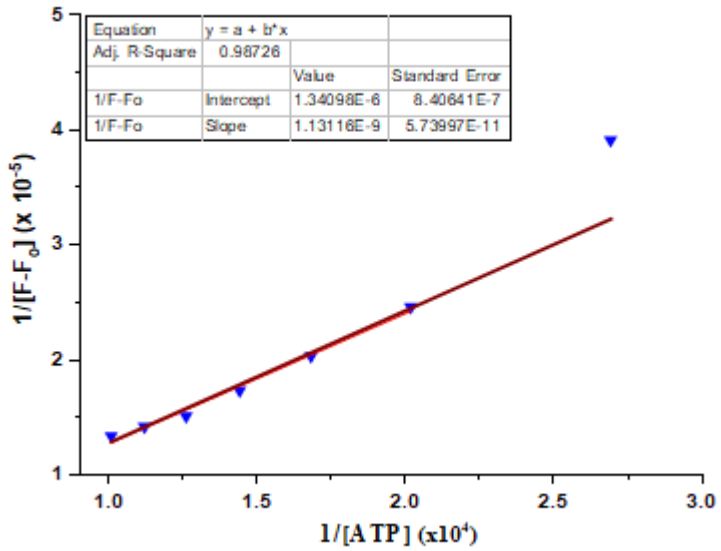


Figure S12. Binding constant (in Tris buffer 1 mM, pH 6.8) between **1*Z*** and ATP was determined from the plot of 1/[F-F_0] against 1/[ATP]; the stoichiometry of **1*Z***-ATP association, obtained from the slope/intercept, is 8.435 x 10^{-4}. Following the equation, binding constant is 1.1 x 10^{3} M^{-1}.

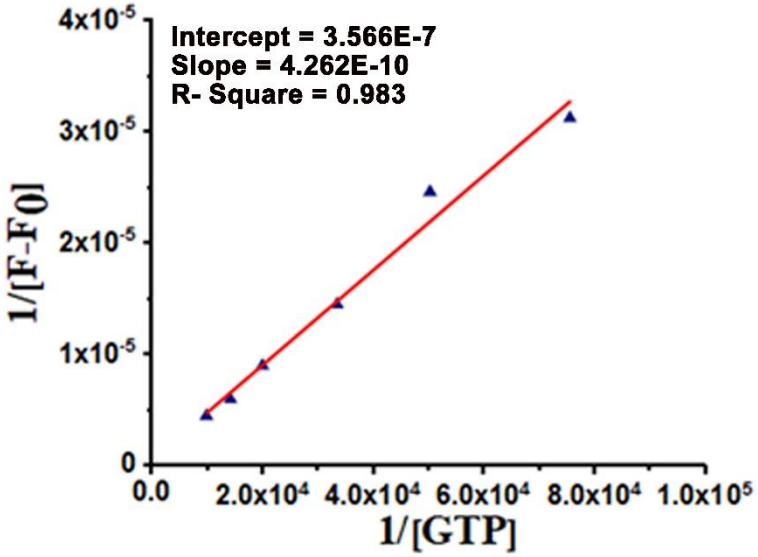


Figure S13. Binding constant (in Tris buffer 1 mM, pH 6.8) between **1*E*** and GTP was determined from the plot of 1/ [F-F_0] against 1/ [GTP]; the stoichiometry of **1*E***-GTP association, obtained from the slope/intercept, is 1.12 x 10^{-3}. Following the equation, binding constant is 8.92 x 10^{2} M^{-1}.

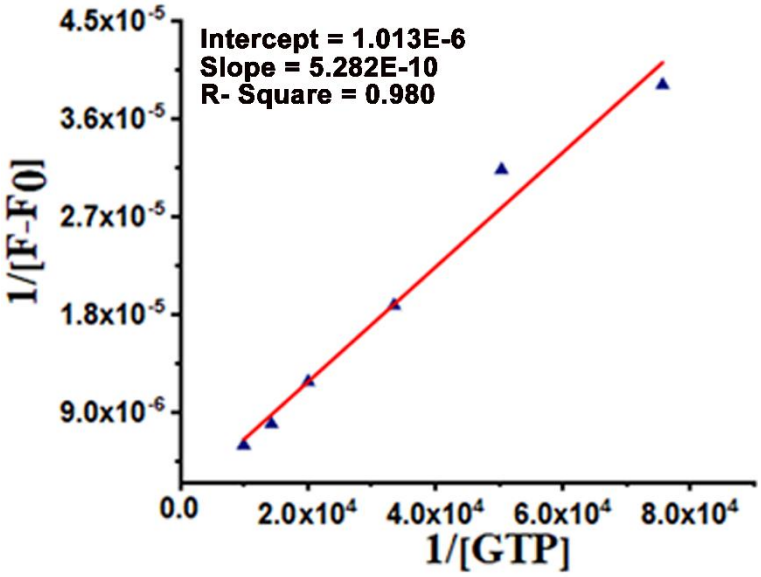


Figure S14. Binding constant (in Tris buffer 1 mM, pH 6.8) between **1*Z*** and GTP was determined from the plot of $1/[F\text{-}F_0]$ against 1/[GTP]; the stoichiometry of **1*Z***-GTP association, obtained from the slope/intercept, is 5.214×10^{-4}. Following the equation, binding constant is $1.9 \times 10^3\ M^{-1}$.

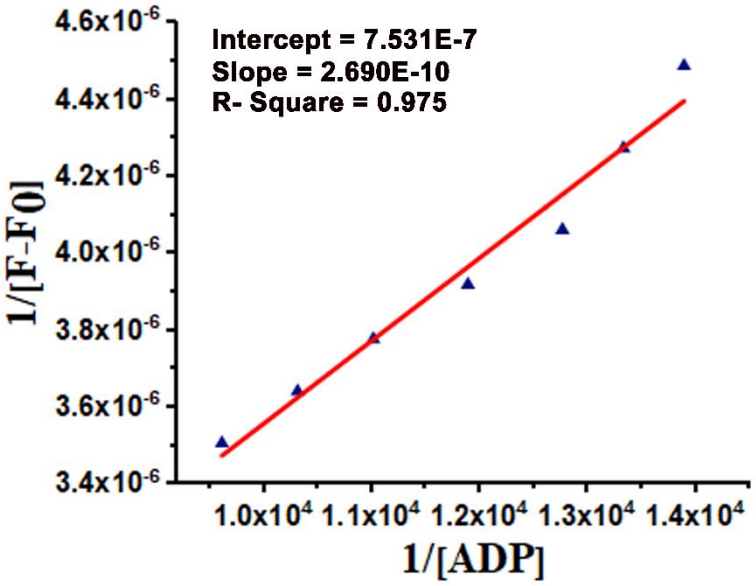


Figure S15. Binding constant (in Tris buffer 1 mM, pH 6.8) between **1*E*** and ADP was determined from the plot of $1/[F\text{-}F_0]$ against 1/ [ADP]; the stoichiometry of **1*E***-ADP association, obtained from the slope/intercept, is 3.57×10^{-4}. Following the equation, binding constant is $2.8 \times 10^3\ M^{-1}$.

Determination of binding constant between **1*Z*** and ADP is not possible due to very small spectral changes upon addition of analytes (Figure S7).
For the same reason, determination of binding constant for both the analytes, AMP and P_i in the (***Z***) forms are not possible (See Figure S6-S7).

Selection of pH range:

In order to optimize the best pH range for the sensing, the effect of the pH on the fluorescence response was investigated by systematic variation of the pH of solutions containing **1*E***⊂ATP (10 μM). It was observed that the emission response was highest in the range between pH 5.0 to pH 7.0 which demonstrated its efficacy at the physiologically relevant pH conditions.

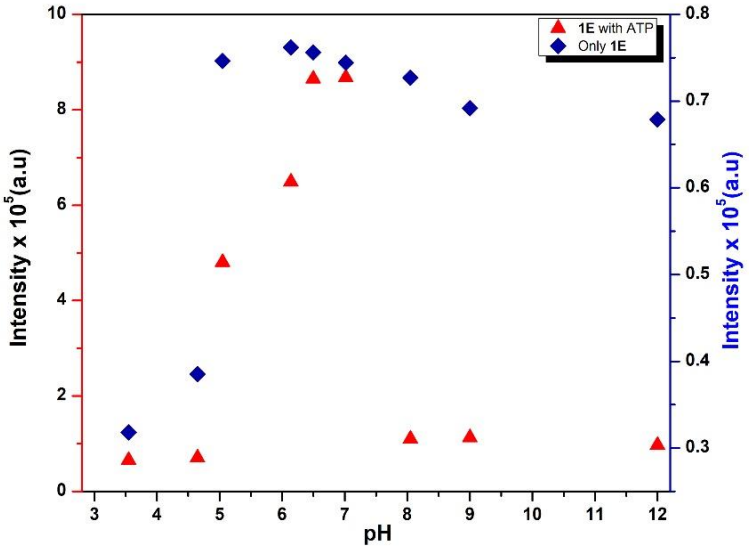


Figure S16. Fluorescence response of **1*E*** (10 μM, blue) and **1*E*•** ATP (100 μM, red) monitored at 393 nm in Tris buffer of different pH at 25 ^{o}C.

Optimized geometry: DFT studies of 1*E* and 1*Z* isomer and interaction of 1*E* isomer with ATP

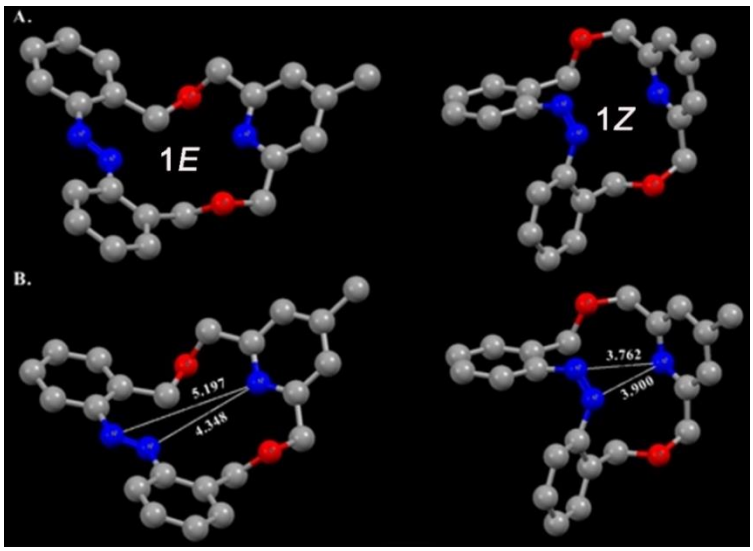


Figure S17. Optimized geometry of (A) **1*E*** and **1*Z*** (B) distances between **-N=N-** to pyridine **N** using B3LYP DFT method taking 6-311G as the basis set.

Table S2: Cartesian coordinate of receptor **1** in the ***E*** isomer

0 1	X	Y	Z
C	-3.05534000	-0.87421300	0.37917800
C	-4.31577500	-0.79615300	-0.21081200
C	-6.14940000	0.54393300	-1.33828100
C	-2.53353400	-2.16970700	0.95320100
C	-2.65692400	1.38491800	-0.03822800
C	-3.92379900	1.53170900	-0.61920500
C	-1.69001200	2.55665600	-0.02460600
C	-4.78004000	0.43068600	-0.71607600
C	2.86138700	4.40538500	-0.01407500
C	3.96676400	3.70798500	-0.51049800
C	-0.07038400	-2.22714500	1.11987300
C	1.13604000	-2.77233600	0.39988300
C	2.16988100	-1.94385100	-0.08303300
C	1.23957000	-4.15590700	0.18534800
C	3.27518800	-2.49597400	-0.75167900
C	0.40321800	1.60689100	0.83941000
C	2.33387500	-4.70408100	-0.48193800
C	3.35849200	-3.86903500	-0.95135600
C	1.72328700	3.71158600	0.40682900
C	2.77956600	1.61262700	-0.15030300
C	1.65035800	2.31381700	0.35333700
C	3.91452800	2.31912300	-0.58139100
H	4.74288900	1.74467100	-0.97040100
H	-2.39902800	-2.07832500	2.03487300
H	-3.24164700	-2.97448000	0.76196500
H	-4.23701300	2.49708300	-0.99481700
H	-1.16828700	2.60577600	-0.98771100
H	-6.92981200	0.29473300	-0.61571300
H	-6.25629900	-0.14698200	-2.17738700
H	-6.33853000	1.55211700	-1.70437400
H	2.88187800	5.48526700	0.04452400
H	4.84918300	4.23766900	-0.84084600
H	0.10185900	0.81766400	0.16177300
H	0.58594100	1.12686100	1.80052800
H	0.86576100	4.24802100	0.78345000
H	-4.93604100	-1.68016500	-0.27812500
H	4.21139700	-4.29098900	-1.46517800
H	2.39339700	-5.77317200	-0.63367100
H	4.04846000	-1.83063300	-1.10450400
H	0.44796200	-4.79915600	0.54409800
H	-0.15820000	-2.68853500	2.11001100
H	-0.01265000	-1.15210200	1.23082600
H	-2.24028200	3.48768900	0.09921600
N	2.89978600	0.19546900	-0.31553200
N	2.03495300	-0.52843600	0.14173200
N	-2.23840400	0.20646600	0.46565800
O	-0.71959300	2.52402100	1.05666200
O	-1.26877700	-2.58639500	0.33896100

Table S3: Cartesian coordinate of receptor **1** in the ***Z*** isomer

0 1	X	Y	Z
C	-2.67322200	-1.11457900	0.82125700
C	-3.35138200	-1.45443300	-0.35238200
C	-4.59565900	-0.78690700	-2.45941500
C	-2.06851300	-2.17033900	1.70981700
C	-2.89266000	1.16256000	0.34627400
C	-3.57328100	0.87824900	-0.83938200
C	-2.53145200	2.57384600	0.73096400
C	-3.82774600	-0.45099700	-1.20594900
C	3.41421000	3.40608700	0.20809800
C	3.72487700	2.50744700	-0.81297800
C	0.35218400	-1.67698800	1.55285500
C	1.51685000	-2.00182500	0.65815000
C	1.63476500	-1.45762400	-0.63624700
C	2.47712200	-2.93761300	1.06882100
C	2.64695000	-1.88299900	-1.50402100
C	-0.12185600	2.34993000	1.16293800
C	3.51417000	-3.33781700	0.22438300
C	3.59225900	-2.81298600	-1.06876900
C	2.16484300	3.33847000	0.83190600
C	1.54724600	1.47109600	-0.56209100
C	1.20667300	2.38927300	0.45604700
C	2.79400200	1.53970600	-1.19784900
H	3.02671000	0.86114700	-2.00364300
H	-1.97621500	-1.79381600	2.72965300
H	-2.66479700	-3.07954100	1.70776900
H	-3.89931600	1.68872400	-1.47725600
H	-3.17089400	3.29346500	0.22644800
H	-5.66335900	-0.88411200	-2.24330700
H	-4.26257300	-1.73243600	-2.88743800
H	-4.48470000	-0.00895300	-3.21451700
H	4.13110800	4.15563500	0.51260600
H	4.68282500	2.55454600	-1.31194800
H	-0.40529600	1.33339200	1.42486300
H	-0.07102200	2.93745700	2.08363300
H	1.92285800	4.03490200	1.62399700
H	-3.50002100	-2.49648800	-0.60137900
H	4.38158300	-3.12521800	-1.73854300
H	4.24391900	-4.05864000	0.56541300
H	2.68837200	-1.49490100	-2.51192800
H	2.39969800	-3.35753700	2.06334500
H	0.61805000	-1.82568600	2.60210700
H	0.01617400	-0.65123000	1.42529500
H	-2.61633600	2.70525900	1.81190400
N	0.50578800	0.59983500	-1.09761900
N	0.55711300	-0.61485900	-1.16427300
N	-2.46093100	0.17709800	1.17605700

O	**-1.16550500**	**2.92330900**	**0.29698900**
O	**-0.74859900**	**-2.59578800**	**1.20541300**

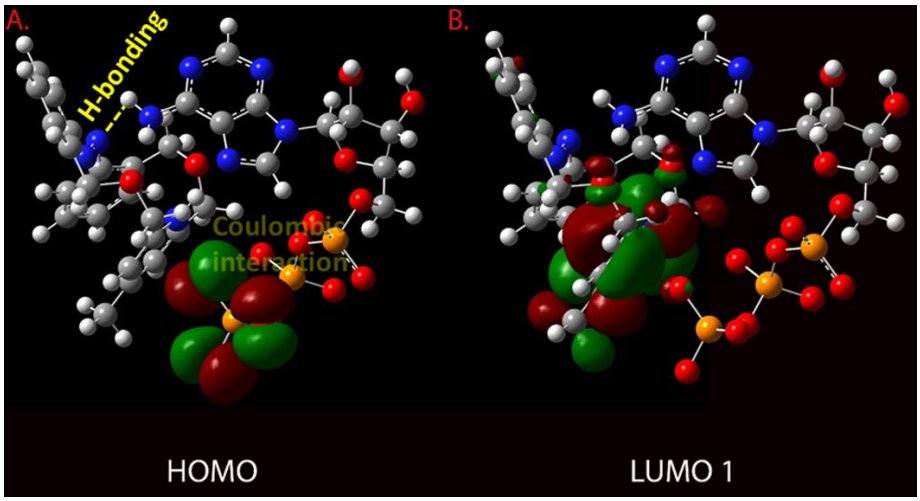


Figure S18. Interaction between **1*E*** with ATP^{4-} (taking 3-21G as the basis set) using DFT method at the B3LYP level.

Table S4: Cartesian coordinate of interaction between receptor **1** in the ***E*** isomer and ATP

-3 1	**X**	**Y**	**Z**
O	**-1.52056000**	**1.14487900**	**-2.12667800**
O	**-2.30233800**	**-0.46790600**	**2.47321500**
N	**-1.26087600**	**-1.07204000**	**-0.31119900**
N	**-4.67320400**	**0.34260300**	**0.57436800**
N	**-4.64483900**	**1.08657400**	**-0.43241000**
C	**-1.52212200**	**-1.24832600**	**-1.63529600**
C	**-3.91832900**	**0.73280300**	**-2.80012900**
C	**-5.00087800**	**0.92809100**	**1.83208800**
C	**-1.65086400**	**-1.95034700**	**0.64668800**
C	**-4.70800700**	**0.37307600**	**-1.68389900**
C	**-4.17131000**	**0.08605700**	**-4.02225100**
H	**-3.57625500**	**0.36038800**	**-4.88801200**
C	**-4.54546800**	**0.25981900**	**2.99237900**
C	**-2.76230100**	**1.69566600**	**-2.71921200**
H	**-2.52505800**	**2.06185700**	**-3.72449700**
H	**-2.98345500**	**2.54392300**	**-2.07002200**
C	**-1.05100800**	**-0.16566800**	**-2.57315200**
H	**-1.36392800**	**-0.39130400**	**-3.59609500**
H	**0.04132900**	**-0.13103700**	**-2.52736900**
C	**-2.20045900**	**-2.39120000**	**-2.03490000**

H	**-2.42165800**	**-2.53135600**	**-3.08548600**
C	**-5.68723200**	**-0.63075900**	**-1.80490300**
H	**-6.28392000**	**-0.87993500**	**-0.93546800**
C	**-2.61873900**	**-3.34666800**	**-1.08811700**
C	**-3.64975900**	**-0.93797400**	**2.86768600**
H	**-3.56712900**	**-1.47242300**	**3.81981500**
H	**-4.03180200**	**-1.61762200**	**2.09947200**
C	**-6.19329400**	**2.54320000**	**3.19218700**
H	**-6.83927100**	**3.41078300**	**3.27157600**
C	**-4.91303700**	**0.76801500**	**4.24376600**
H	**-4.55733700**	**0.27228100**	**5.14115200**
C	**-5.82784300**	**2.06112400**	**1.93343800**
H	**-6.19332500**	**2.53016500**	**1.02685000**
C	**-5.16016200**	**-0.89556000**	**-4.14901100**
H	**-5.33774600**	**-1.36661400**	**-5.10956800**
C	**-5.91424700**	**-1.26292100**	**-3.02897300**
H	**-6.68343900**	**-2.02350700**	**-3.10922400**
C	**-2.33913700**	**-3.09883300**	**0.26454200**
H	**-2.64571300**	**-3.80580000**	**1.02483400**
C	**-5.73401100**	**1.89861900**	**4.34878200**
H	**-6.01858800**	**2.26981600**	**5.32722000**
C	**-1.38851400**	**-1.55403200**	**2.07481000**
H	**-1.50147000**	**-2.41354400**	**2.73722200**
H	**-0.38139800**	**-1.16049600**	**2.18232700**
C	**-3.35973700**	**-4.58195300**	**-1.52362900**
H	**-4.28240900**	**-4.31160300**	**-2.05049400**
H	**-3.62116600**	**-5.21527700**	**-0.67308700**
H	**-2.75251900**	**-5.17237500**	**-2.21965100**
H	**-0.67699600**	**-0.24884800**	**-0.00925600**
P	**4.86270600**	**-1.03126200**	**1.22266100**
O	**6.01065500**	**-2.08616500**	**0.83343000**
O	**3.40440600**	**-1.23786400**	**0.30351800**
O	**5.27645000**	**0.56703500**	**0.60043100**
C	**5.67927700**	**0.70300600**	**-0.79953600**
H	**5.19626600**	**-0.05979200**	**-1.42058000**
H	**6.76727000**	**0.58604800**	**-0.87701100**
C	**5.28610100**	**2.08972800**	**-1.27388500**
H	**5.77249300**	**2.30862800**	**-2.22870200**
O	**3.81219500**	**2.13842700**	**-1.51341700**
C	**3.19081300**	**3.10646400**	**-0.62826000**
H	**2.97293700**	**4.04016500**	**-1.15457200**
N	**1.91418200**	**2.57792600**	**-0.17476700**
C	**1.62987900**	**1.28000200**	**0.22788400**
H	**2.36571100**	**0.48601400**	**0.24048300**
N	**0.33602300**	**1.12926900**	**0.51898300**
C	**-0.24825500**	**2.38001000**	**0.30286800**
C	**-1.58618600**	**2.82316900**	**0.36627000**
N	**-2.61301700**	**2.05758000**	**0.80704800**

H	**-3.50730100**	**2.52766300**	**0.83318200**
H	**-2.41550300**	**1.31813800**	**1.46740700**
N	**-1.85296700**	**4.09204200**	**-0.07289900**
C	**-0.83370800**	**4.86928000**	**-0.50983300**
H	**-1.10431000**	**5.86254000**	**-0.84787600**
N	**0.47801900**	**4.55154200**	**-0.56625900**
C	**0.71368600**	**3.28325900**	**-0.15793400**
C	**5.56533700**	**3.21047700**	**-0.26803500**
H	**6.39290800**	**2.97069000**	**0.40583300**
C	**4.22548700**	**3.37600800**	**0.47804900**
H	**4.13946000**	**2.64200000**	**1.27959200**
O	**4.04524700**	**4.73514800**	**0.95246500**
H	**4.29473600**	**4.81436700**	**1.89355300**
O	**5.83730800**	**4.43644100**	**-1.00328700**
H	**5.48890700**	**5.17789100**	**-0.45600800**
O	**4.46283000**	**-0.76643300**	**2.75373700**
P	**2.96669000**	**-2.22358500**	**-1.09848400**
O	**2.74472700**	**-3.76935900**	**-0.42948500**
O	**1.59198100**	**-1.55999000**	**-1.63038100**
O	**4.21769400**	**-2.25679500**	**-2.11969700**
P	**1.99090100**	**-4.36171700**	**1.16757600**
O	**0.83051500**	**-3.27311700**	**1.53719400**
O	**3.25613600**	**-4.40300400**	**2.19344600**
O	**1.44727100**	**-5.81550400**	**0.67965900**

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Linear discrimination analysis (LDA):

To glean the inherent characterisation patterns of information about the 5 types of ions, the data were subjected to linear discriminant analysis (LDA). Maintaining the class-discriminatory information as much as possible, the high dimensional dataset was projected onto a subspace (smaller than the original) using LDA. This statistical method takes the components, which were nothing but the linear combination of the experimental variables, thereby maximizing the measure between classes while minimizing the measure within the same. A new set of variables (also known as factors) were generated in this process for the efficient differentiation of the coenzymes. The dimension of the dataset was reduced using this LDA which resorted to keeping only the best two or three factors and rejecting the rest of the information. This gave rise to a transformed dataset which comprised of points associated with factor scores (a doublet or triplet of numbers), which could be taken to be coordinates in a two- or three-dimensional score plots. LDA was also employed to classify unknown coenzymes. This technique is usually exploited in machine learning for the prevention of over fitting of the data

and for getting a clue as to how this model would generalize to independent dataset. The accuracy of the model was ascertained by comparing the model's predictions on the test set and their actual labels. A confusion matrix was shown regarding the performance of the classifier on test data where each row corresponds to predicted class and each column the actual class. Overall 200 (5 × 8 × 5) raw data points (no. of variables were 8) acquired by taking 5 replicates obtained from each coenzyme were subjected to linear discrimination analysis (LDA). In the case of **1*E***, the most contributing emission variables were found to be 350 nm, 375 nm and 500 nm.[4]

Table S5. The confusion matrix trained on full data set and challenged with the unknown coenzymes of the given class which was not present in the training data set.

Actual Class

Predicted Class: Analytes with 1*E*	ATP	ADP	AMP	PO_4^{3-}	GTP	Total	% correct
ATP	5	0	0	0	0	5	100.00
ADP	0	5	0	0	0	5	100.00
AMP	0	0	4	1	0	5	80.00
PO_4^{3-}	0	0	1	4	0	5	80.00
GTP	0	0	0	0	5	5	100.00
Total	5	5	5	5	5	25	100.00
N= 25		N correct = 23			Percentage Correct= 92		

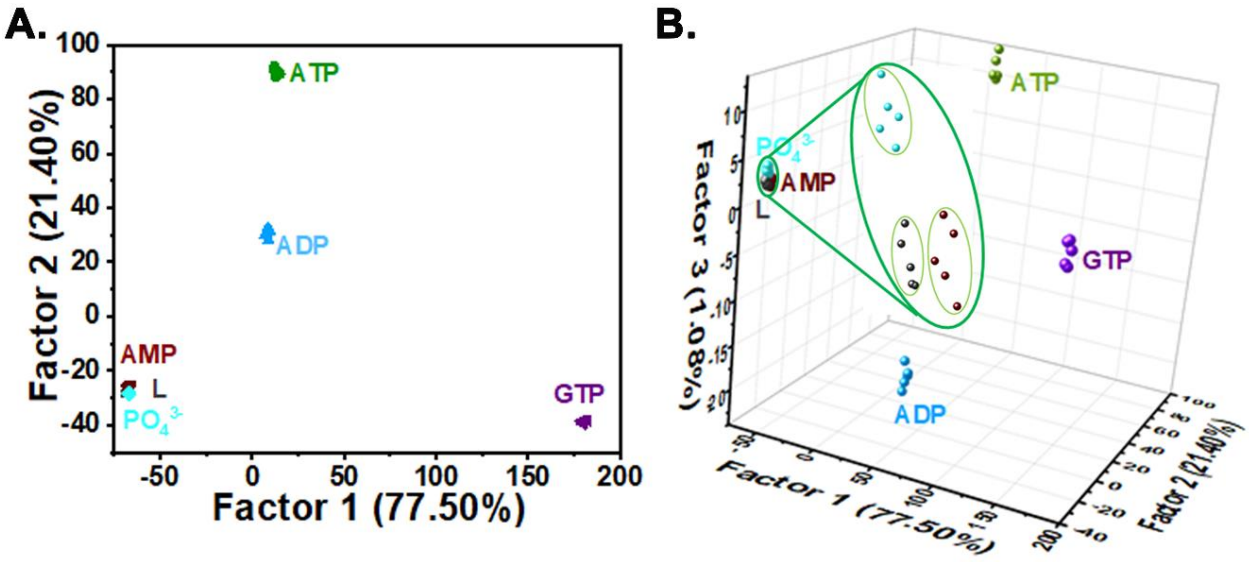

Figure S19. (A) Two-dimensional and (B) three-dimensional LDA score plots for **1*E*** (10 μM) as a single photoswitchable sensor discriminating the given analytes (10 equiv. each) along with the probe itself in aqueous solution at pH 6.8 (in 1 mM Tris buffer).

Table S6. The confusion matrix **A** obtained as a classification accuracy trained on the full data set for all the analytes along with the probe itself and challenged with the unknown coenzymes of the given class which was not present in the training data set (showed in the table **B**).

A.

Predicted Class \ Actual Class	L	ATP	ADP	AMP	PO_4^{3-}	GTP	Total	% correct
L	5	0	0	0	0	0	5	100.00
ATP	0	5	0	0	0	0	5	100.00
ADP	0	0	5	0	0	0	5	100.00
AMP	0	0	0	5	0	0	5	100.00
PO_4^{3-}	0	0	0	0	5	0	5	100.00
GTP	0	0	0	0	0	5	5	100.00
Total	5	5	5	5	5	5	30	100.00

B.

Predicted Class \ Actual Class	L	ATP	ADP	AMP	PO_4^{3-}	GTP	Total	% correct
L	5	0	0	0	0	0	5	100.00
ATP	0	5	0	0	0	0	5	100.00
ADP	0	0	5	0	0	0	5	100.00
AMP	0	0	0	5	0	0	5	100.00
PO_4^{3-}	0	0	0	0	5	0	5	100.00
GTP	0	0	0	0	0	5	5	100.00
Total	5	5	5	5	5	5	30	100.00
N= 30			N Correct= 30			% Correct= 100		

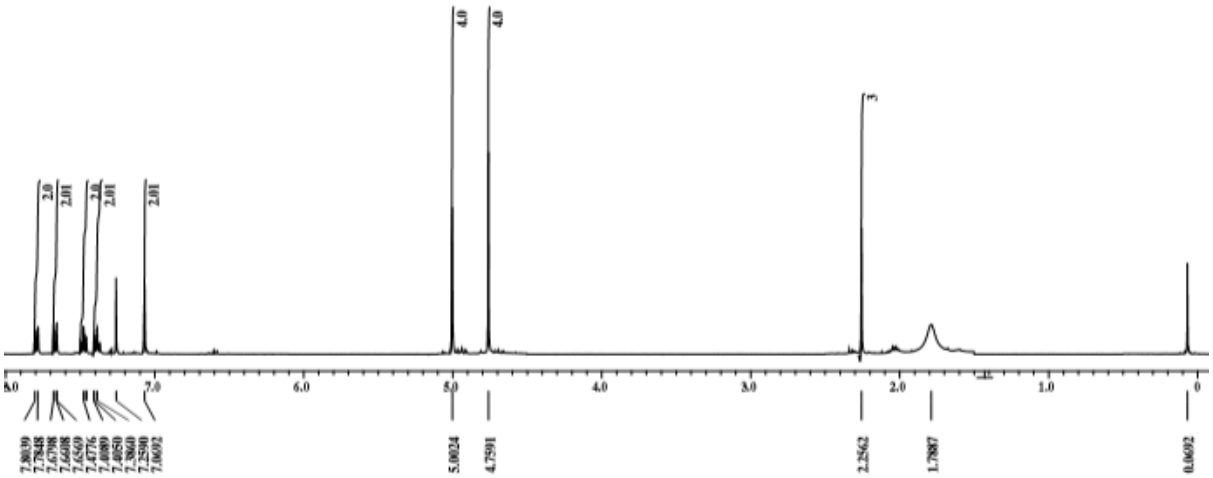

Figure S20. ^{1}H NMR spectrum of receptor **1** in $CDCl_3$.

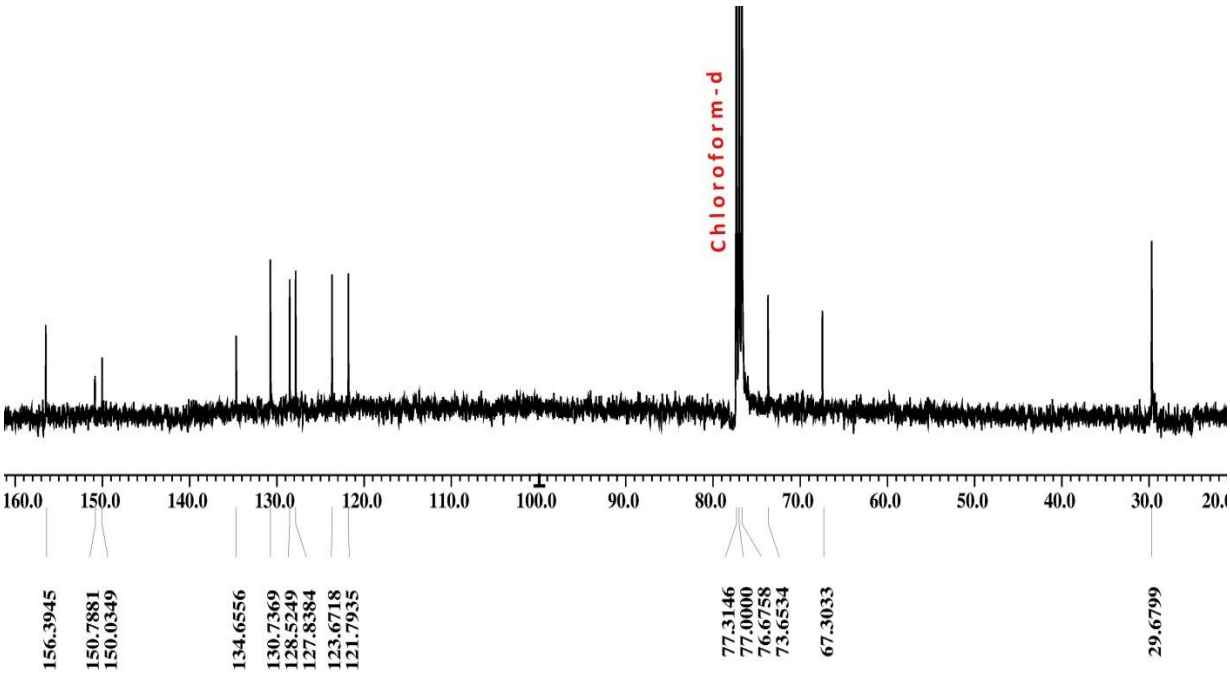

Figure S21. ^{13}C NMR spectrum of compound **1** in $CDCl_3$.

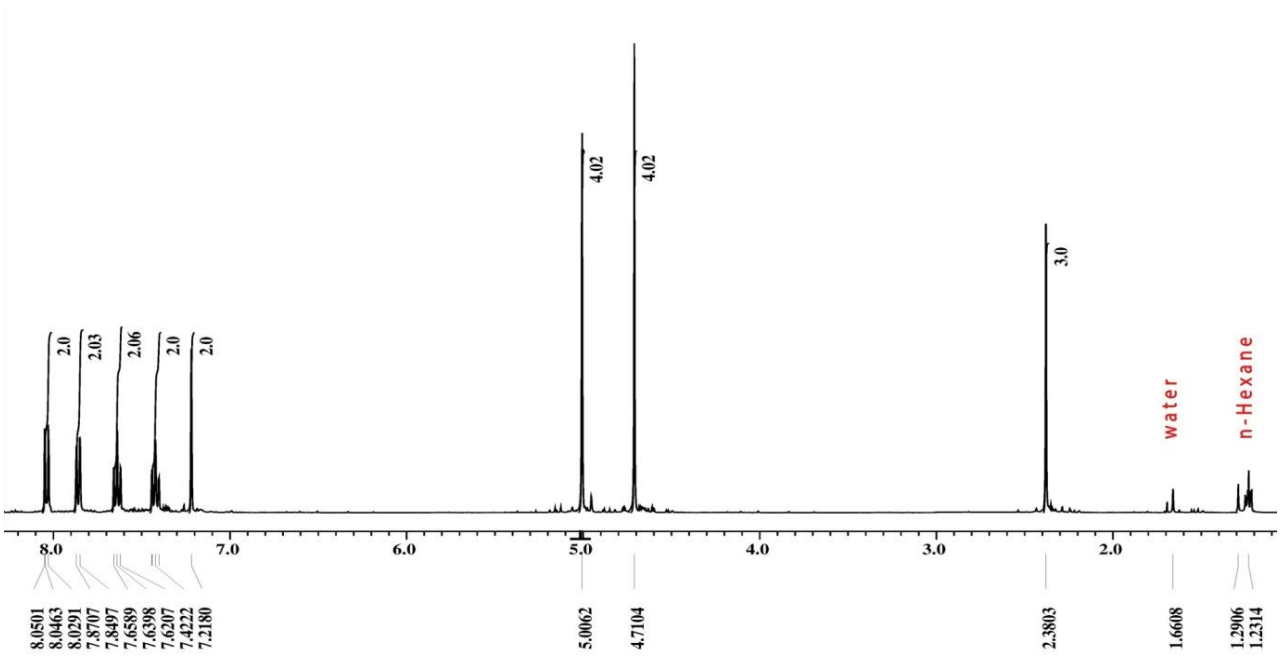

Figure S22. ^{1}H NMR spectrum of compound **2** in $CDCl_3$.

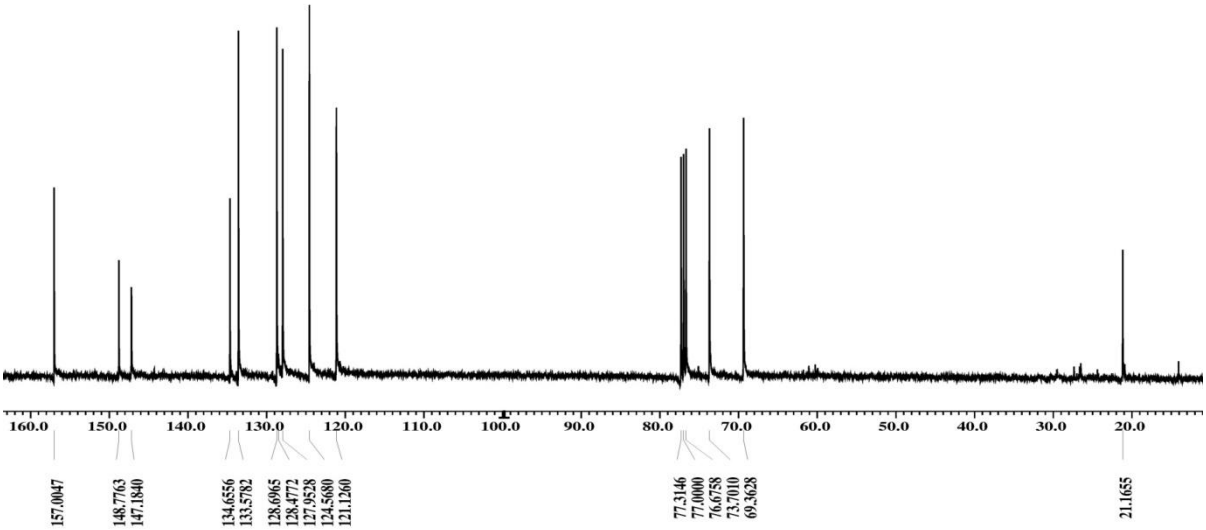

Figure S23. ^{13}C NMR spectrum of compound **2** in $CDCl_3$.

Crystallographic Details:

Single crystals of $C_{22}H_{21}N_3O_2$ (CCDC Number **1941103**) and $C_{22}H_{22}N_3O_2$ (CCDC Number **1941161**) were obtained by slow diffusion of CH_2Cl_2/cyclohexane (1:1, v/v) as well as CH_2Cl_2/MeOH (1:1, v/v) solution respectively. Suitable crystals for each sample were selected on a SuperNova, Dual, Cu at zero, Eos diffractometer using graphite monochromatic Mo K_α radiation (λ= 0.71073 Å). The crystals were kept at 100(2) K and 100.01(10) K respectively during data collection. Using Olex2 the structures were solved with the Super flip3 structure solution program using Charge Flipping and refined with the ShelXL4 refinement package using Least Squares minimisation. All hydrogen atoms were added according to the riding model. Crystallographic parameters for **1*E*** and protonated **1*E*** are given in the Table. [5, 6, 7]

Experimental details (**1*E*)**

Crystal data	
Chemical formula	$C_{22}H_{21}N_3O_2$

M_r	359.43
Crystal system, space group	Monoclinic, $P2_1$
Temperature (K)	100
a, *b*, *c* (Å)	14.2375 (10), 4.3802 (3), 15.0293 (14)
β (°)	104.466 (9)
V (Å^3)	907.56 (13)
Z	17
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.12
Crystal size (mm)	0.21 × 0.16 × 0.1
Data collection	
Diffractometer	SuperNova, Dual, Cu at zero, Eos
Absorption correction	Multi-scan *CrysAlis PRO*, Agilent Technologies, Version 1.171.37.34 (release 22-05-2014 CrysAlis171 .NET) (compiled May 22 2014,16:03:01) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.851, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	3796, 2693, 2358
R_{int}	0.025
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.588
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.055, 0.129, 1.10
No. of reflections	2693
No. of parameters	245
No. of restraints	1
H-atom treatment	H-atom parameters constrained
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	0.34, -0.20
Absolute structure	Flack x determined using 703 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259).
Absolute structure parameter	-0.4 (10)

Computing details (CCDC Number 1941103)

Data collection: *CrysAlis PRO*, Agilent Technologies, Version 1.171.37.34 (release 22-05-2014 CrysAlis171 .NET) (compiled May 22 2014,16:03:01); cell refinement: *CrysAlis PRO*, Agilent Technologies, Version 1.171.37.34 (release 22-05-2014 CrysAlis171 .NET) (compiled May 22

2014,16:03:01); data reduction: *CrysAlis PRO*, Agilent Technologies, Version 1.171.37.34 (release 22-05-2014 CrysAlis171 .NET) (compiled May 22 2014,16:03:01); program(s) used to solve structure: ShelXT (Sheldrick, 2015); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015); molecular graphics: Olex2 (Dolomanov *et al.*, 2009); software used to prepare material for publication: Olex2 (Dolomanov *et al.*, 2009).

($C_{22}H_{21}N_3O_2$)	$F(000)$ = 374
M_r = 359.43	D_x = 1.338 Mg m^{-3}
Monoclinic, $P2_1$	Mo $K\alpha$ radiation, λ = 0.71073 Å
a = 14.2375 (10) Å	Cell parameters from 1438 reflections
b = 4.3802 (3) Å	θ = 2.3–26.2°
c = 15.0293 (14) Å	μ = 0.12 mm^{-1}
β = 104.466 (9)°	T = 100 K
V = 907.56 (13) Å^3	Plate, red
Z = 17	0.21 × 0.16 × 0.1 mm
$R[F^2 > 2\sigma(F^2)]$ = 0.055	$w = 1/[\sigma^2(F_o^2) + (0.0496P)^2 + 0.4593P]$ where $P = (F_o^2 + 2F_c^2)/3$
Refinement on F2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
R[F2 > 2s(F2)] = 0.055	w = 1/[s2(Fo2) + (0.0496P)2 + 0.4593P] where P = (Fo2 + 2Fc2)/3
wR(F2) = 0.129	(D/s)max = 0.001
S = 1.10	Dρmax = 0.34 e Å-3
2693 reflections	Dρmin = -0.20 e Å-3
245 parameters	Absolute structure: Flack x determined using 703 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259).
1 restraint	Absolute structure parameter: -0.4 (10)
Primary atom site location: dual	

Compound 1

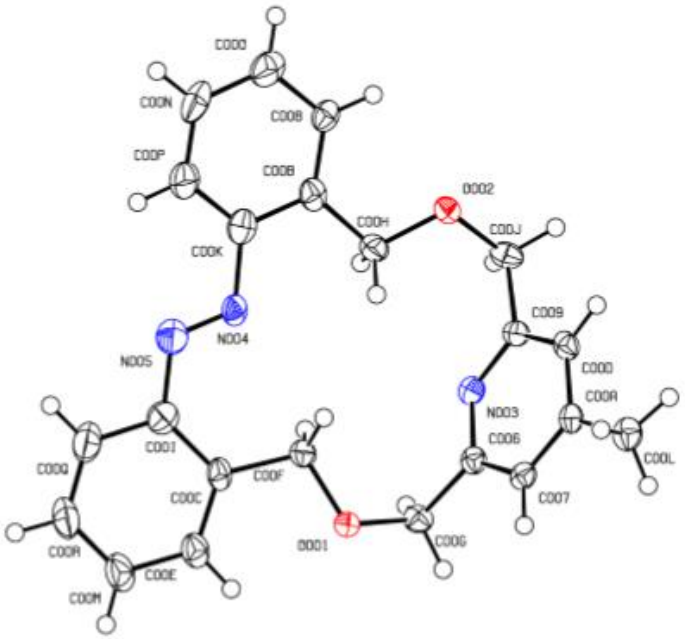

Table S7: Crystallographic parameters of 1*E*

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for (**1*E*)*

	x	*y*	*z*	U_{iso}*/U_{eq}
O001	0.6160 (2)	0.4071 (7)	0.08779 (18)	0.0222 (7)
O002	0.6045 (2)	0.3084 (7)	0.46316 (18)	0.0241 (7)
N003	0.5253 (3)	0.1482 (8)	0.2513 (2)	0.0206 (8)
N004	0.8108 (2)	0.6311 (9)	0.3379 (3)	0.0265 (9)
N005	0.8691 (3)	0.7725 (11)	0.3040 (3)	0.0380 (11)
C006	0.4908 (3)	0.2681 (10)	0.1669 (3)	0.0213 (10)
C007	0.4105 (3)	0.4587 (10)	0.1465 (3)	0.0213 (10)
H007	0.3873	0.5331	0.0871	0.026*
C008	0.7669 (3)	0.5824 (11)	0.5701 (3)	0.0258 (11)
H008	0.7217	0.4924	0.5971	0.031*
C009	0.4834 (3)	0.2311 (10)	0.3185 (3)	0.0216 (10)
C00A	0.3647 (3)	0.5383 (10)	0.2143 (3)	0.0215 (10)
C00B	0.7588 (3)	0.5444 (11)	0.4772 (3)	0.0263 (11)
C00C	0.7765 (3)	0.6025 (11)	0.1437 (3)	0.0248 (10)

C00D	0.4036 (3)	0.4227 (11)	0.3021 (3)	0.0232 (10)
H00D	0.3759	0.4744	0.3499	0.028*
C00E	0.7805 (3)	0.6067 (12)	0.0527 (3)	0.0308 (12)
H00E	0.7293	0.5221	0.0087	0.037*
C00F	0.6907 (3)	0.4562 (12)	0.1707 (3)	0.0260 (11)
H00A	0.7099	0.2635	0.2017	0.031*
H00B	0.6672	0.5894	0.2119	0.031*
C00G	0.5459 (3)	0.1816 (11)	0.0979 (3)	0.0243 (11)
H00C	0.5791	-0.0103	0.1164	0.029*
H00F	0.5004	0.1500	0.0388	0.029*
C00H	0.6785 (3)	0.3620 (12)	0.4167 (3)	0.0285 (11)
H00G	0.6518	0.4725	0.3601	0.034*
H00H	0.7038	0.1688	0.4013	0.034*
C00I	0.8559 (3)	0.7368 (12)	0.2081 (3)	0.0329 (12)
C00J	0.5301 (3)	0.1086 (11)	0.4127 (3)	0.0266 (11)
H00I	0.4809	0.0823	0.4466	0.032*
H00J	0.5580	-0.0901	0.4068	0.032*
C00K	0.8261 (3)	0.6801 (12)	0.4366 (3)	0.0299 (12)
C00L	0.2754 (3)	0.7374 (11)	0.1937 (3)	0.0289 (11)
H00K	0.2944	0.9482	0.1961	0.043*
H00L	0.2389	0.7001	0.2384	0.043*
H00M	0.2360	0.6907	0.1335	0.043*
C00M	0.8574 (3)	0.7312 (14)	0.0242 (4)	0.0430 (15)
H00N	0.8574	0.7266	-0.0377	0.052*
C00N	0.9093 (3)	0.8926 (13)	0.5812 (4)	0.0404 (13)
H00O	0.9598	1.0093	0.6161	0.049*
C00O	0.8422 (3)	0.7542 (13)	0.6231 (3)	0.0391 (13)
H00P	0.8482	0.7776	0.6858	0.047*
C00P	0.9002 (3)	0.8553 (13)	0.4887 (3)	0.0380 (13)
H00Q	0.9442	0.9488	0.4610	0.046*
C00Q	0.9318 (4)	0.8666 (14)	0.1766 (4)	0.0451 (15)
H00R	0.9828	0.9597	0.2188	0.054*
C00R	0.9332 (4)	0.8607 (15)	0.0865 (4)	0.0502 (17)
H00S	0.9852	0.9439	0.0676	0.060*

*Atomic displacement parameters (Å^2) for (**1E**)*

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O001	0.0210 (15)	0.0266 (17)	0.0191 (14)	-0.0026 (15)	0.0052 (13)	-0.0008 (14)
O002	0.0230 (15)	0.0283 (18)	0.0227 (15)	-0.0015 (15)	0.0089 (13)	-0.0023 (14)
N003	0.0227 (18)	0.0142 (19)	0.0246 (19)	-0.0043 (18)	0.0050 (16)	-0.0023 (16)

N004	0.0164 (18)	0.032 (2)	0.030 (2)	0.0058 (19)	0.0051 (17)	0.0080 (19)
N005	0.031 (2)	0.045 (3)	0.038 (2)	-0.003 (2)	0.008 (2)	0.004 (2)
C006	0.021 (2)	0.019 (2)	0.024 (2)	-0.003 (2)	0.0061 (19)	-0.002 (2)
C007	0.022 (2)	0.017 (2)	0.023 (2)	-0.005 (2)	0.0030 (19)	0.0015 (19)
C008	0.019 (2)	0.026 (3)	0.031 (3)	0.005 (2)	0.003 (2)	-0.001 (2)
C009	0.026 (2)	0.018 (2)	0.020 (2)	-0.008 (2)	0.0061 (19)	-0.001 (2)
C00A	0.022 (2)	0.016 (2)	0.027 (2)	-0.008 (2)	0.007 (2)	0.0004 (19)
C00B	0.020 (2)	0.027 (3)	0.034 (3)	0.009 (2)	0.009 (2)	0.005 (2)
C00C	0.017 (2)	0.025 (3)	0.033 (2)	0.006 (2)	0.008 (2)	0.007 (2)
C00D	0.026 (2)	0.020 (2)	0.026 (2)	-0.007 (2)	0.0105 (19)	-0.002 (2)
C00E	0.023 (2)	0.034 (3)	0.037 (3)	0.006 (2)	0.011 (2)	0.006 (2)
C00F	0.019 (2)	0.037 (3)	0.023 (2)	0.005 (2)	0.0064 (19)	0.002 (2)
C00G	0.028 (2)	0.021 (3)	0.024 (2)	0.000 (2)	0.008 (2)	-0.004 (2)
C00H	0.025 (2)	0.038 (3)	0.023 (2)	0.004 (2)	0.008 (2)	0.001 (2)
C00I	0.025 (2)	0.039 (3)	0.033 (3)	0.010 (3)	0.004 (2)	0.009 (3)
C00J	0.036 (3)	0.023 (3)	0.022 (2)	0.001 (2)	0.010 (2)	-0.002 (2)
C00K	0.021 (2)	0.029 (3)	0.039 (3)	0.009 (2)	0.006 (2)	0.002 (2)
C00L	0.028 (2)	0.024 (3)	0.035 (3)	-0.003 (2)	0.009 (2)	-0.004 (2)
C00M	0.024 (3)	0.064 (4)	0.044 (3)	0.011 (3)	0.014 (2)	0.017 (3)
C00N	0.019 (2)	0.041 (3)	0.056 (3)	0.001 (3)	0.000 (2)	-0.012 (3)
C00O	0.026 (3)	0.049 (4)	0.040 (3)	0.013 (3)	0.003 (2)	-0.009 (3)
C00P	0.023 (2)	0.048 (4)	0.043 (3)	0.007 (3)	0.009 (2)	-0.002 (3)
C00Q	0.024 (2)	0.059 (4)	0.050 (3)	-0.005 (3)	0.006 (2)	0.007 (3)
C00R	0.029 (3)	0.073 (5)	0.052 (3)	-0.010 (3)	0.017 (3)	0.013 (4)

*Geometric parameters (Å, º) for (**1E**)*

O001—C00F	1.437 (5)	C00E—H00E	0.9300
O001—C00G	1.439 (5)	C00E—C00M	1.384 (6)
O002—C00H	1.421 (5)	C00F—H00A	0.9700
O002—C00J	1.436 (5)	C00F—H00B	0.9700
N003—C006	1.347 (5)	C00G—H00C	0.9700
N003—C009	1.344 (5)	C00G—H00F	0.9700
N004—N005	1.242 (5)	C00H—H00G	0.9700
N004—C00K	1.460 (6)	C00H—H00H	0.9700
N005—C00I	1.414 (6)	C00I—C00Q	1.404 (7)
C006—C007	1.387 (6)	C00J—H00I	0.9700
C006—C00G	1.497 (6)	C00J—H00J	0.9700
C007—H007	0.9300	C00K—C00P	1.379 (7)
C007—C00A	1.385 (6)	C00L—H00K	0.9600
C008—H008	0.9300	C00L—H00L	0.9600

C008—C00B	1.381 (6)	C00L—H00M	0.9600
C008—C00O	1.387 (7)	C00M—H00N	0.9300
C009—C00D	1.384 (6)	C00M—C00R	1.363 (7)
C009—C00J	1.505 (6)	C00N—H00O	0.9300
C00A—C00D	1.393 (6)	C00N—C00O	1.406 (7)
C00A—C00L	1.509 (6)	C00N—C00P	1.374 (7)
C00B—C00H	1.501 (6)	C00O—H00P	0.9300
C00B—C00K	1.392 (6)	C00P—H00Q	0.9300
C00C—C00E	1.383 (6)	C00Q—H00R	0.9300
C00C—C00F	1.522 (6)	C00Q—C00R	1.360 (7)
C00C—C00I	1.419 (6)	C00R—H00S	0.9300
C00D—H00D	0.9300		
C00F—O001—C00G	113.1 (3)	H00C—C00G—H00F	107.7
C00H—O002—C00J	112.4 (3)	O002—C00H—C00B	109.7 (3)
C009—N003—C006	118.4 (4)	O002—C00H—H00G	109.7
N005—N004—C00K	113.4 (4)	O002—C00H—H00H	109.7
N004—N005—C00I	115.5 (4)	C00B—C00H—H00G	109.7
N003—C006—C007	122.0 (4)	C00B—C00H—H00H	109.7
N003—C006—C00G	115.0 (4)	H00G—C00H—H00H	108.2
C007—C006—C00G	123.0 (4)	N005—C00I—C00C	128.5 (4)
C006—C007—H007	119.9	C00Q—C00I—N005	112.4 (4)
C00A—C007—C006	120.1 (4)	C00Q—C00I—C00C	119.1 (4)
C00A—C007—H007	119.9	O002—C00J—C009	112.0 (4)
C00B—C008—H008	119.9	O002—C00J—H00I	109.2
C00B—C008—C00O	120.2 (4)	O002—C00J—H00J	109.2
C00O—C008—H008	119.9	C009—C00J—H00I	109.2
N003—C009—C00D	121.9 (4)	C009—C00J—H00J	109.2
N003—C009—C00J	115.8 (4)	H00I—C00J—H00J	107.9
C00D—C009—C00J	122.3 (4)	C00B—C00K—N004	116.0 (4)
C007—C00A—C00D	117.2 (4)	C00P—C00K—N004	123.9 (4)
C007—C00A—C00L	121.5 (4)	C00P—C00K—C00B	120.1 (4)
C00D—C00A—C00L	121.3 (4)	C00A—C00L—H00K	109.5
C008—C00B—C00H	122.3 (4)	C00A—C00L—H00L	109.5
C008—C00B—C00K	119.9 (4)	C00A—C00L—H00M	109.5
C00K—C00B—C00H	117.7 (4)	H00K—C00L—H00L	109.5
C00E—C00C—C00F	120.2 (4)	H00K—C00L—H00M	109.5
C00E—C00C—C00I	116.6 (4)	H00L—C00L—H00M	109.5
C00I—C00C—C00F	123.2 (4)	C00E—C00M—H00N	119.9
C009—C00D—C00A	120.2 (4)	C00R—C00M—C00E	120.2 (5)

C009—C00D—H00D	119.9	C00R—C00M—H00N	119.9
C00A—C00D—H00D	119.9	C00O—C00N—H00O	120.0
C00C—C00E—H00E	118.6	C00P—C00N—H00O	120.0
C00C—C00E—C00M	122.8 (5)	C00P—C00N—C00O	119.9 (5)
C00M—C00E—H00E	118.6	C008—C00O—C00N	119.4 (5)
O001—C00F—C00C	107.5 (3)	C008—C00O—H00P	120.3
O001—C00F—H00A	110.2	C00N—C00O—H00P	120.3
O001—C00F—H00B	110.2	C00K—C00P—H00Q	119.8
C00C—C00F—H00A	110.2	C00N—C00P—C00K	120.4 (5)
C00C—C00F—H00B	110.2	C00N—C00P—H00Q	119.8
H00A—C00F—H00B	108.5	C00I—C00Q—H00R	118.9
O001—C00G—C006	113.4 (3)	C00R—C00Q—C00I	122.2 (5)
O001—C00G—H00C	108.9	C00R—C00Q—H00R	118.9
O001—C00G—H00F	108.9	C00M—C00R—H00S	120.5
C006—C00G—H00C	108.9	C00Q—C00R—C00M	119.1 (5)
C006—C00G—H00F	108.9	C00Q—C00R—H00S	120.5

Computing details (CCDC Number 1941161)

Data collection: *CrysAlis PRO*, Agilent Technologies, Version 1.171.37.34 (release 22-05-2014 CrysAlis171 .NET) (compiled May 22 2014,16:03:01); cell refinement: *CrysAlis PRO*, Agilent Technologies, Version 1.171.37.34 (release 22-05-2014 CrysAlis171 .NET) (compiled May 22 2014,16:03:01); data reduction: *CrysAlis PRO*, Agilent Technologies, Version 1.171.37.34 (release 22-05-2014 CrysAlis171 .NET) (compiled May 22 2014,16:03:01); program(s) used to solve structure: ShelXT (Sheldrick, 2015); program(s) used to refine structure: olex2.refine (Bourhis *et al.*, 2015); molecular graphics: Olex2 (Dolomanov *et al.*, 2009); software used to prepare material for publication: Olex2 (Dolomanov *et al.*, 2009).

Crystal data	
Chemical formula	$2(ClO_4)\cdot 2(C_{22}H_{22}N_3O_2)\cdot 1(H_2O)$
M_r	936.25
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	100
a, *b*, *c* (Å)	11.7556 (9), 13.9168 (8), 14.9786 (10)
α, β, γ (°)	97.472 (5), 106.582 (6), 110.609 (6)
V (Å^3)	2124.5 (3)
Z	30

Radiation type	Mo *K*α
μ (mm^{-1})	0.23
Crystal size (mm)	0.22 × 0.14 × 0.11
Data collection	
Diffractometer	SuperNova, Dual, Cu at zero, Eos
Absorption correction	Multi-scan *CrysAlis PRO*, Agilent Technologies, Version 1.171.37.34 (release 22-05-2014 CrysAlis171 .NET) (compiled May 22 2014,16:03:01) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.851, 1.000
No. of measured, independent and observed [$I \geq 2u(I)$] reflections	16157, 7491, 5405
R_{int}	0.061
$(\sin \theta/\lambda)_{max}$ ($Å^{-1}$)	0.595
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.065, 0.164, 1.12
No. of reflections	7491
No. of parameters	623
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e $Å^{-3}$)	0.98, -1.13
$wR(F^2)$ = 0.164	$w = 1/[\sigma^2(F_o^2) + (0.0545P)^2 + 1.2466P]$ where $P = (F_o^2 + 2F_c^2)/3$

Protonated form of 1*E*

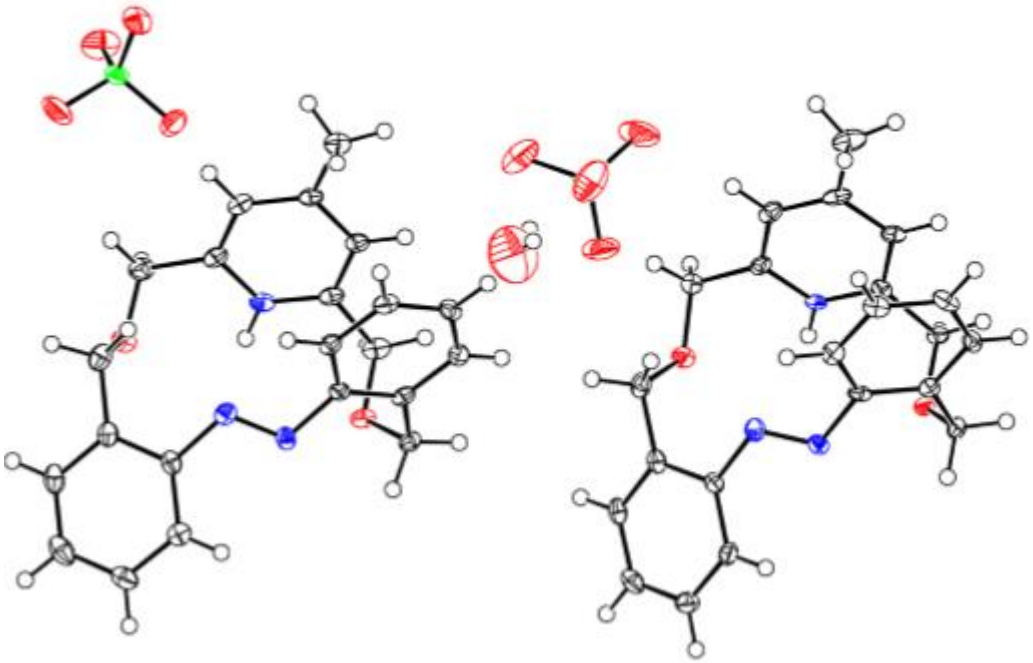

Table S8: Crystallographic parameters of protonated form 1*E*

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for (*protonated form of **1*E**)*

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl01	1.28074 (9)	1.05592 (7)	0.96566 (6)	0.0182 (2)
Cl02	0.63467 (10)	0.41413 (8)	0.43544 (9)	0.0332 (3)
O003	-0.0532 (2)	-0.07878 (18)	0.40195 (17)	0.0143 (6)
O004	0.9164 (2)	0.41749 (18)	0.90585 (17)	0.0171 (6)
O005	0.3345 (2)	0.21109 (19)	0.61421 (18)	0.0204 (6)
O006	1.3372 (2)	0.71605 (19)	1.05884 (18)	0.0196 (6)
O007	1.2807 (3)	1.0765 (2)	0.87387 (19)	0.0292 (7)
O008	1.1807 (3)	0.9527 (2)	0.9495 (2)	0.0313 (7)
N009	0.1190 (3)	0.1434 (2)	0.4457 (2)	0.0133 (7)
N00A	1.0878 (3)	0.6389 (2)	0.9225 (2)	0.0160 (7)
O00B	1.2549 (3)	1.1343 (2)	1.0175 (2)	0.0393 (8)
N00C	0.3207 (3)	0.0022 (2)	0.4794 (2)	0.0165 (7)
N00D	1.1518 (3)	0.4068 (2)	0.8779 (2)	0.0163 (7)
N00E	0.2149 (3)	-0.0736 (2)	0.4286 (2)	0.0151 (7)
N00F	1.2588 (3)	0.4868 (2)	0.9120 (2)	0.0164 (7)

O00G	1.4038 (3)	1.0584 (3)	1.0192 (2)	0.0451 (9)
O00H	0.5957 (3)	0.3371 (2)	0.4878 (2)	0.0433 (9)
O00I	0.6887 (3)	0.3770 (2)	0.3717 (3)	0.0489 (9)
O00J	0.7327 (3)	0.5132 (2)	0.5017 (3)	0.0462 (9)
C00K	0.0227 (3)	0.0882 (3)	0.3597 (3)	0.0132 (8)
C00L	1.0753 (3)	0.4008 (3)	0.7822 (3)	0.0136 (8)
C00M	0.0363 (4)	-0.1197 (3)	0.2792 (3)	0.0143 (8)
C00N	0.9399 (4)	0.3513 (3)	0.7552 (3)	0.0150 (8)
O00O	0.5248 (3)	0.4315 (3)	0.3837 (3)	0.0649 (12)
C00P	0.3675 (3)	-0.0056 (3)	0.5757 (3)	0.0141 (8)
C00Q	0.9764 (4)	0.5779 (3)	0.8482 (3)	0.0162 (8)
C00R	0.2279 (3)	0.2263 (3)	0.4562 (3)	0.0160 (8)
C00S	0.1707 (4)	-0.0707 (3)	0.3296 (3)	0.0153 (8)
C00T	1.0522 (4)	0.4220 (3)	0.6228 (3)	0.0184 (9)
H00T	1.0890 (4)	0.4461 (3)	0.5783 (3)	0.0220 (10)*
C00U	0.9625 (4)	0.5960 (3)	0.7578 (3)	0.0158 (8)
H00U	0.8854 (4)	0.5557 (3)	0.7061 (3)	0.0189 (10)*
C00V	1.0649 (4)	0.6752 (3)	0.7443 (3)	0.0158 (8)
C00W	0.9173 (4)	0.3704 (3)	0.5949 (3)	0.0175 (8)
H00W	0.8646 (4)	0.3586 (3)	0.5315 (3)	0.0210 (10)*
C00X	1.1312 (4)	0.4373 (3)	0.7162 (3)	0.0164 (8)
H00X	1.2211 (4)	0.4718 (3)	0.7348 (3)	0.0197 (10)*
C00Y	-0.0105 (4)	-0.1228 (3)	0.1819 (3)	0.0161 (8)
H00Y	-0.0995 (4)	-0.1556 (3)	0.1472 (3)	0.0193 (10)*
C00Z	0.4335 (3)	0.0900 (3)	0.6485 (3)	0.0152 (8)
C010	1.3372 (4)	0.3974 (3)	1.0338 (3)	0.0180 (8)
H010	1.2786 (4)	0.3310 (3)	0.9932 (3)	0.0216 (10)*
C011	-0.0558 (4)	-0.1620 (3)	0.3309 (3)	0.0163 (8)
H01a	-0.0331 (4)	-0.2125 (3)	0.3627 (3)	0.0196 (10)*
H01b	-0.1435 (4)	-0.1994 (3)	0.2840 (3)	0.0196 (10)*
C012	1.4303 (3)	0.5898 (3)	1.0639 (3)	0.0171 (8)
C013	-0.0934 (3)	-0.0032 (3)	0.3612 (3)	0.0151 (8)
H01c	-0.1557 (3)	-0.0375 (3)	0.2961 (3)	0.0182 (10)*
H01d	-0.1356 (3)	0.0235 (3)	0.3991 (3)	0.0182 (10)*
C014	0.0360 (4)	0.1184 (3)	0.2780 (3)	0.0161 (8)
H014	-0.0309 (4)	0.0838 (3)	0.2186 (3)	0.0194 (10)*
C015	0.2564 (4)	-0.0251 (3)	0.2840 (3)	0.0178 (8)
H015	0.3457 (4)	0.0070 (3)	0.3179 (3)	0.0213 (10)*
C016	1.3410 (3)	0.4891 (3)	1.0043 (3)	0.0161 (8)
C017	0.8810 (4)	0.3236 (3)	0.8311 (3)	0.0166 (8)

C018	0.1508 (4)	0.2013 (3)	0.2849 (3)	0.0179 (9)
C019	0.4514 (4)	0.1937 (3)	0.6233 (3)	0.0188 (9)
H01e	0.4670 (4)	0.1920 (3)	0.5630 (3)	0.0226 (10)*
H01f	0.5258 (4)	0.2509 (3)	0.6733 (3)	0.0226 (10)*
C01A	0.3989 (4)	-0.1040 (3)	0.6941 (3)	0.0217 (9)
H01g	0.3909 (4)	-0.1681 (3)	0.7094 (3)	0.0261 (11)*
C01B	0.4749 (3)	0.0850 (3)	0.7431 (3)	0.0181 (8)
H01h	0.5156 (3)	0.1475 (3)	0.7921 (3)	0.0217 (10)*
C01C	0.8620 (4)	0.3368 (3)	0.6611 (3)	0.0163 (8)
H01u	0.7720 (4)	0.3042 (3)	0.6426 (3)	0.0196 (10)*
C01D	0.3526 (3)	-0.1019 (3)	0.5990 (3)	0.0182 (8)
H01i	0.3113 (3)	-0.1648 (3)	0.5505 (3)	0.0219 (10)*
C01E	1.1750 (4)	0.7382 (3)	0.8248 (3)	0.0180 (8)
H01v	1.2419 (4)	0.7935 (3)	0.8179 (3)	0.0216 (10)*
C01F	0.0745 (4)	-0.0774 (3)	0.1362 (3)	0.0202 (9)
H01j	0.0425 (4)	-0.0799 (3)	0.0712 (3)	0.0242 (10)*
C01G	0.2073 (4)	-0.0282 (3)	0.1878 (3)	0.0194 (9)
H01k	0.2639 (4)	0.0031 (3)	0.1571 (3)	0.0233 (10)*
C01H	1.2988 (4)	0.7840 (3)	1.0052 (3)	0.0221 (9)
C01I	0.2452 (4)	0.2558 (3)	0.3751 (3)	0.0183 (8)
H01l	0.3207 (4)	0.3127 (3)	0.3810 (3)	0.0220 (10)*
C01J	1.1869 (4)	0.7203 (3)	0.9146 (3)	0.0170 (8)
C01K	0.8728 (4)	0.4945 (3)	0.8713 (3)	0.0202 (9)
H01y	0.7954 (4)	0.4587 (3)	0.8138 (3)	0.0243 (11)*
H	0.8500 (4)	0.5289 (3)	0.9198 (3)	0.0243 (11)*
C01L	0.4573 (4)	-0.0106 (3)	0.7665 (3)	0.0205 (9)
H01m	0.4847 (4)	-0.0122 (3)	0.8308 (3)	0.0246 (11)*
C01M	0.3195 (4)	0.2844 (3)	0.5584 (3)	0.0228 (9)
H01n	0.2857 (4)	0.3293 (3)	0.5874 (3)	0.0274 (11)*
H01o	0.4037 (4)	0.3295 (3)	0.5579 (3)	0.0274 (11)*
C01N	1.4325 (4)	0.6878 (3)	1.0322 (3)	0.0218 (9)
C01O	1.4202 (4)	0.4056 (3)	1.1230 (3)	0.0225 (9)
H01	1.4190 (4)	0.3446 (3)	1.1425 (3)	0.0269 (11)*
C01P	1.0571 (4)	0.6878 (3)	0.6454 (3)	0.0205 (9)
H0aa	1.095 (2)	0.6458 (15)	0.6186 (7)	0.0308 (13)*
Ha	0.9676 (4)	0.6645 (17)	0.6051 (5)	0.0308 (13)*
Hb	1.1038 (19)	0.7611 (4)	0.6489 (3)	0.0308 (13)*
C01Q	1.5062 (4)	0.5055 (3)	1.1841 (3)	0.0266 (10)
H1aa	1.5608 (4)	0.5113 (3)	1.2452 (3)	0.0319 (12)*
C01R	1.5103 (4)	0.5962 (3)	1.1536 (3)	0.0230 (9)

H2aa	1.5682 (4)	0.6625 (3)	1.1947 (3)	0.0277 (11)*
C01S	0.1691 (4)	0.2286 (3)	0.1944 (3)	0.0282 (10)
H01p	0.214 (2)	0.1905 (16)	0.1721 (11)	0.0423 (15)*
H01q	0.0857 (4)	0.2093 (19)	0.1457 (6)	0.0423 (15)*
H01r	0.219 (2)	0.3036 (5)	0.2080 (5)	0.0423 (15)*
O01T	0.6505 (6)	0.4664 (5)	0.6742 (4)	0.1051 (16)
H009	0.111 (4)	0.126 (3)	0.497 (3)	0.022 (11)*
H01s	0.785 (3)	0.284 (3)	0.800 (2)	0.007 (9)*
H01t	0.919 (3)	0.281 (3)	0.868 (2)	0.010 (9)*
H01z	1.516 (4)	0.747 (3)	1.067 (3)	0.025 (11)*
Hc	1.408 (4)	0.680 (3)	0.965 (3)	0.029 (12)*
H01w	1.371 (4)	0.832 (3)	0.992 (3)	0.015 (10)*
H01x	1.260 (4)	0.816 (3)	1.041 (3)	0.022 (10)*
H00A	1.100 (4)	0.624 (3)	0.979 (3)	0.027 (12)*
H3aa	0.645 (8)	0.446 (7)	0.616 (2)	0.158 (2)*
Hd	0.596 (7)	0.494 (7)	0.670 (5)	0.158 (2)*

*Atomic displacement parameters (Å^2) for (*protonated form of **1*E**)*

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl01	0.0211 (5)	0.0189 (5)	0.0156 (5)	0.0086 (4)	0.0063 (4)	0.0068 (4)
Cl02	0.0227 (6)	0.0310 (6)	0.0598 (8)	0.0146 (5)	0.0219 (6)	0.0293 (6)
O003	0.0176 (14)	0.0123 (13)	0.0139 (14)	0.0068 (11)	0.0056 (11)	0.0038 (10)
O004	0.0251 (15)	0.0147 (13)	0.0166 (14)	0.0100 (11)	0.0112 (12)	0.0060 (11)
O005	0.0187 (15)	0.0191 (14)	0.0248 (16)	0.0096 (12)	0.0061 (12)	0.0083 (12)
O006	0.0235 (16)	0.0207 (14)	0.0176 (15)	0.0120 (12)	0.0082 (12)	0.0043 (12)
O007	0.0311 (18)	0.0415 (18)	0.0173 (15)	0.0124 (14)	0.0120 (14)	0.0143 (13)
O008	0.0330 (18)	0.0199 (15)	0.0297 (17)	0.0007 (13)	0.0077 (14)	0.0065 (13)
N009	0.0172 (18)	0.0140 (16)	0.0126 (17)	0.0079 (14)	0.0071 (14)	0.0077 (14)
N00A	0.0237 (19)	0.0173 (17)	0.0139 (18)	0.0118 (15)	0.0108 (15)	0.0067 (14)
O00B	0.068 (2)	0.0285 (17)	0.0295 (18)	0.0264 (16)	0.0227 (17)	0.0038 (14)
N00C	0.0170 (18)	0.0168 (16)	0.0135 (17)	0.0062 (14)	0.0048 (14)	0.0009 (14)
N00D	0.0133 (18)	0.0173 (17)	0.0175 (17)	0.0075 (14)	0.0039 (14)	0.0018 (14)
N00E	0.0173 (18)	0.0151 (16)	0.0136 (17)	0.0087 (14)	0.0043 (14)	0.0028 (13)
N00F	0.0177 (18)	0.0137 (16)	0.0191 (18)	0.0076 (14)	0.0078 (15)	0.0020 (14)
O00G	0.0248 (18)	0.060 (2)	0.049 (2)	0.0171 (16)	0.0024 (16)	0.0339 (18)
O00H	0.036 (2)	0.0410 (19)	0.069 (2)	0.0174 (16)	0.0275 (18)	0.0400 (18)
O00I	0.043 (2)	0.0385 (19)	0.059 (2)	0.0044 (16)	0.0292 (19)	0.0019 (17)
O00J	0.044 (2)	0.0234 (17)	0.073 (3)	0.0093 (15)	0.0293 (19)	0.0102 (16)
C00K	0.016 (2)	0.0132 (18)	0.0127 (19)	0.0107 (16)	0.0034 (16)	0.0011 (15)
C00L	0.018 (2)	0.0101 (18)	0.014 (2)	0.0083 (16)	0.0046 (17)	0.0016 (15)

C00M	0.019 (2)	0.0095 (18)	0.016 (2)	0.0088 (16)	0.0054 (17)	-0.0004 (15)
C00N	0.018 (2)	0.0097 (18)	0.021 (2)	0.0074 (15)	0.0108 (17)	0.0035 (16)
O00O	0.027 (2)	0.078 (3)	0.110 (3)	0.0274 (19)	0.025 (2)	0.073 (3)
C00P	0.012 (2)	0.0184 (19)	0.013 (2)	0.0062 (16)	0.0051 (16)	0.0058 (16)
C00Q	0.021 (2)	0.0128 (18)	0.021 (2)	0.0108 (16)	0.0115 (18)	0.0058 (16)
C00R	0.014 (2)	0.0097 (18)	0.026 (2)	0.0065 (16)	0.0061 (17)	0.0049 (16)
C00S	0.023 (2)	0.0129 (18)	0.014 (2)	0.0116 (16)	0.0073 (17)	0.0055 (16)
C00T	0.028 (2)	0.0146 (19)	0.016 (2)	0.0092 (17)	0.0109 (18)	0.0045 (16)
C00U	0.018 (2)	0.0136 (19)	0.021 (2)	0.0101 (16)	0.0090 (17)	0.0057 (16)
C00V	0.020 (2)	0.0132 (19)	0.020 (2)	0.0104 (16)	0.0101 (18)	0.0066 (16)
C00W	0.023 (2)	0.018 (2)	0.012 (2)	0.0103 (17)	0.0044 (17)	0.0026 (16)
C00X	0.016 (2)	0.0134 (18)	0.022 (2)	0.0065 (16)	0.0088 (17)	0.0042 (16)
C00Y	0.018 (2)	0.0152 (19)	0.013 (2)	0.0086 (16)	0.0014 (17)	-0.0005 (16)
C00Z	0.0093 (19)	0.020 (2)	0.018 (2)	0.0079 (16)	0.0051 (16)	0.0026 (16)
C010	0.019 (2)	0.019 (2)	0.021 (2)	0.0092 (17)	0.0106 (18)	0.0054 (17)
C011	0.018 (2)	0.0110 (18)	0.015 (2)	0.0048 (16)	0.0021 (17)	-0.0015 (15)
C012	0.013 (2)	0.021 (2)	0.019 (2)	0.0067 (16)	0.0071 (17)	0.0034 (17)
C013	0.017 (2)	0.0131 (18)	0.019 (2)	0.0081 (16)	0.0082 (17)	0.0068 (16)
C014	0.024 (2)	0.0145 (19)	0.016 (2)	0.0126 (17)	0.0092 (18)	0.0059 (16)
C015	0.017 (2)	0.018 (2)	0.022 (2)	0.0088 (17)	0.0090 (18)	0.0043 (17)
C016	0.013 (2)	0.022 (2)	0.015 (2)	0.0074 (16)	0.0062 (17)	0.0044 (16)
C017	0.020 (2)	0.0123 (19)	0.016 (2)	0.0054 (17)	0.0069 (18)	0.0021 (16)
C018	0.027 (2)	0.0133 (19)	0.025 (2)	0.0138 (17)	0.0182 (19)	0.0095 (17)
C019	0.013 (2)	0.018 (2)	0.023 (2)	0.0058 (16)	0.0054 (17)	0.0017 (17)
C01A	0.020 (2)	0.021 (2)	0.025 (2)	0.0079 (18)	0.0081 (19)	0.0111 (18)
C01B	0.015 (2)	0.021 (2)	0.013 (2)	0.0062 (17)	0.0015 (17)	-0.0025 (16)
C01C	0.014 (2)	0.0142 (19)	0.021 (2)	0.0079 (16)	0.0058 (17)	0.0026 (16)
C01D	0.013 (2)	0.0148 (19)	0.023 (2)	0.0035 (16)	0.0035 (17)	0.0031 (17)
C01E	0.021 (2)	0.0135 (19)	0.024 (2)	0.0072 (17)	0.0129 (19)	0.0061 (17)
C01F	0.031 (2)	0.023 (2)	0.012 (2)	0.0194 (19)	0.0054 (18)	0.0041 (17)
C01G	0.025 (2)	0.022 (2)	0.019 (2)	0.0141 (18)	0.0125 (19)	0.0079 (17)
C01H	0.029 (2)	0.020 (2)	0.017 (2)	0.0089 (19)	0.0090 (19)	0.0055 (17)
C01I	0.017 (2)	0.0135 (19)	0.028 (2)	0.0071 (16)	0.0116 (18)	0.0059 (17)
C01J	0.021 (2)	0.0107 (18)	0.022 (2)	0.0087 (16)	0.0102 (18)	0.0025 (16)
C01K	0.025 (2)	0.021 (2)	0.026 (2)	0.0137 (18)	0.0174 (19)	0.0106 (18)
C01L	0.017 (2)	0.032 (2)	0.016 (2)	0.0115 (18)	0.0065 (18)	0.0105 (18)
C01M	0.020 (2)	0.017 (2)	0.026 (2)	0.0060 (17)	0.0007 (18)	0.0072 (17)
C01N	0.022 (2)	0.019 (2)	0.021 (2)	0.0050 (19)	0.010 (2)	0.0006 (18)
C01O	0.017 (2)	0.034 (2)	0.026 (2)	0.0151 (19)	0.0128 (19)	0.0174 (19)
C01P	0.026 (2)	0.021 (2)	0.019 (2)	0.0116 (18)	0.0114 (18)	0.0068 (17)

C01Q	0.021 (2)	0.045 (3)	0.019 (2)	0.016 (2)	0.0084 (19)	0.012 (2)
C01R	0.018 (2)	0.028 (2)	0.016 (2)	0.0054 (18)	0.0053 (18)	-0.0007 (18)
C01S	0.040 (3)	0.026 (2)	0.032 (3)	0.016 (2)	0.026 (2)	0.016 (2)
O01T	0.094 (4)	0.121 (5)	0.096 (4)	0.047 (3)	0.030 (3)	0.018 (4)

*Geometric parameters (Å, º) for (*protonated form of **1*E**)*

Cl01—O007	1.440 (3)	C00Z—C01B	1.380 (5)
Cl01—O008	1.436 (3)	C010—H010	0.9300
Cl01—O00B	1.426 (3)	C010—C016	1.393 (5)
Cl01—O00G	1.426 (3)	C010—C01O	1.374 (5)
Cl02—O00H	1.433 (3)	C011—H01a	0.9700
Cl02—O00I	1.425 (3)	C011—H01b	0.9700
Cl02—O00J	1.444 (3)	C012—C016	1.403 (5)
Cl02—O00O	1.423 (3)	C012—C01N	1.496 (5)
O003—C011	1.452 (4)	C012—C01R	1.374 (5)
O003—C013	1.433 (4)	C013—H01c	0.9700
O004—C017	1.451 (4)	C013—H01d	0.9700
O004—C01K	1.434 (4)	C014—H014	0.9300
O005—C019	1.450 (4)	C014—C018	1.399 (5)
O005—C01M	1.426 (4)	C015—H015	0.9300
O006—C01H	1.426 (5)	C015—C01G	1.380 (5)
O006—C01N	1.446 (4)	C017—H01s	0.99 (3)
N009—C00K	1.352 (4)	C017—H01t	0.99 (3)
N009—C00R	1.338 (4)	C018—C01I	1.385 (5)
N009—H009	0.86 (4)	C018—C01S	1.506 (5)
N00A—C00Q	1.347 (5)	C019—H01e	0.9700
N00A—C01J	1.356 (5)	C019—H01f	0.9700
N00A—H00A	0.89 (4)	C01A—H01g	0.9300
N00C—N00E	1.251 (4)	C01A—C01D	1.380 (5)
N00C—C00P	1.423 (5)	C01A—C01L	1.386 (5)
N00D—N00F	1.258 (4)	C01B—H01h	0.9300
N00D—C00L	1.432 (5)	C01B—C01L	1.381 (5)
N00E—C00S	1.436 (5)	C01C—H01u	0.9300
N00F—C016	1.431 (5)	C01D—H01i	0.9300
C00K—C013	1.512 (5)	C01E—H01v	0.9300
C00K—C014	1.376 (5)	C01E—C01J	1.376 (5)
C00L—C00N	1.399 (5)	C01F—H01j	0.9300
C00L—C00X	1.391 (5)	C01F—C01G	1.388 (5)
C00M—C00S	1.399 (5)	C01G—H01k	0.9300
C00M—C00Y	1.393 (5)	C01H—C01J	1.485 (5)

C00M—C011	1.506 (5)	C01H—H01w	0.97 (4)
C00N—C017	1.515 (5)	C01H—H01x	0.96 (4)
C00N—C01C	1.387 (5)	C01I—H01l	0.9300
C00P—C00Z	1.405 (5)	C01K—H01y	0.9700
C00P—C01D	1.392 (5)	C01K—H	0.9700
C00Q—C00U	1.384 (5)	C01L—H01m	0.9300
C00Q—C01K	1.516 (5)	C01M—H01n	0.9700
C00R—C01I	1.378 (5)	C01M—H01o	0.9700
C00R—C01M	1.510 (5)	C01N—H01z	0.98 (4)
C00S—C015	1.393 (5)	C01N—Hc	0.94 (4)
C00T—H00T	0.9300	C01O—H01	0.9300
C00T—C00W	1.396 (5)	C01O—C01Q	1.394 (6)
C00T—C00X	1.381 (5)	C01P—H0aa	0.9600
C00U—H00U	0.9300	C01P—Ha	0.9600
C00U—C00V	1.403 (5)	C01P—Hb	0.9600
C00V—C01E	1.390 (5)	C01Q—H1aa	0.9300
C00V—C01P	1.496 (5)	C01Q—C01R	1.387 (5)
C00W—H00W	0.9300	C01R—H2aa	0.9300
C00W—C01C	1.378 (5)	C01S—H01p	0.9600
C00X—H00X	0.9300	C01S—H01q	0.9600
C00Y—H00Y	0.9300	C01S—H01r	0.9600
C00Y—C01F	1.387 (5)	O01T—H3aa	0.8500
C00Z—C019	1.496 (5)	O01T—Hd	0.8500
O008—Cl01—O007	108.86 (17)	C010—C016—N00F	122.9 (3)
O00B—Cl01—O007	109.28 (17)	C012—C016—N00F	116.3 (3)
O00B—Cl01—O008	109.41 (18)	C012—C016—C010	120.7 (3)
O00G—Cl01—O007	109.79 (18)	C00N—C017—O004	111.5 (3)
O00G—Cl01—O008	109.40 (18)	H01s—C017—O004	112.3 (18)
O00G—Cl01—O00B	110.1 (2)	H01s—C017—C00N	109.5 (19)
O00I—Cl02—O00H	109.36 (19)	H01t—C017—O004	102.4 (19)
O00J—Cl02—O00H	109.8 (2)	H01t—C017—C00N	111.0 (19)
O00J—Cl02—O00I	108.50 (19)	H01t—C017—H01s	110 (3)
O00O—Cl02—O00H	109.15 (18)	C01I—C018—C014	118.8 (3)
O00O—Cl02—O00I	111.1 (2)	C01S—C018—C014	119.5 (4)
O00O—Cl02—O00J	108.9 (2)	C01S—C018—C01I	121.7 (3)
C013—O003—C011	113.5 (3)	C00Z—C019—O005	108.5 (3)
C01K—O004—C017	113.9 (3)	H01e—C019—O005	109.99 (18)
C01M—O005—C019	113.4 (3)	H01e—C019—C00Z	109.99 (19)
C01N—O006—C01H	112.2 (3)	H01f—C019—O005	109.99 (18)
C00R—N009—C00K	123.6 (3)	H01f—C019—C00Z	110.0 (2)

H009—N009—C00K	119 (3)	H01f—C019—H01e	108.4
H009—N009—C00R	117 (3)	C01D—C01A—H01g	120.0 (2)
C01J—N00A—C00Q	123.6 (3)	C01L—C01A—H01g	120.0 (2)
H00A—N00A—C00Q	119 (3)	C01L—C01A—C01D	119.9 (4)
H00A—N00A—C01J	117 (3)	H01h—C01B—C00Z	119.2 (2)
C00P—N00C—N00E	112.9 (3)	C01L—C01B—C00Z	121.5 (3)
C00L—N00D—N00F	113.2 (3)	C01L—C01B—H01h	119.2 (2)
C00S—N00E—N00C	113.6 (3)	C00W—C01C—C00N	120.4 (3)
C016—N00F—N00D	113.7 (3)	H01u—C01C—C00N	119.8 (2)
C013—C00K—N009	116.5 (3)	H01u—C01C—C00W	119.8 (2)
C014—C00K—N009	118.8 (3)	C01A—C01D—C00P	120.1 (3)
C014—C00K—C013	124.7 (3)	H01i—C01D—C00P	120.0 (2)
C00N—C00L—N00D	117.2 (3)	H01i—C01D—C01A	120.0 (2)
C00X—C00L—N00D	122.2 (3)	H01v—C01E—C00V	119.3 (2)
C00X—C00L—C00N	120.5 (3)	C01J—C01E—C00V	121.4 (3)
C00Y—C00M—C00S	118.7 (3)	C01J—C01E—H01v	119.3 (2)
C011—C00M—C00S	120.4 (3)	H01j—C01F—C00Y	120.0 (2)
C011—C00M—C00Y	120.8 (3)	C01G—C01F—C00Y	119.9 (3)
C017—C00N—C00L	119.4 (3)	C01G—C01F—H01j	120.0 (2)
C01C—C00N—C00L	119.3 (3)	C01F—C01G—C015	120.7 (3)
C01C—C00N—C017	121.1 (3)	H01k—C01G—C015	119.6 (2)
C00Z—C00P—N00C	116.8 (3)	H01k—C01G—C01F	119.6 (2)
C01D—C00P—N00C	123.0 (3)	C01J—C01H—O006	110.5 (3)
C01D—C00P—C00Z	120.2 (3)	H01w—C01H—O006	111 (2)
C00U—C00Q—N00A	118.9 (3)	H01w—C01H—C01J	111 (2)
C01K—C00Q—N00A	116.4 (3)	H01x—C01H—O006	105 (2)
C01K—C00Q—C00U	124.6 (4)	H01x—C01H—C01J	102 (2)
C01I—C00R—N009	118.6 (3)	H01x—C01H—H01w	116 (3)
C01M—C00R—N009	116.4 (3)	C018—C01I—C00R	120.4 (3)
C01M—C00R—C01I	124.9 (3)	H01l—C01I—C00R	119.8 (2)
C00M—C00S—N00E	116.7 (3)	H01l—C01I—C018	119.8 (2)
C015—C00S—N00E	122.3 (3)	C01E—C01J—N00A	118.0 (4)
C015—C00S—C00M	121.0 (3)	C01H—C01J—N00A	116.4 (3)
C00W—C00T—H00T	119.9 (2)	C01H—C01J—C01E	125.6 (3)
C00X—C00T—H00T	119.9 (2)	C00Q—C01K—O004	111.7 (3)
C00X—C00T—C00W	120.2 (3)	H01y—C01K—O004	109.27 (19)
H00U—C00U—C00Q	120.0 (2)	H01y—C01K—C00Q	109.3 (2)
C00V—C00U—C00Q	119.9 (4)	H—C01K—O004	109.27 (17)
C00V—C00U—H00U	120.0 (2)	H—C01K—C00Q	109.27 (19)
C01E—C00V—C00U	118.1 (3)	H—C01K—H01y	107.9

C01P—C00V—C00U	120.5 (3)	C01B—C01L—C01A	119.8 (4)
C01P—C00V—C01E	121.4 (3)	H01m—C01L—C01A	120.1 (2)
H00W—C00W—C00T	119.9 (2)	H01m—C01L—C01B	120.1 (2)
C01C—C00W—C00T	120.2 (3)	C00R—C01M—O005	110.7 (3)
C01C—C00W—H00W	119.9 (2)	H01n—C01M—O005	109.50 (19)
C00T—C00X—C00L	119.5 (3)	H01n—C01M—C00R	109.5 (2)
H00X—C00X—C00L	120.3 (2)	H01o—C01M—O005	109.50 (19)
H00X—C00X—C00T	120.3 (2)	H01o—C01M—C00R	109.5 (2)
H00Y—C00Y—C00M	119.7 (2)	H01o—C01M—H01n	108.1
C01F—C00Y—C00M	120.5 (4)	C012—C01N—O006	107.5 (3)
C01F—C00Y—H00Y	119.7 (2)	H01z—C01N—O006	106 (2)
C019—C00Z—C00P	120.2 (3)	H01z—C01N—C012	110 (2)
C01B—C00Z—C00P	118.3 (3)	Hc—C01N—O006	105 (2)
C01B—C00Z—C019	121.4 (3)	Hc—C01N—C012	115 (2)
C016—C010—H010	120.1 (2)	Hc—C01N—H01z	112 (3)
C01O—C010—H010	120.1 (2)	H01—C01O—C010	120.1 (2)
C01O—C010—C016	119.8 (4)	C01Q—C01O—C010	119.9 (4)
C00M—C011—O003	112.7 (3)	C01Q—C01O—H01	120.1 (2)
H01a—C011—O003	109.05 (17)	H0aa—C01P—C00V	109.5
H01a—C011—C00M	109.05 (19)	Ha—C01P—C00V	109.5
H01b—C011—O003	109.05 (18)	Ha—C01P—H0aa	109.5
H01b—C011—C00M	109.0 (2)	Hb—C01P—C00V	109.5
H01b—C011—H01a	107.8	Hb—C01P—H0aa	109.5
C01N—C012—C016	120.4 (3)	Hb—C01P—Ha	109.5
C01R—C012—C016	118.5 (3)	H1aa—C01Q—C01O	120.1 (2)
C01R—C012—C01N	121.1 (3)	C01R—C01Q—C01O	119.9 (4)
C00K—C013—O003	110.3 (3)	C01R—C01Q—H1aa	120.1 (2)
H01c—C013—O003	109.59 (18)	C01Q—C01R—C012	121.2 (4)
H01c—C013—C00K	109.6 (2)	H2aa—C01R—C012	119.4 (2)
H01d—C013—O003	109.59 (17)	H2aa—C01R—C01Q	119.4 (2)
H01d—C013—C00K	109.59 (18)	H01p—C01S—C018	109.5
H01d—C013—H01c	108.1	H01q—C01S—C018	109.5
H014—C014—C00K	120.2 (2)	H01q—C01S—H01p	109.5
C018—C014—C00K	119.6 (4)	H01r—C01S—C018	109.5
C018—C014—H014	120.2 (2)	H01r—C01S—H01p	109.5
H015—C015—C00S	120.4 (2)	H01r—C01S—H01q	109.5
C01G—C015—C00S	119.2 (4)	Hd—O01T—H3aa	104.5
C01G—C015—H015	120.4 (2)		

References for the Supporting Information

(1) Samanta, M.; Krishna, V. S. R.; Bandyopadhyay, S. *Chem. Commun*. **2014**, *50*, 10577.
(2) Li, J.; Wang, H.; Liu, L.; Sun, J. *RSC Advances* **2014,** *4*, 49974.
(3) Fischer, E. *J. Phys. Chem*. **1967**, *71*, 3704**.**

(4) Roy, B.; Roy, T.S.; Rahaman, S. A.; Das, K.; Bandyopadhyay, S. *ACS Sens.* **2018**, *3*, 2166.
(5) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. J. *Appl. Cryst*., **2009**, *42*, 339.
(6) Palatinus, L.; Chapuis, G. J. *Appl. Cryst*., **2007**, *40*, 786.
(7) Sheldrick, G. M. *Acta Cryst*., *A* **2008**, *64*, 112.