# Two Fluorescein-based Chemosensors for the Fast Detection of 2, 4, 6-Trinitrophenol (TNP) in Water

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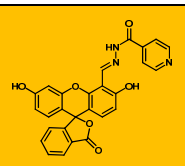
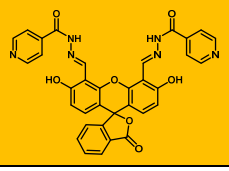
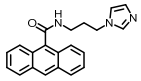
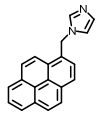
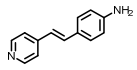
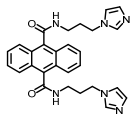
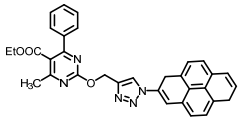
## 1. Some reported work for the detection of TNP.

Table S1. A comparison about ours and some reported work for the detection of TNP.

| Probe | | Solvent | Ex (nm) | Reference |
|---|---|---|---|---|
| **F1** |  | Ethanol | 500 | ***This work*** |
| | | HEPES buffer(pH=7.0) | 400 | |
| **F2** |  | Ethanol | 517 | |
| | | HEPES buffer(pH=7.0) | 400 | |
| **A** |  | EtOH | 362 | (1) |
| **B** |  | Toluene Acetonitrile | 342 | (2) |
| **C** |  | THF | 350 | (3) |
| **D** |  | EtOH-$H_2O$ (1/1, v/v, pH=7.0) | 366 | (4) |
| **E** |  | THF-HEPES (1/9, v/v, pH=6.99) | 342 | (5) |


(1) A. Pandith, A. Kumar, J.-Y. Lee, H.-S. Kim, *Tetrahedron Lett.*, 2015, **56**, 7094–7099.

(2) R. Sodkhomkhum, M. Masik, S. Watchasit, C. Suksai, J. Boonmak, S. Youngme, N. Wanichacheva, V. Ervithayasuporn, *Sens. Actuators, B*, 2017, **245**, 665–673.

(3) J. Pan, F. Tang, A. Ding, L. Kong, L. Yang, X. Tao, Y. Tian, J. Yang, *RSC Adv.*, 2015, **5**, 191–195.

(4) A. Pandith, A. Kumar and H.S. Kim, *RSC Adv.*, 2016, **6**, 68628–68637.

(5) R. Chopra, P. Kaur, K. Singh, *Anal. Chim. Acta*, 2015, **864**, 55–63.

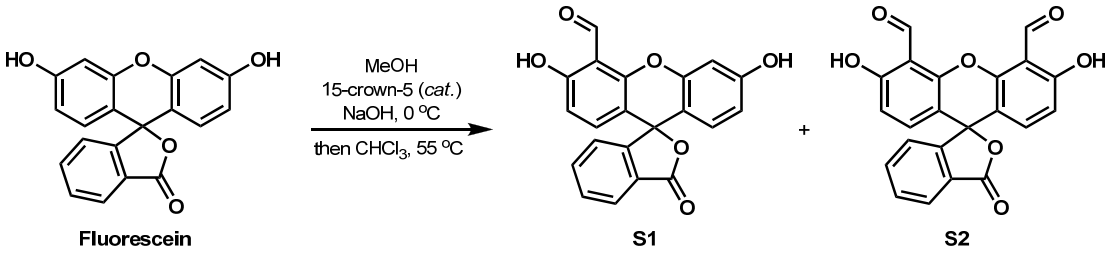
## 2. General information.

The commercially available chemicals were used without further purification. All of solvents used in experiments were analytical-reagent grade. $^{1}H$ and $^{13}C$ NMR spectra were measured on the Bruker ADVANCE III 400 MHz, JEOL JNM-ECS M Hz or Varian Mercury plus 300 MHz instruments using TMS as an internal standard. The single-crustal X-ray was performed on a Bruker smart CCD area detector diffractometer by the use of graphite-monochromated Mo Kα radiation (λ= 0.71072 Å). Lorentz-plarization and absorption corrections were applied for the compounds. The structures were solved with direct methods and refined by full-matrix least-squares on F2 by the use of the SHELXL-97 program package. Mass spectra were determined on a Bruker esquire 6000 spectrometer. IR spectra were recorded on Nicolet FT-170SX instrument using KBr discs in the 400–4000 $cm^{-1}$ region. UV-vis spectra were performed on an Agilent Carry 5000 UV-Vis-NIR spectrophotometer. Fluorescence spectra were recorded on a Hitachi F-7000 spectrophotometer equipped with quartz cuvettes of 1 cm path length. All pH measurements were made with a pH-10C digital pH meter.

Various stock solutions of NACs such as P (phenol), TNP (2,4,6-trinitrophenol), 3, 5-DMP (3,5-dimethoxyphenol), 4-NB (4-nitrobenzene), 1, 3-DNB (1,3-dinitrobenzene), 4-NT (4-nitrotol-uene), 2,4-DNT (2,4-dinitrotoluene), 3, 5-DMT (3,5-methylcatechol), TNT (2,4,6-trinitrotoluene), PAP (*p*-aminophenol), 2-IP (2-iodophenol), 4-MP (4-methoxyphenol), 2-CP (2-chlorophenol) and 4-BP (4-bromophenol) in DMSO or ethanol were prepared. Stock solutions of **F1** and **F2** (10.0 mM) were also prepared in DMSO. Test solutions were prepared by placing 2.0 $\mu$L of the probe stock solution into a test tube, and then diluting to 2.0 mL, followed by the addition of an appropriate aliquot of NACs's stock solution. Fluorescence quantum yields were determined in solution, using rhodamin 6G ($\Phi$ = 0.76 in $H_2O$ and $\Phi$ = 0.88 in ethanol ) as a standard.[6]

(6) J. Olmsted, *J. Phys. Chem.*, 1979, **83**, 2581–2584.

## 3. Synthesis of fluorescein-derived aldehydes S1 and S2.




This procedure was adapted from a known literature.[7] To a 250 mL three-neck round-bottom flask were added fluorescein (5.0 g, 15.0 mmol) and MeOH (12 mL) at room temperature. The whole system was then cooled to 0 °C, followed by the addition of a mixture of NaOH aqueous solution (40 g, 50%) and 15-crown-5 (60 $\mu$L) within 5 min. The resulting mixture was stirred for 10 min, and then allowed to warm gradually in an oil bath. $CHCl_3$ (20 mL) was added dropwise while the reaction temperature was maintained at 55 °C. The reaction mixture was further stirred for 10 h at this temperature, and then cooled to room temperature. The mixture is acidified with $H_2SO_4$ (5 mL, 10 M), and the purple-black precipitate appeared. This solid was filtered and dried and purified by flash column chromatography (DCM/EtOAc = 85:15) on silica gel to afford the crude products, which could be recrystallized in acetone (10 mL) to give pure sample (**S1**, 708 mg, 13% yield) as a pale-yellow solid and (**S2**, 136 mg, 2.3% yield) as a white solid.

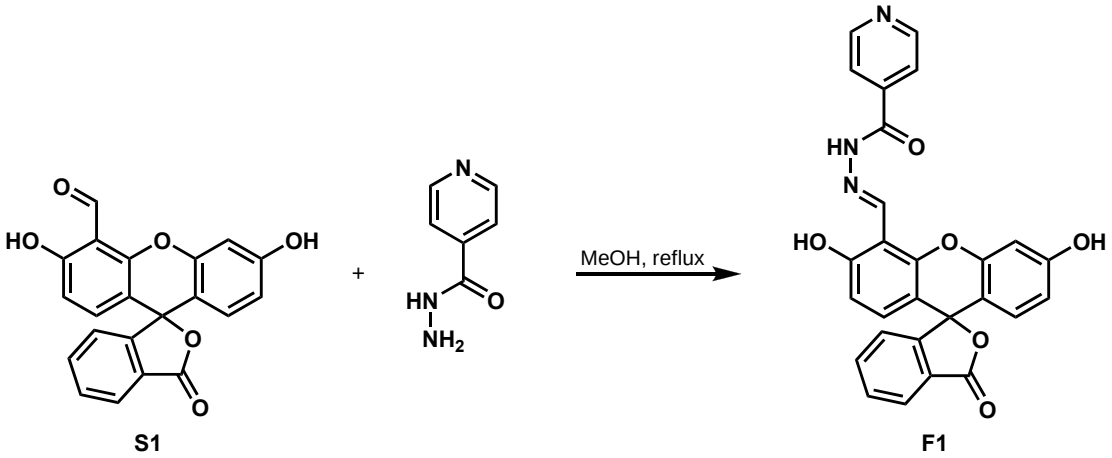
**S1**. Mp: 272–276 °C. $^1$H NMR (DMSO-$d_6$, 300 MHz): $\delta$ = 11.89 (s, 1H), 10.63 (s, 1H), 10.29 (s, 1H), 8.02 (d, $J$ = 7.5 Hz, 1H), 7.81 (d, $J$ = 7.2 Hz, 1H), 7.73 (d, $J$ = 7.2 Hz, 1H), 7.32 (d, $J$ = 7.5 Hz, 1H), 6.95 (d, $J$ = 9.0 Hz, 1H), 6.85 (s, 1H), 6.71 (d, $J$ = 9.0 Hz, 1H), 6.61 (brs, 2H) ppm. $^{13}$C NMR (DMSO-$d_6$, 75 MHz) $\delta$ = 192.9, 168.5, 162.9, 159.6, 152.4, 152.2, 150.9, 136.5, 135.8, 130.3, 129.0, 125.9, 124.8, 124.0, 113.5, 113.4, 109.7, 109.2, 109.1, 102.7, 81.8 ppm. ESI−MS: $m/z$ 361.1 $[M + H]^+$.

**S2**. Mp: 311–313 °C. $^1$H NMR (DMSO-$d_6$, 400 MHz): $\delta$ = 11.85 (s, 2H), 10.68 (s, 2H), 8.04 (d, $J$ = 7.6 Hz, 1H), 7.82 (td, $J$ = 1.2, 7.6 Hz, 1H), 7.73–7.77 (m, 1H), 7.37 (d, $J$ = 7.6 Hz, 1H), 6.99 (d, $J$ = 8.8 Hz, 2H), 6.79 (d, $J$ = 9.2 Hz, 2H) ppm. $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ = 192.3 (2C), 168.5, 163.3 (2C), 152.0, 151.0 (2C), 136.2

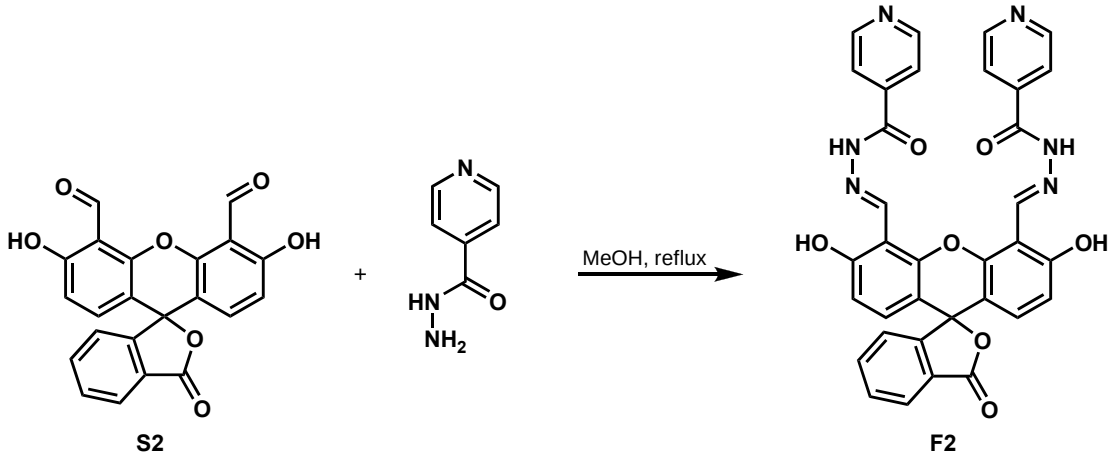
(2C), 136.1, 130.7, 125.8, 125.1, 124.1, 114.4 (2C), 109.7 (2C), 109.4 (2C), 80.8 ppm. ESI−MS: *m/z* 389.0454 $[M + H]^+$.

(7) W. Wang, O. Rusin, X. Xu, K. K. Kim, J. O. Escobedo, S. O. Fakayode, K. A. Fletcher, M. Lowry, C. M. Schowalter, C. M. Lawrence, F. R. Fronczek, I. M. Warner, R. M. Strongin, *J. Am. Chem. Soc.*, 2005, **127**, 15949–15958.

**4. Synthesis of F1 and F2.**




The isonicotinohydrazide (206 mg, 1.5 mmol) was added to a solution of aldehyde **S1** (360 mg, 1.0 mmol) in methanol (15 mL). The reaction mixture was then stirred for 8 h at reflux. The resulting solid was filtered and washed with methanol, dried over vacuum to afford **F1**. (256 mg, 53.4%). Mp: 350–353°C. $^1$H NMR (DMSO-$d_6$, 400 MHz): $\delta$= 12.71 (brs, 1H), 12.60 (brs, 1H), 10.31 (brs, 1H), 9.26 (s, 1H), 8.86 (d, $J$ = 5.6 Hz, 2H), 8.02 (d, $J$ = 7.6 Hz, 1H), 7.91 (d, $J$ = 5.6 Hz, 2H), 7.81 (t, $J$ = 7.6 Hz, 1H), 7.74 (t, $J$ = 7.6 Hz, 1H), 7.34 (d, $J$ = 7.6 Hz, 1H), 6.75 (d, $J$ = 8.8 Hz, 2H), 6.72 (d, $J$ = 9.2 Hz, 1H), 6.62 (d, $J$ = 0.8 Hz, 2H) ppm. $^{13}$C NMR (DMSO-$d_6$, 100 MHz): $\delta$ = 168.6, 161.3, 160.1, 159.7, 152.2, 151.2 (2C), 150.52, 150.50, 149.7, 145.5, 139.5, 139.4, 135.7, 131.1, 130.3, 129.2, 126.1, 124.8, 124.1, 121.5, 113.4, 109.6, 109.4, 105.6, 102.1, 82.4 ppm. ESI−MS: *m/z* 480.1362 $[M + H]^+$. IR (KBr): $\nu_{max}$ = 3480, 3157, 3055, 2943, 2837, 1749, 1654, 1632, 1609, 1579, 1507, 1441, 1357, 1309, 1244, 1158, 1119, 1092, 1030, 839, 763, 703, 692 $cm^{-1}$.




The isonicotinohydrazide (412 mg, 3.0 mmol) was added to a solution of aldehyde **S2** (388 mg, 1.0 mmol) in methanol (15 mL). The reaction mixture was then stirred for 8 h at reflux. The resulting solid was filtered and washed with methanol, dried over vacuum to afford **F2** (428 mg, 68.3%). Mp: 296–298 $^{o}$C. $^{1}$H NMR (DMSO-$d_6$, 400 MHz): $\delta$ = 12.43 (brs, 2H), 12.05 (brs, 2H), 9.59 (s, 2H), 8.70 (d, $J$ = 5.6 Hz, 4H), 8.04 (d, $J$ = 7.6 Hz, 1H), 7.85 (d, $J$ = 5.6 Hz, 4H), 7.84 (t, $J$ = 7.6 Hz, 1H), 7.76 (t, $J$ = 7.6 Hz, 1H), 7.41 (d, $J$ = 7.6 Hz, 1H), 6.78 (d, $J$ = 8.8 Hz, 2H), 6.74 (d, $J$ = 8.8 Hz, 2H) ppm. $^{13}$C NMR (DMSO-$d_6$, 100 MHz): $\delta$= 168.7, 162.2 (2C), 160.2 (2C), 152.3, 150.3 (4C), 149.3 (2C), 147.0 (2C), 139.7 (2C), 135.9, 131.1 (2C), 130.4, 126.1, 124.9, 124.3, 121.7 (4C), 113.4 (2C), 109.5 (2C), 106.9 (2C), 82.4 ppm. ESI−MS: $m/z$ 627.5 $[M + H]^+$. IR (KBr): $\nu_{max}$ = 3435, 3251, 3047, 2849, 1744, 1665, 1638, 1611, 1542, 1466, 1434, 1353, 1290, 1229, 1162, 1117, 1065, 1014, 839, 823, 756, 692 $cm^{-1}$.

## 5. $^{1}$H, $^{13}$C NMR, IR and ESI-MS copies of compounds.

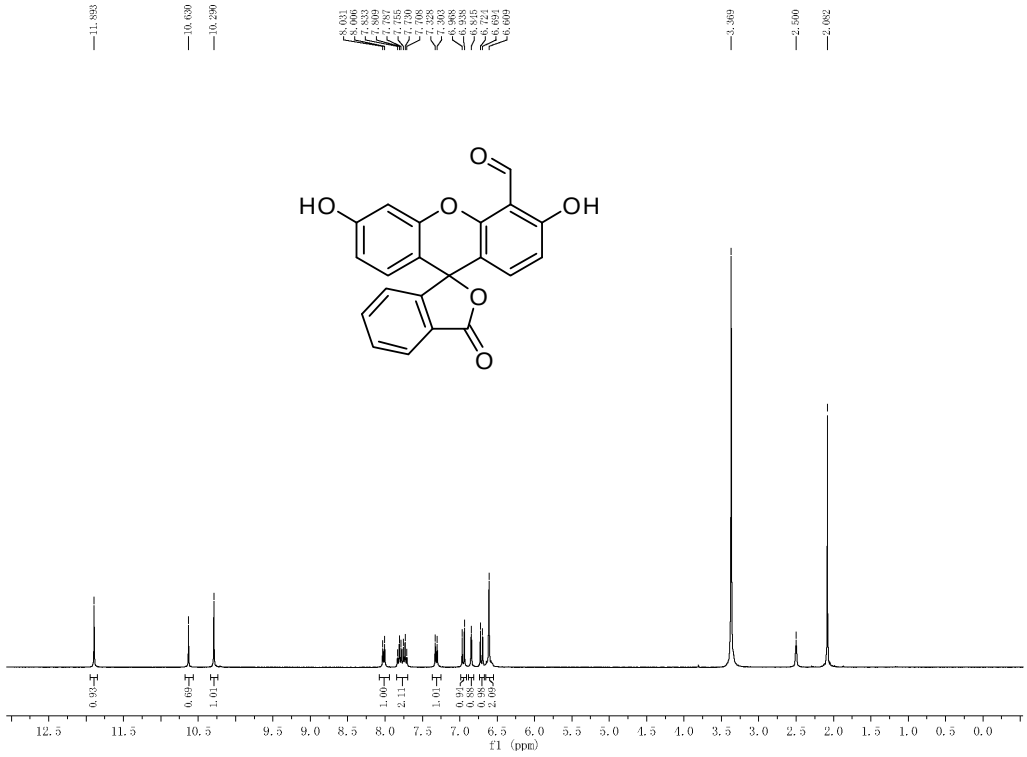



**Figure S1.** $^{1}$H NMR spectrum (300 MHz, DMSO-$d_6$) of **S1**.

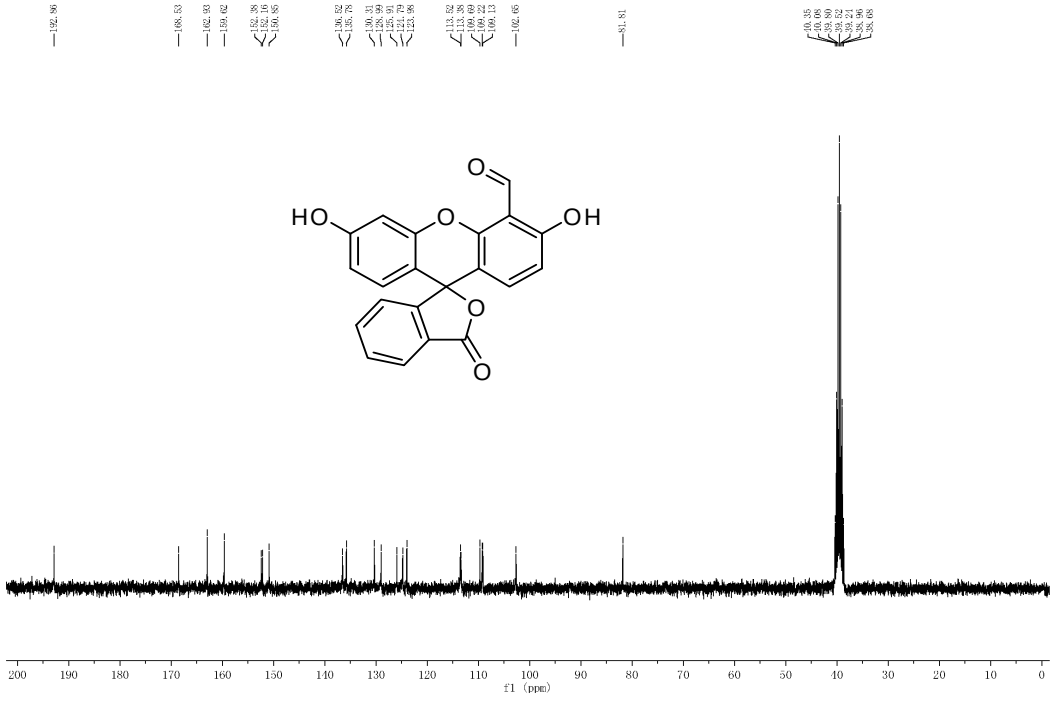



**Figure S2.** $^{13}$C NMR spectrum (75 MHz, DMSO-$d_6$) of **S1**.

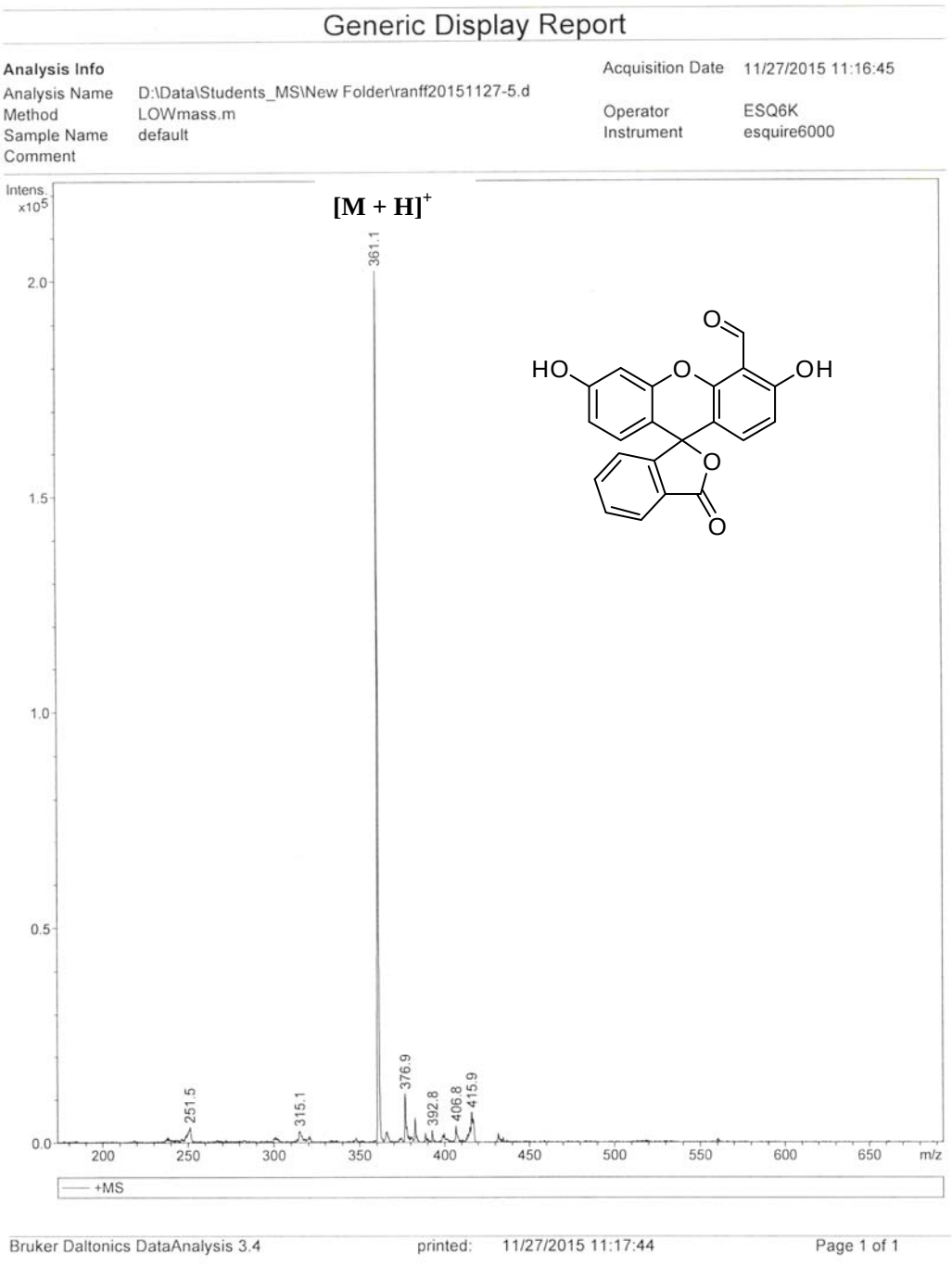



**Figure S3.** ESI-MS spectrum of monoaldehyde -functionalized fluorescein.

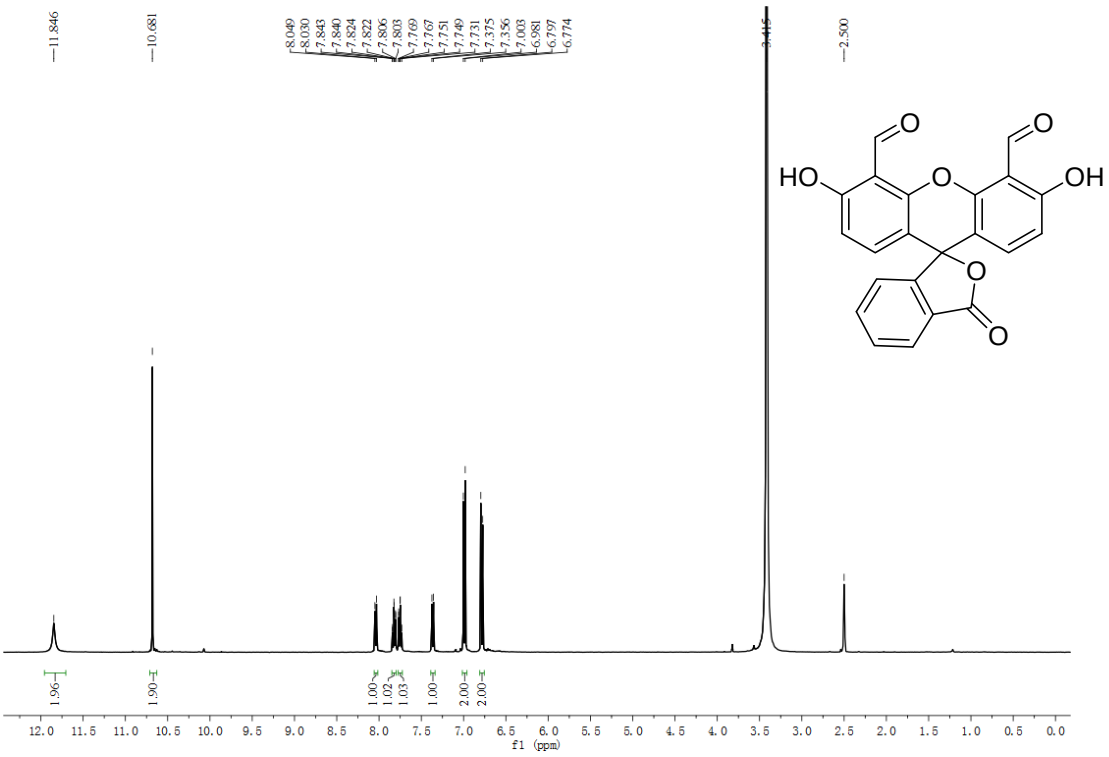



**Figure S4.** $^{1}$H NMR spectrum (400 MHz, DMSO-$d_6$) of **S2.**

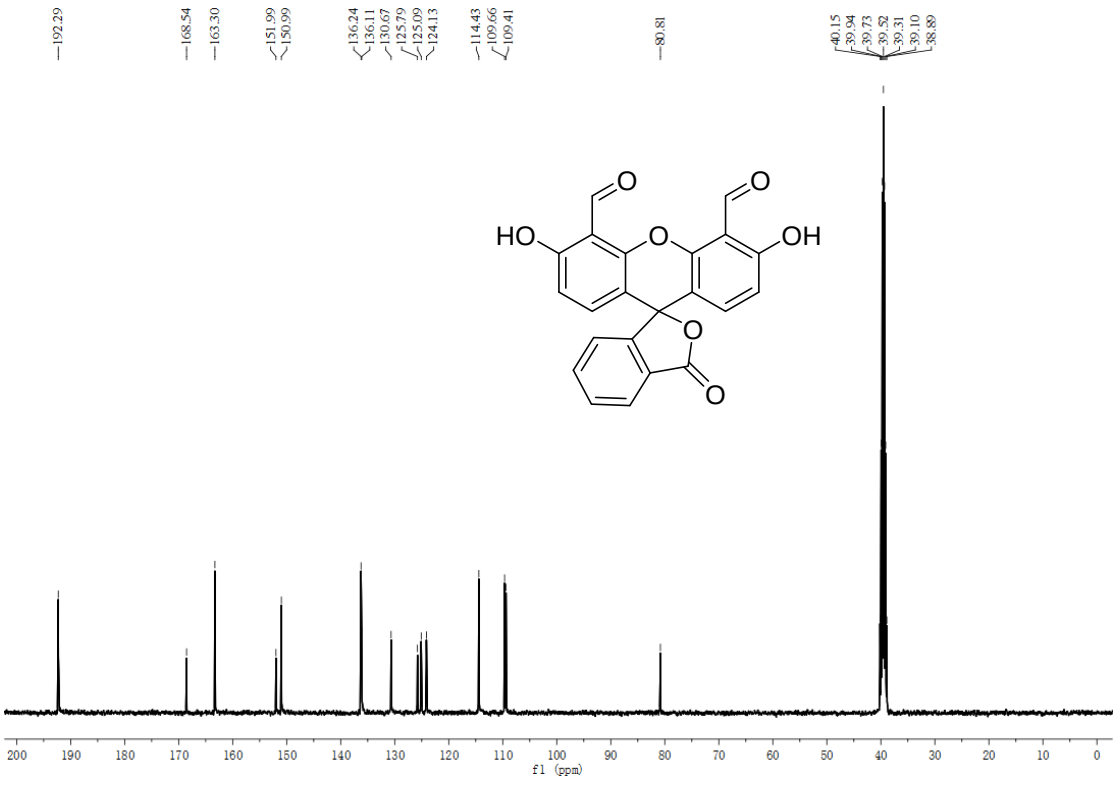



**Figure S5.** $^{13}$C NMR spectrum (100 MHz, DMSO-$d_6$) of **S2**.

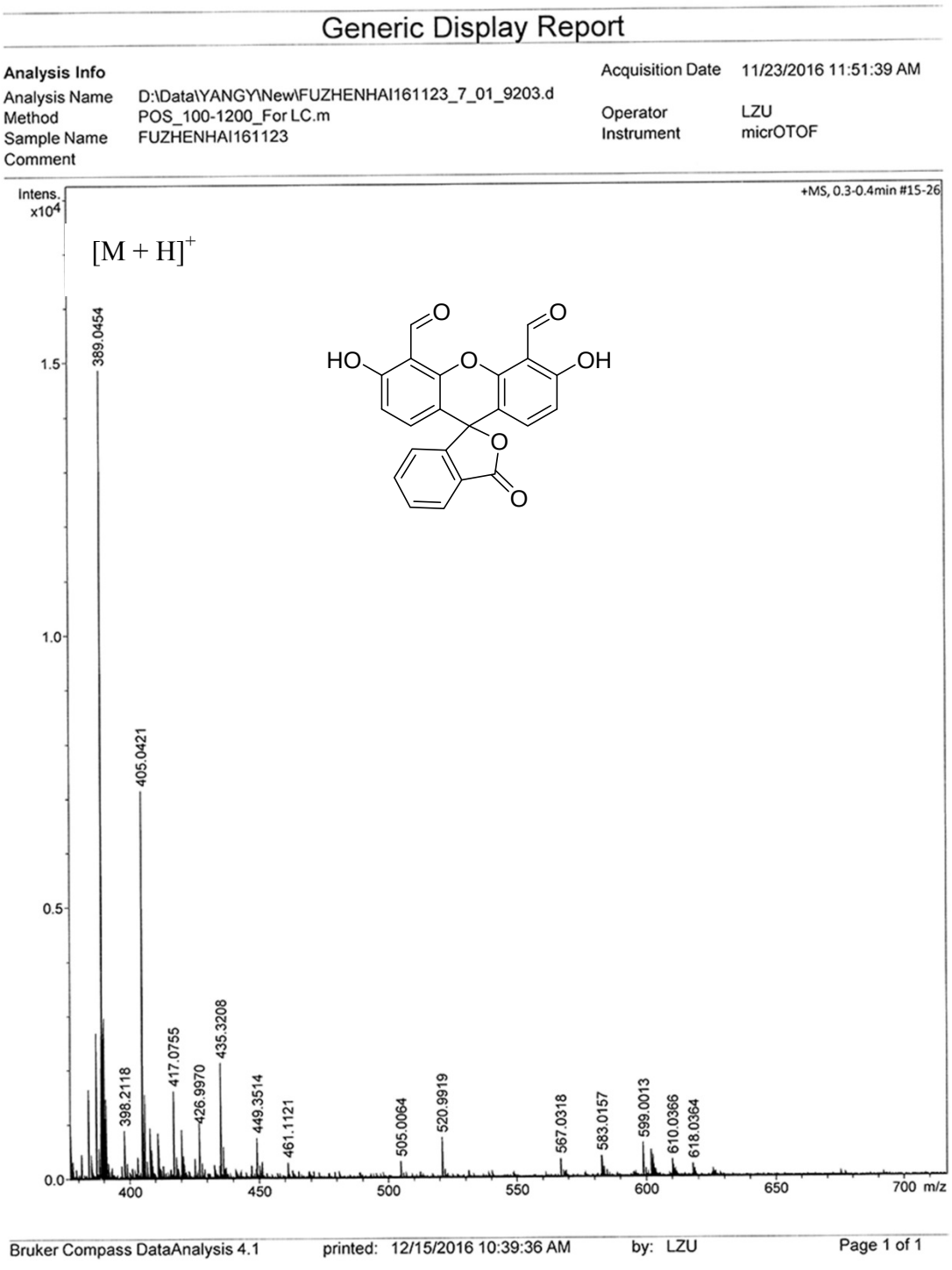



**Figure S6.** ESI-MS spectrum of dialdehyde-functionalized fluorescein**.**

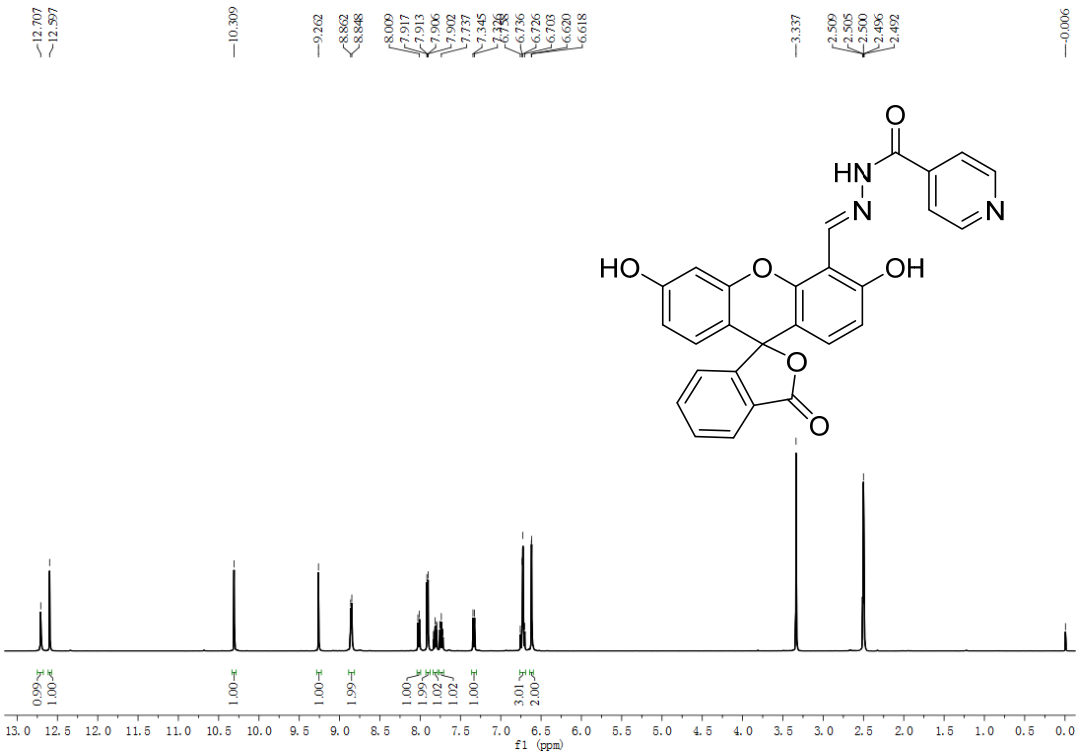



**Figure S7**. $^{1}$H NMR spectrum (400 MHz, DMSO-$d_6$) of **F1**.

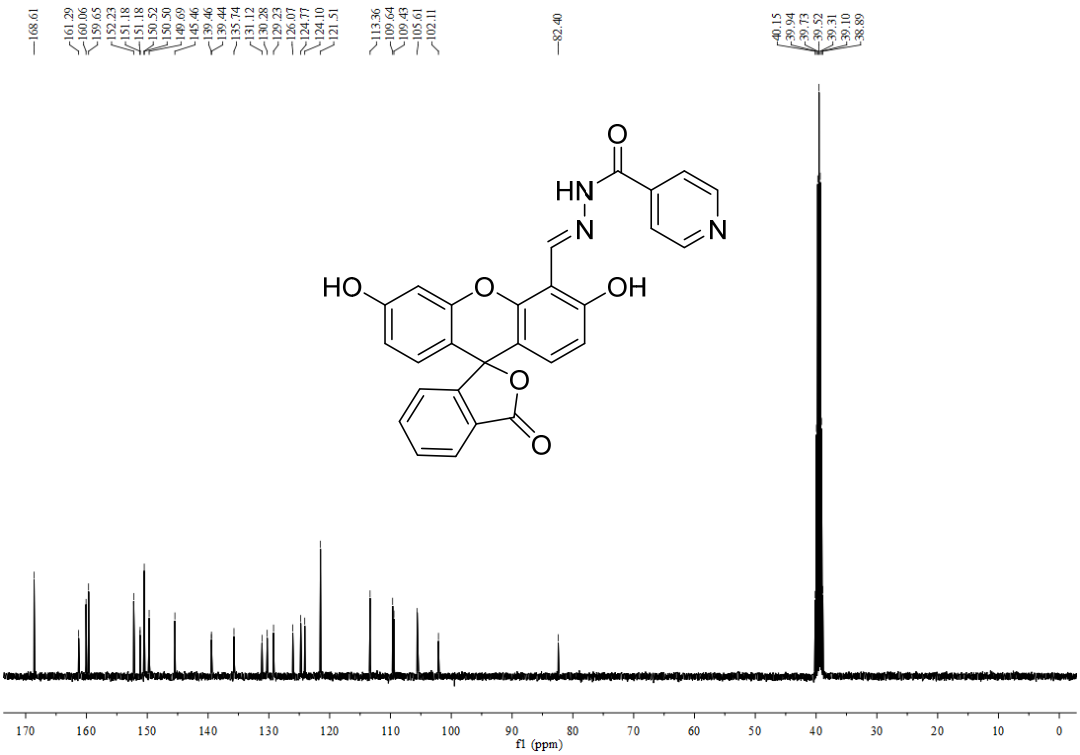



**Figure S8**. $^{13}$C NMR spectrum (100 MHz, DMSO-$d_6$) of **F1**.

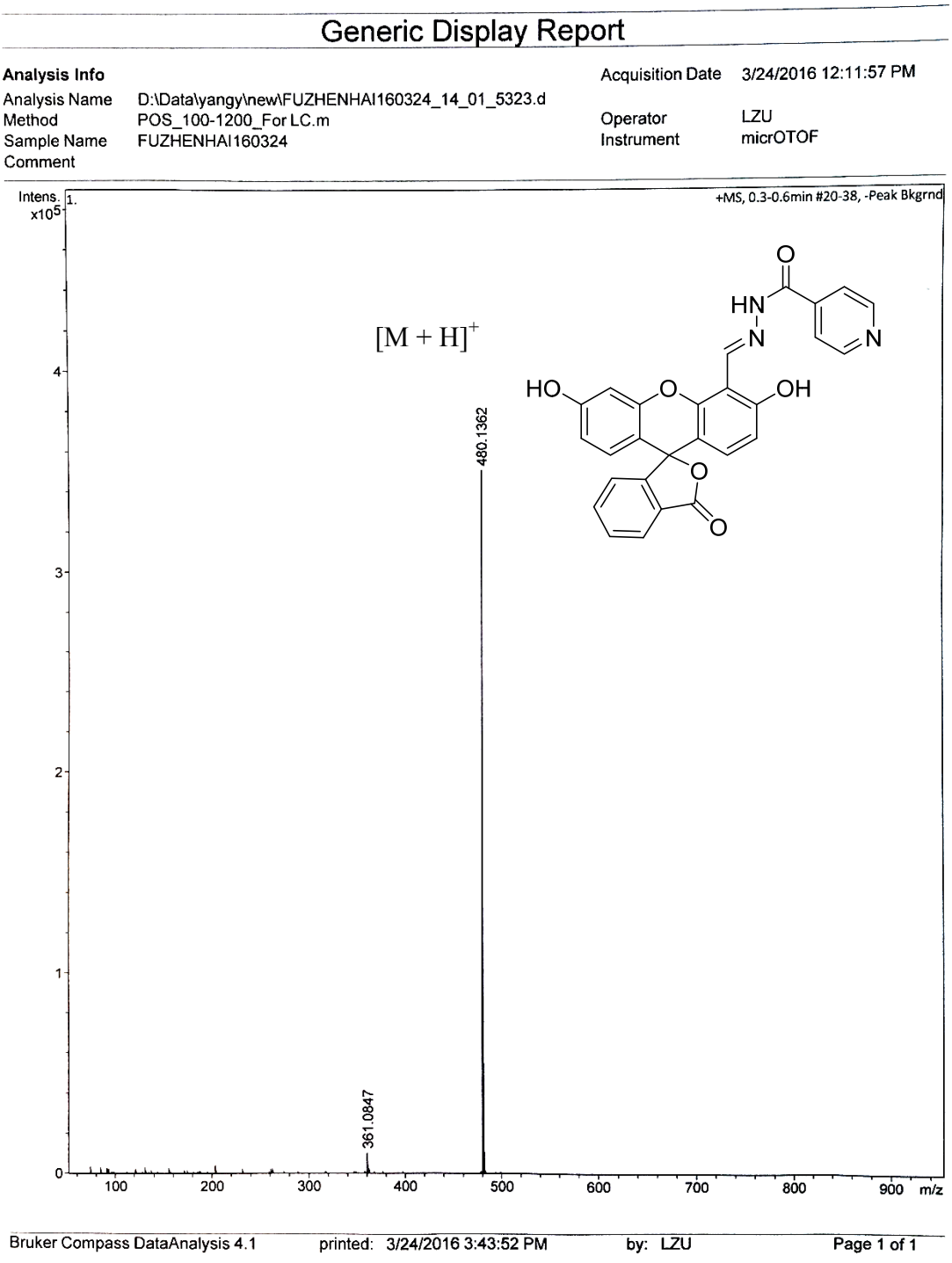



**Figure S9.** ESI-MS spectrum of **F1**.

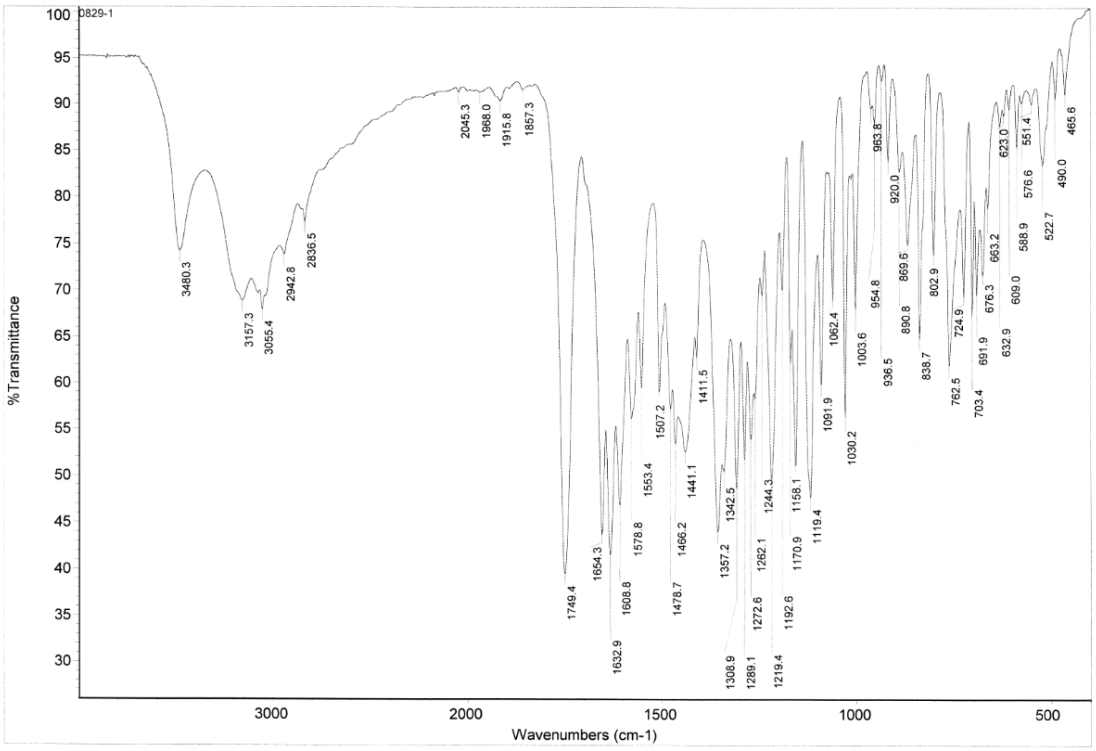



**Figure S10.** FTIR spectrum of **F1**.

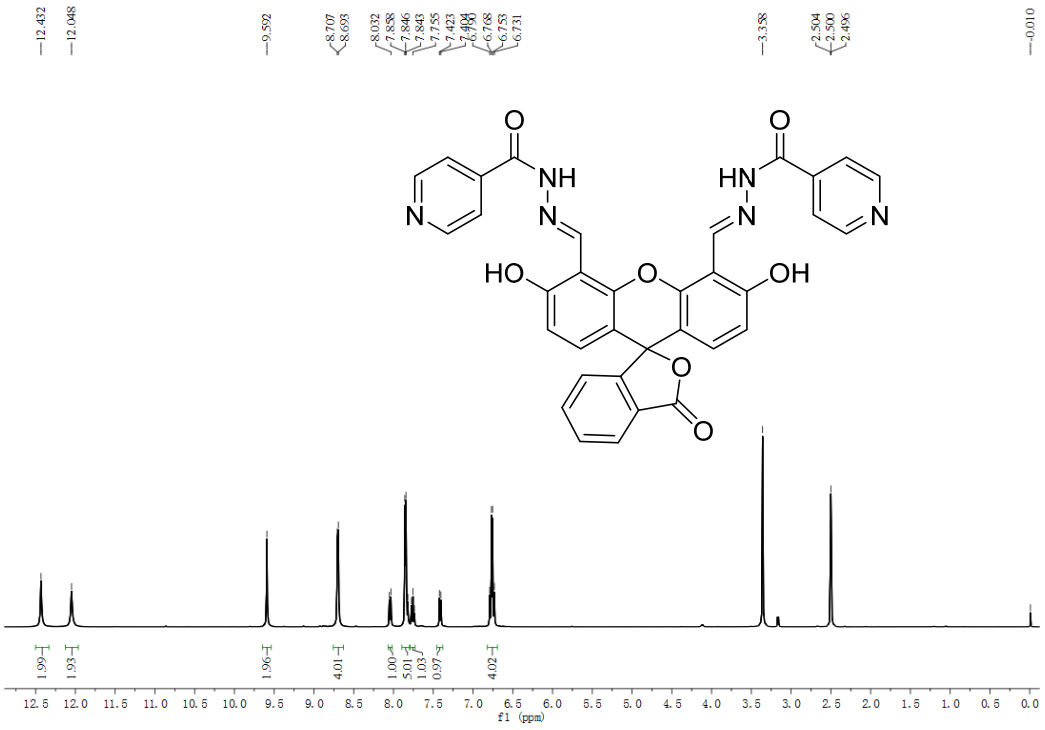



**Figure S11.** $^{1}$H NMR spectrum (400 MHz, DMSO-$d_6$) of **F2**.

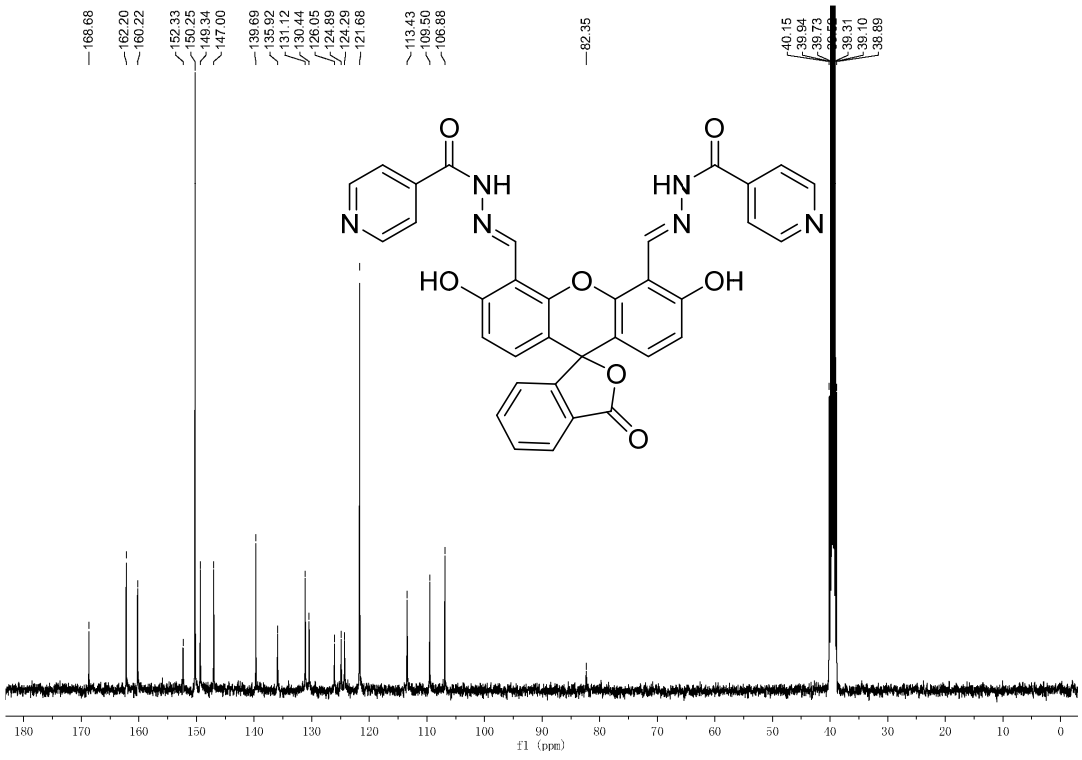



**Figure S12.** $^{13}$C NMR spectrum (100 MHz, DMSO-$d_6$) of **F2.**

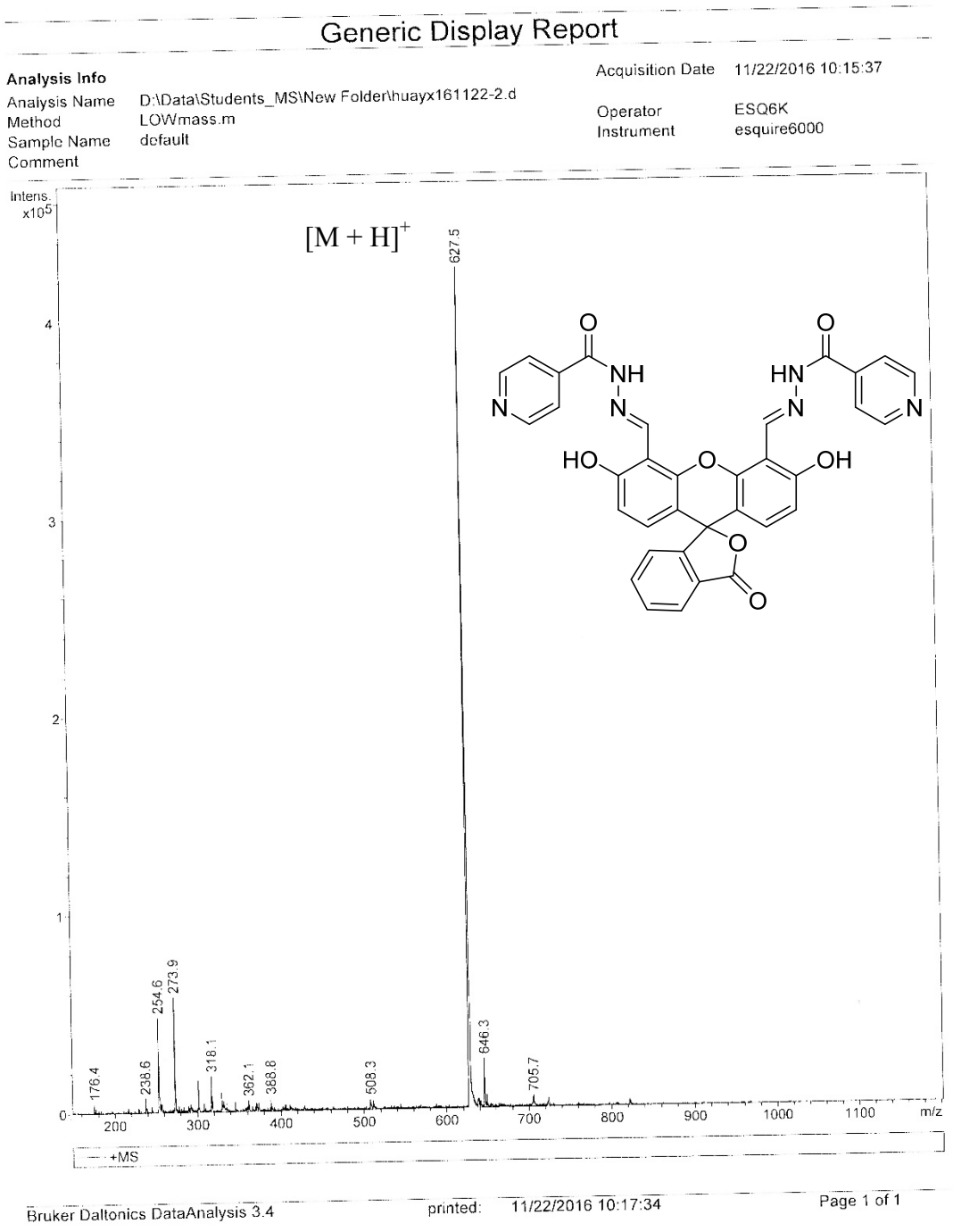



**Figure S13.** ESI-MS spectrum of **F2**.

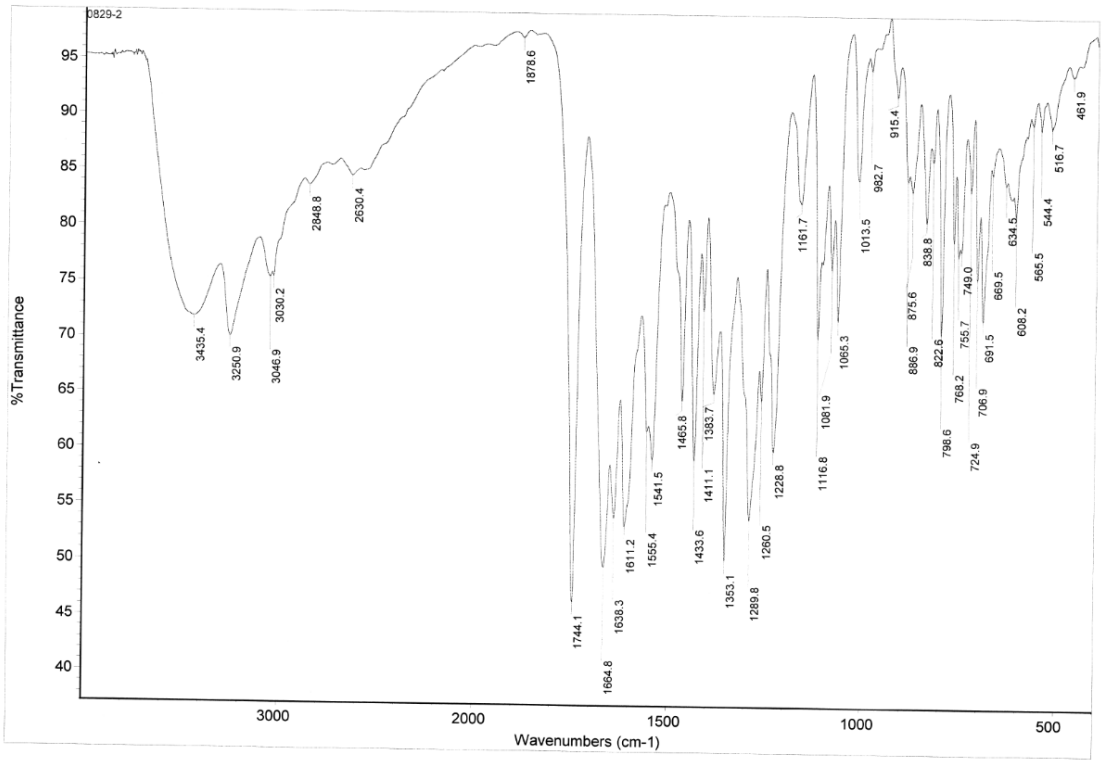



**Figure S14.** FTIR spectrum of **F2**.

## 6. The crystal data and structure refinement parameters.

**Table S2.** Crystal data and structure refinement parameters for **F1** and **F2**

| Compound | **F1** | **F2** |
|---|---|---|
| Empirical formula | $C_{29}H_{23}N_3O_7S$ | $C_{38}H_{34}N_6O_9S_2$ |
| Temperature/K | 293 (2) | 293 (2) |
| *M* | 557.56 | 782.83 |
| Crystal system | Triclinic | Triclinic |
| Space group | *P*-1 | *P*-1 |
| *a*/Å | 7.7595(16) | 8.2956(8) |
| *b*/Å | 13.126(4) | 15.1849(14) |
| *c*/Å | 14.358(3) | 16.4901(16) |
| *a*/° | 106.59(2) | 83.140(8) |
| *β*/° | 94.664(19) | 81.044(8) |
| *γ*/° | 105.99(2) | 87.483(8) |
| *V*/Å$^3$ | 1326.8(6) | 2036.5(3) |
| *Z* | 2 | 2 |
| $D_c$/kg m$^{-3}$ | 1.396 | 1.277 |
| *μ*/mm$^{-1}$ | 0.176 | 0.190 |
| *F*(000) | 580.0 | 816.0 |
| Crystal size/mm | 0.15 × 0.12 × 0.07 | 0.23 × 0.21 × 0.19 |
| *θ* Range for data collection/° | 3.41-26.022 | 3.392-26.014 |
| Index ranges, *hkl* | $-9 \le h \le 9$, $-9 \le k \le 16$, $-17 \le l \le 16$ | $-10 \le h \le 9$, $-18 \le k \le 18$, $-20 \le l \le 19$ |
| Reflections collected/unique | 8550/5225 | 13764/7998 |
| Data/restraints/params | 5225/0/365 | 7998/0/509 |
| Goodness-of-fit on $F^2$ | 1.054 | 0.933 |
| Final *R* indices [$I > 2\sigma(I)$] | $R1 = 0.0941$, $wR2 = 0.2012$ | $R1 = 0.0811$, $wR2 = 0.1995$ |
| *R* indices (all data) | $R1 = 0.1973$, $wR2 = 0.2879$ | $R1 = 0.1648$, $wR2 = 0.2539$ |

**7. UV-vis spectra and images of F1 and F2 in different solution.**

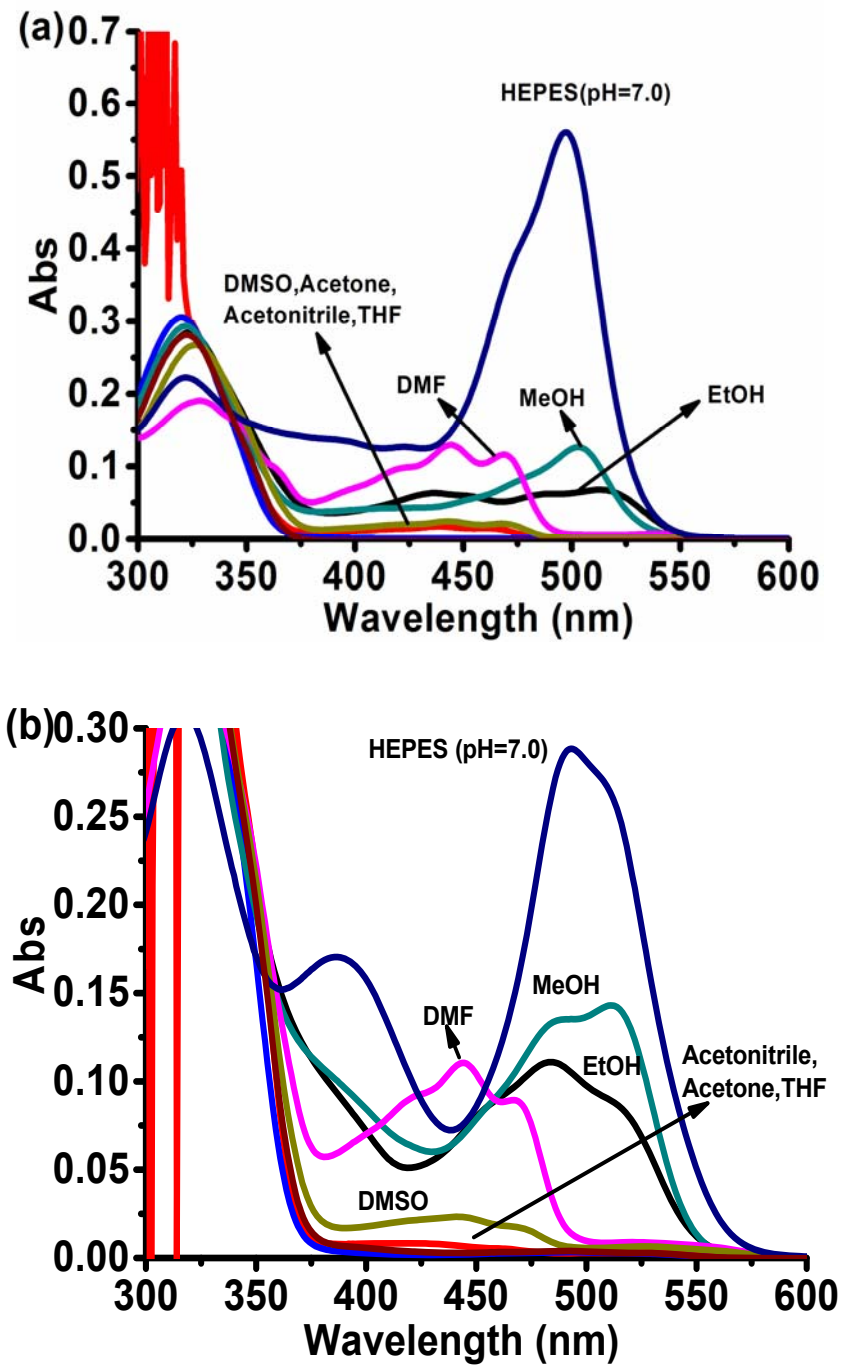



**Figure S15.** The UV-vis spectra of **F1** and **F2** (10.0 $\mu$M) in different solution. (a) for **F1**; (b) for **F2**.

**8. UV-vis spectra and images of F1 and F2 with different NACs in ethanol.**

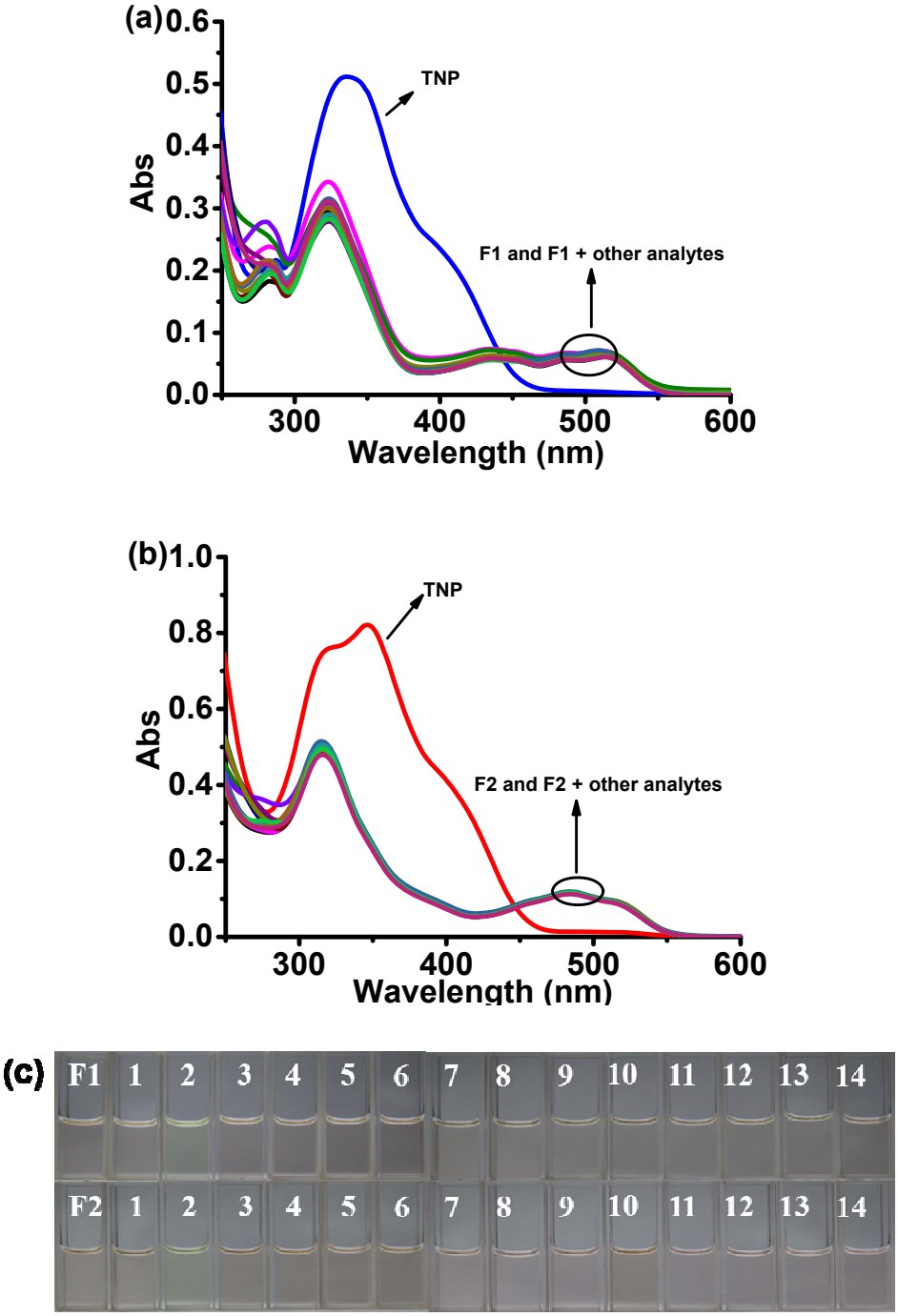



**Figure S16.** The UV-vis spectra and images of **F1** (a) and **F2** (b) (10.0 $\mu$M) toward different NACs (10.0 $\mu$M or 20.0 $\mu$M) in ethanol. (c) From 1 to 14: P, TNP, 3,5-DMP, 4-NB, 1,3-DNB, 4-NT, 2,4-DNT, 3,5-DMT, TNT, PAP, 2-IP, 4-MP, 2-CP, 4-BP**.**

**9. UV-vis spectra and images of F1 and F2 with different NACs in HEPES buffer (pH = 7.0).**

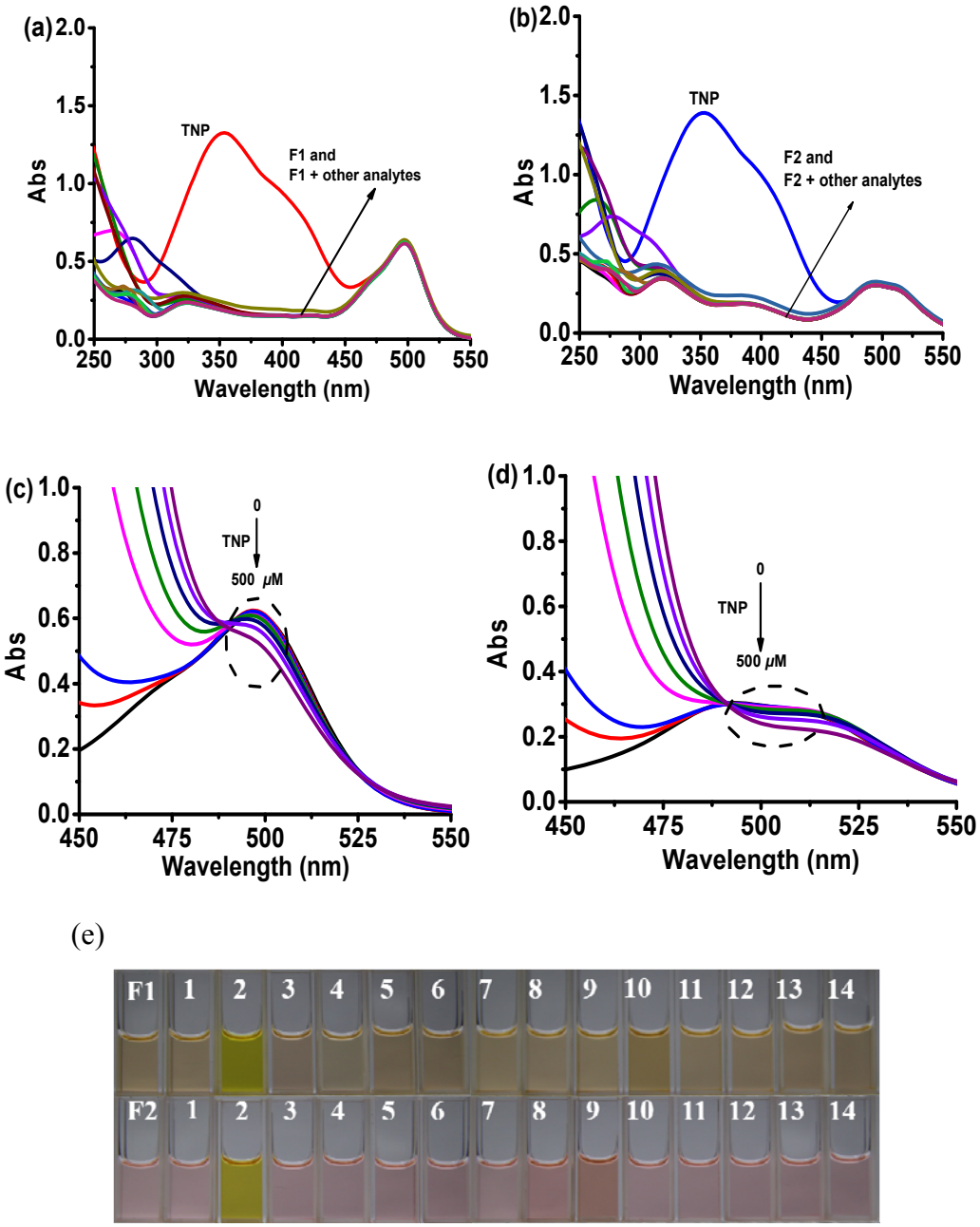



**Figure S17.** (a) (b) The UV-vis spectra of 10.0 $\mu$M **F1** and **F2** toward different NACs (200 $\mu$M) in HEPES buffer (pH= 7.0). (c)(d) The UV-vis spectra of 10.0 $\mu$M **F1** and **F2** toward TNP (0-500 μM) in HEPES buffer (pH= 7.0). (e)The images observed from 1 to 14: P, TNP, 3,5-DMP, 4-NB, 1,3-DNB, 4-NT, 2,4-DNT, 3,5-DMT, TNT, PAP, 2-IP, 4-MP, 2-CP, 4-BP**.**

**10. The fluorescence selectivity of F1 and F2 in ethanol.**

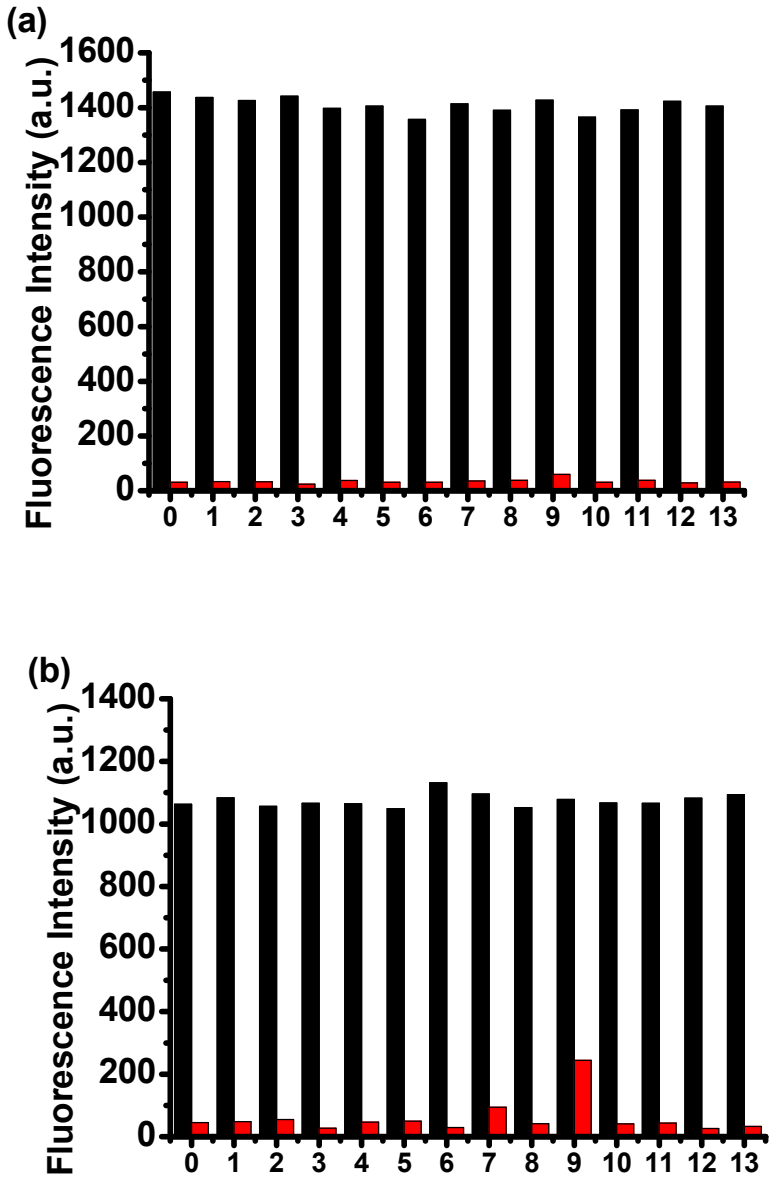



**Figure S18.** The fluorescence selectivity of chemosensors (10.0 $\mu$M), the black bars represent the emission intensity of chemosensors in the presence of NACs (10.0 $\mu$M or 200.0 $\mu$M), the red bars represent the emission intensity that occurs upon the subsequent addition of 10.0 $\mu$M or 200.0 $\mu$M of TNP to the above solution. From 0 to 15: none, P, TNP, 3,5-DMP, 4-NB, 1,3-DNB, 4-NT, 2,4-DNT, 3,5-DMT, TNT, PAP, 2-IP, 4-MP, 2-CP, 4-BP. (a) **F1** in ethanol, (b) **F2** in HEPES buffer (pH=7.0).

**11. The fluorescence spectral changes of F1 and F2 with the addition of TNP in ethanol.**

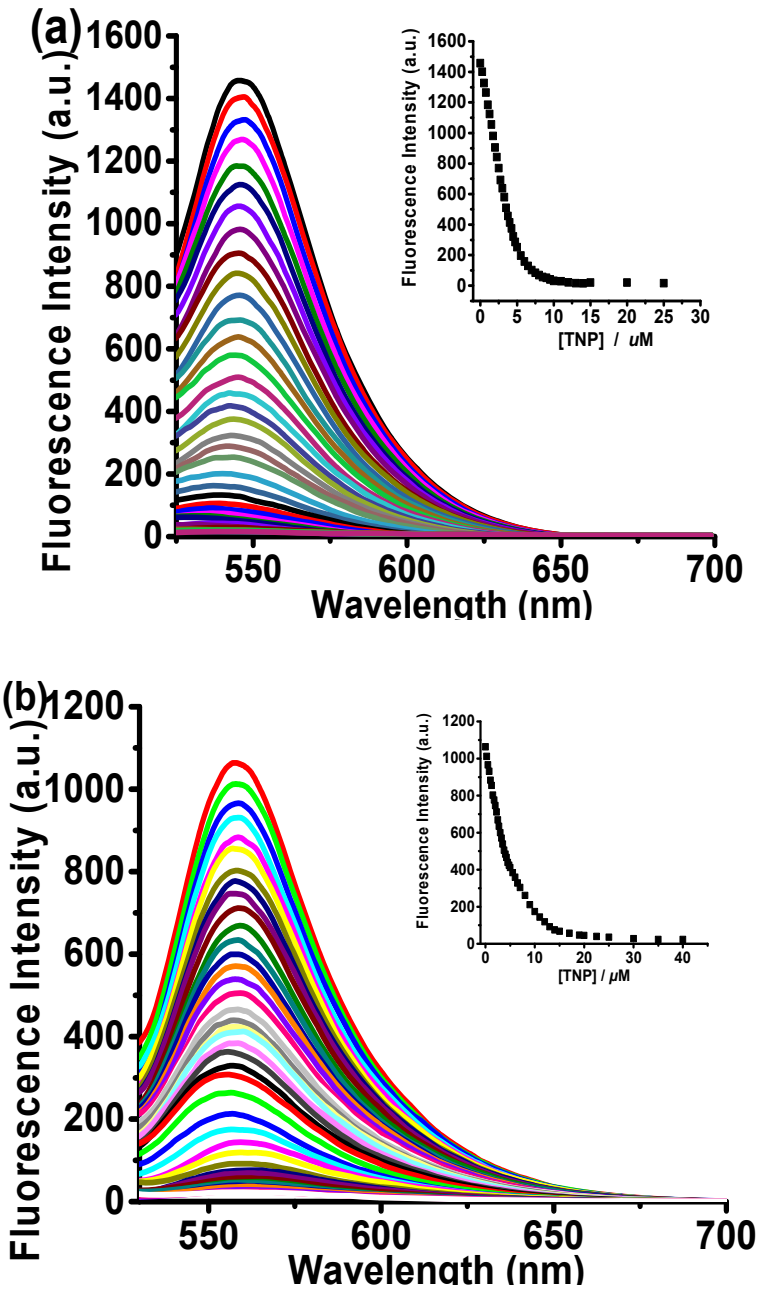



**Figure S19.** Fluorescence spectral changes of chemosensors (10.0 $\mu$M) with the addition of TNP in ethanol. (a) **F1**, Inset: Fluorescence intensity changes at 545 nm upon the addition of TNP ($\lambda_{ex}$= 500 nm). (b) **F2**. Inset: Fluorescence intensity changes at 558 nm upon the addition of TNP ($\lambda_{ex}$ = 517 nm).

**12. Plot of fluorescence intensity against time for F1 and F2 upon addition of TNP in ethanol.**

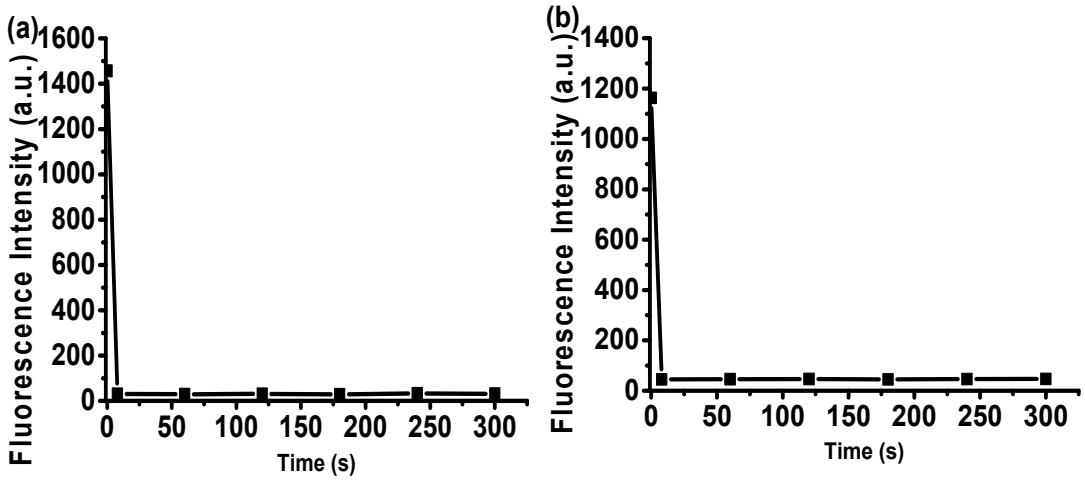



**Figure S20.** Plot of fluorescence intensity against time for chemosensors upon addition of TNP in ethanol. (a) **F1**; (b) **F2**.

**13. The pH dependence of the fluorescence intensity change.**

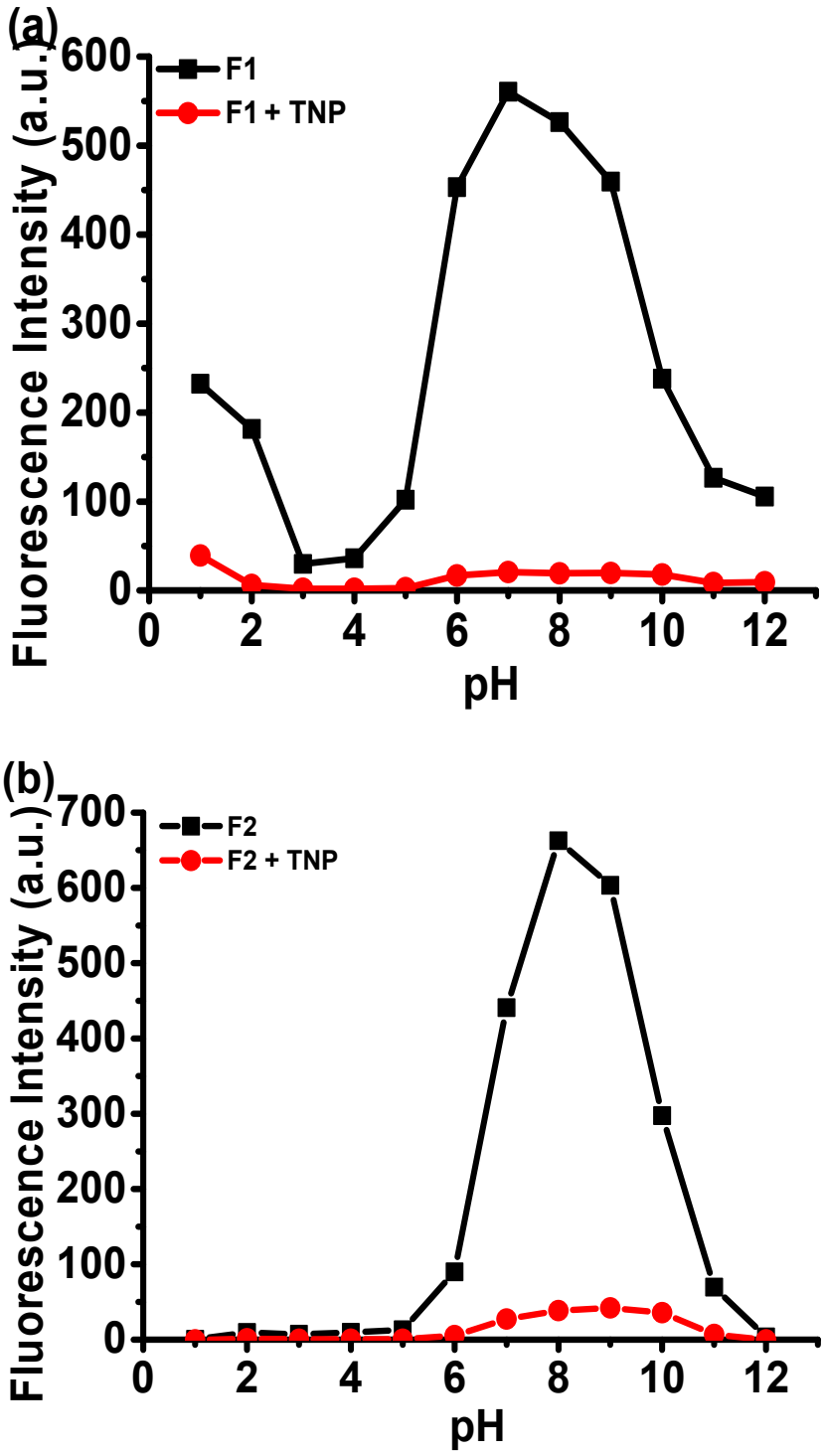



**Figure S21.** Fluorescence intensity of chemosensors (10.0 $\mu$M) in HEPES solution of different pH in the absence and presence of 200.0 $\mu$M TNP ($\lambda_{ex}$ = 400 nm).

**14. The fluorescence spectral changes of F1 and F2 with the addition of TNP in HEPES buffer (pH = 7.0) under different excitation wavelength.**

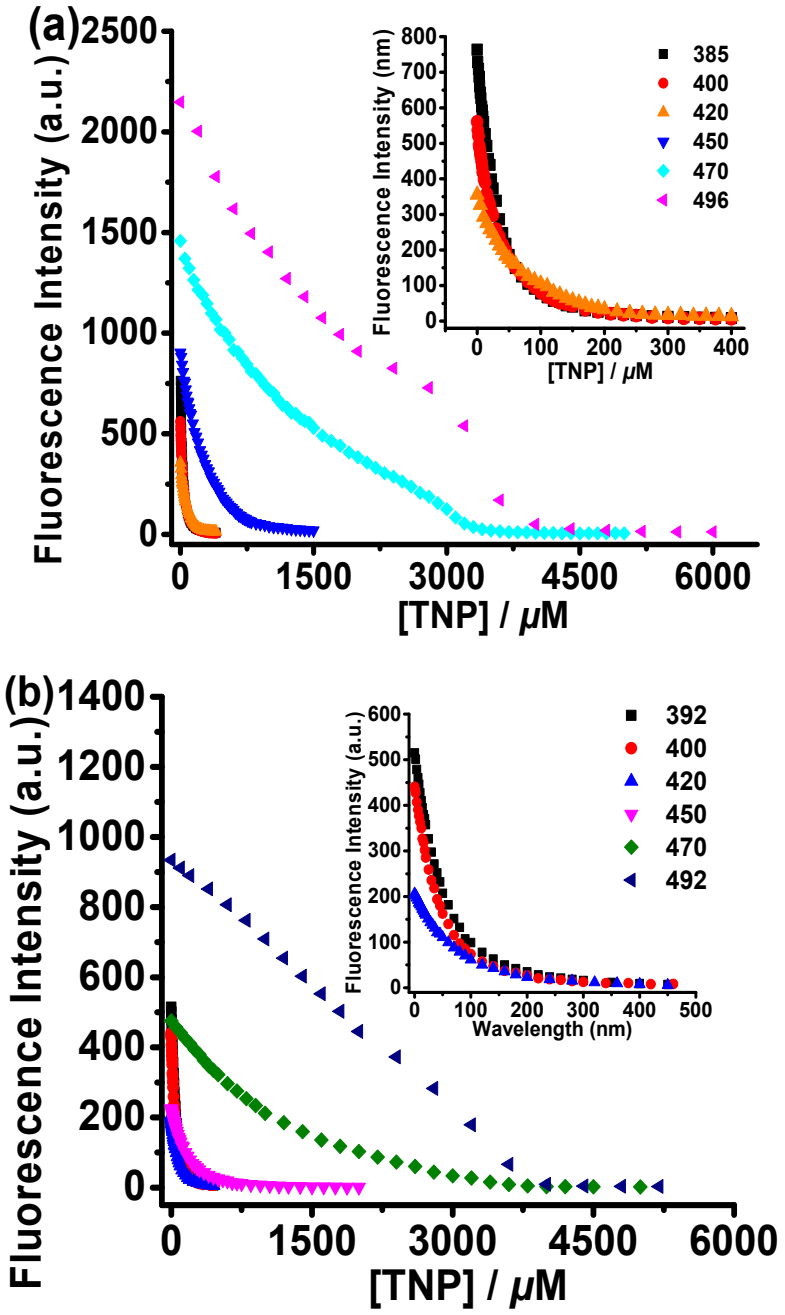



**Figure S22.** The fluorescence spectral changes of **F1** and **F2** with the addition of TNP in HEPES buffer (pH=7.0) under different excitation wavelength. (a) **F1**: $\lambda_{em}$ = 542 nm; (b) **F2**: $\lambda_{em}$ = 555 nm.

**15. The fluorescence spectral changes of F1 and F2 with the addition of TNP in HEPES buffer (pH = 7.0).**

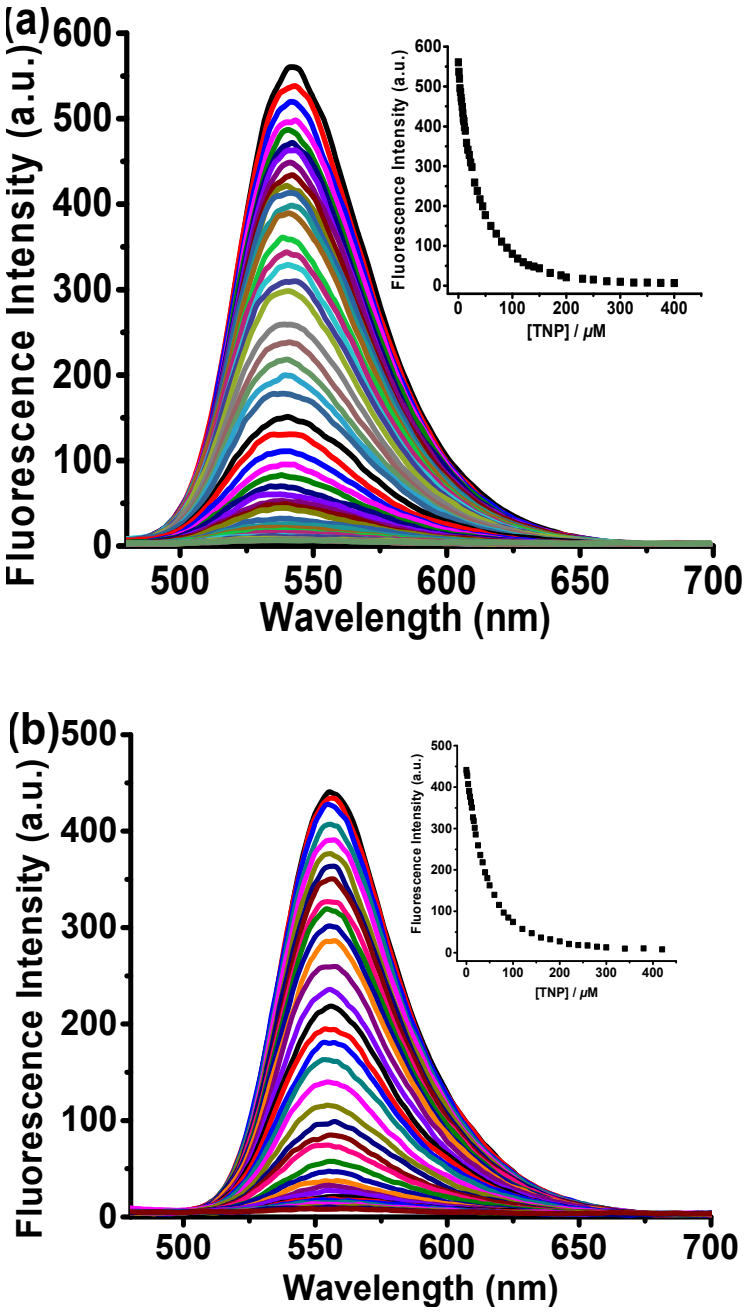



**Figure S23.** Fluorescence spectral changes of chemosensors (10.0 $\mu$M) with the addition of TNP in HEPES buffer (pH=7.0). (a) **F1**, Inset: Fluorescence intensity changes at 542 nm upon the addition of TNP ($\lambda_{ex}$= 400 nm). (b) **F2**. Inset: Fluorescence intensity changes at 555 nm upon the addition of TNP ($\lambda_{ex}$ = 400 nm).

**16. The fluorescence selectivity of F1 and F2 in HEPES buffer (pH=7.0).**

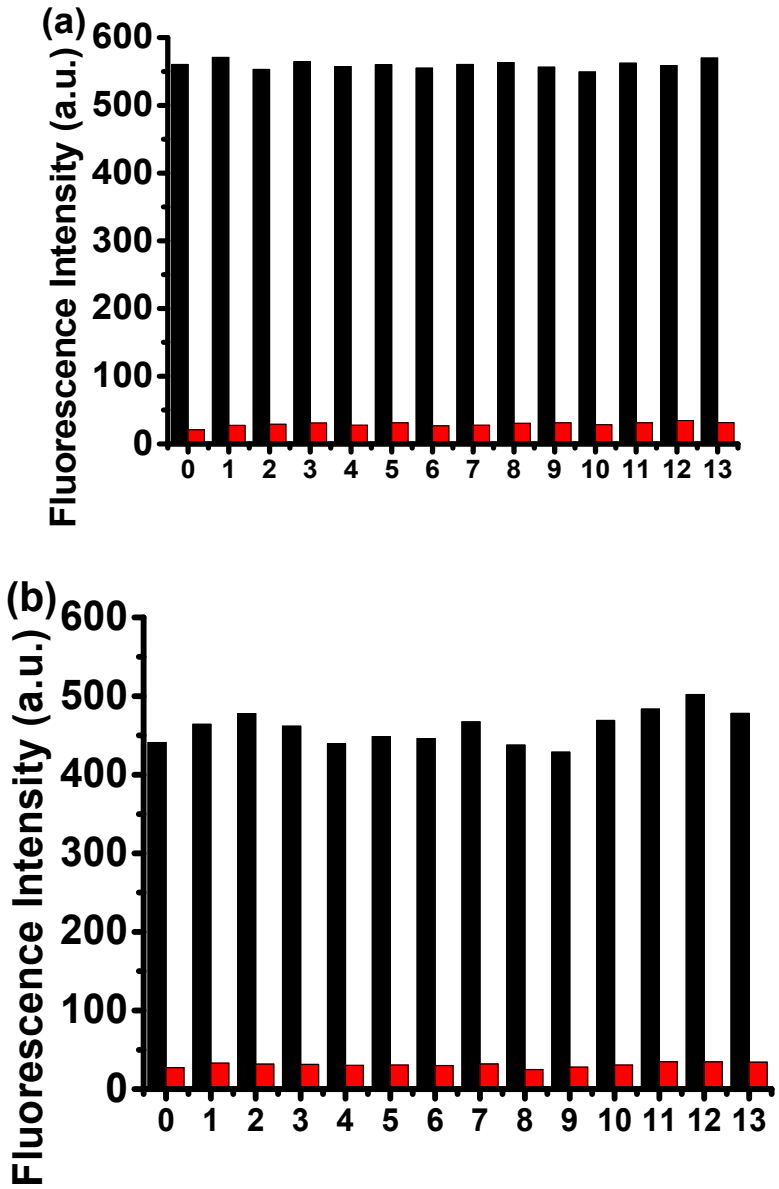



**Figure S24.** The fluorescence selectivity of chemosensors (10.0 $\mu$M) in HEPES buffer (pH = 7.0), the black bars represent the emission intensity of chemosensors in the presence of NACs (200.0 $\mu$M), the red bars represent the emission intensity that occurs upon the subsequent addition of 200.0 $\mu$M of TNP to the above solution. (a) for **F1**; (b) for **F2**. From 0 to 13: none, P, 3,5-DMP, 4-NB, 1,3-DNB, 4-NT, 2,4-DNT, 3,5-DMT, TNT, PAP, 2-IP, 4-MP, 2-CP, 4-BP。

**17. Stern-Volmer plots of F1 and F2 in ethanol.**

The fluorescence quenching process can be analyzed by Stern-Volmer equation:

$$F_0/F\text{-}1 = K_{sv}[Q]$$

Where $F_0$ is the fluorescence intensity in the absence of TNP, $F$ is the fluorescence intensity upon the addition of TNP and [Q] is the concentration of TNP.

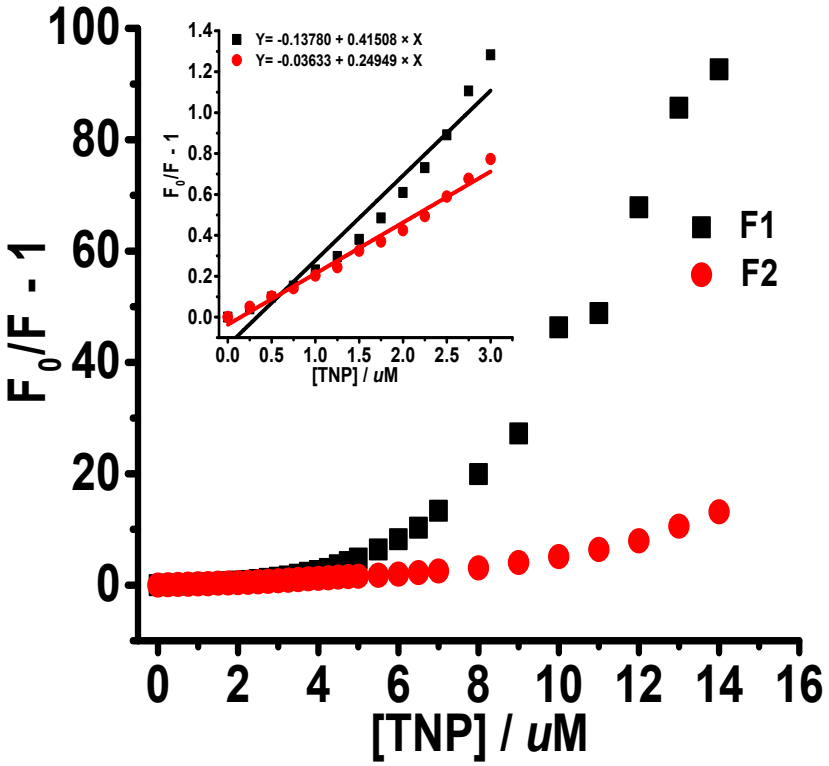



**Figure S25. Stern-Volmer plots of F1 and F2 for TNP in ethanol.**

**18. The detection limit of F1 and F2 with TNP in ethanol.**

The detection limit was calculated accordingly to literature[8]

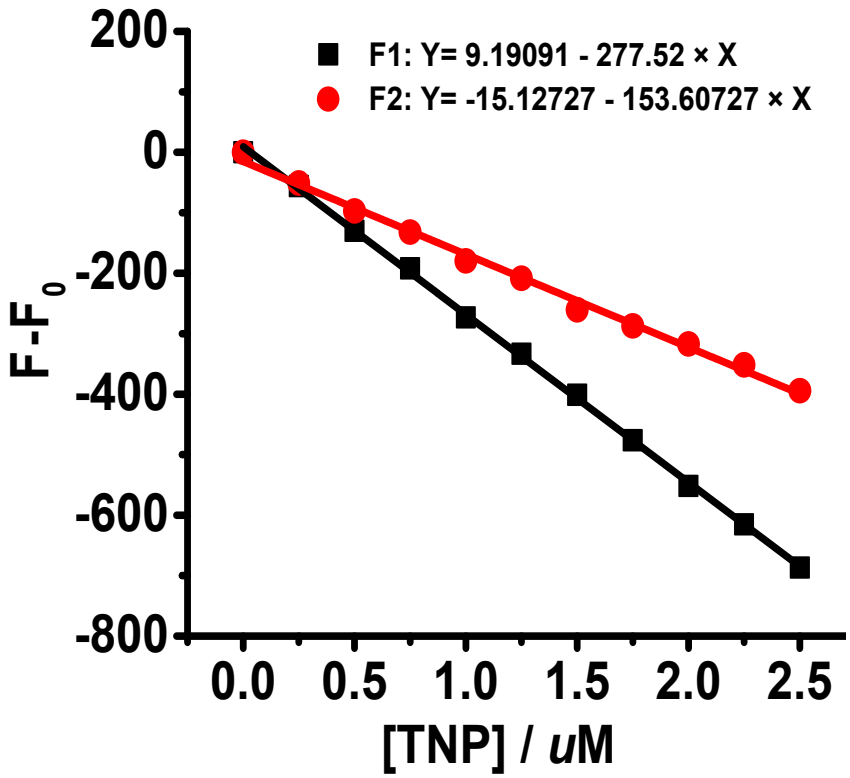



**Figure S26.** Plot of the intensity a mixture of chemosensors and TNP in ethanol.

**Table S3.** The Stern-Volmer quenching constants and detection limits in ethanol.

| | **F1** | **F2** |
|---|---|---|
| | TNP | TNP |
| LOD/ $\mu$M | 0.075 | 0.110 |
| $K_{sv}$ /$M^{-1}$ | $4.15\times10^5$ | $2.5\times10^5$ |

(8) Z.-H. Fu, L.-B. Yan, X. Zhang, F.-F. Zhu, X.-L. Han, J. F, Y.-W. Wang, Y. Peng, *Org. Biomol. Chem.*, 2017, **15**, 4115–4121.

**19. Stern-Volmer plots of F1 and F2 in HEPES buffer (pH = 7.0).**

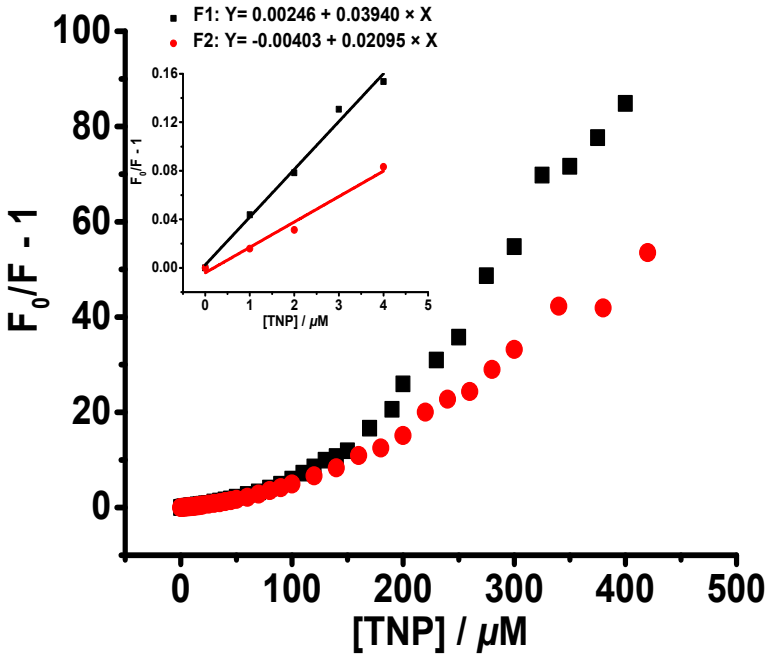



**Figure S27.** Stern-Volmer plots of **F1** and **F2** in HEPES buffer (pH = 7.0).

**20. The detection limit of F1 and F2 with TNP in HEPES buffer (pH = 7.0).**

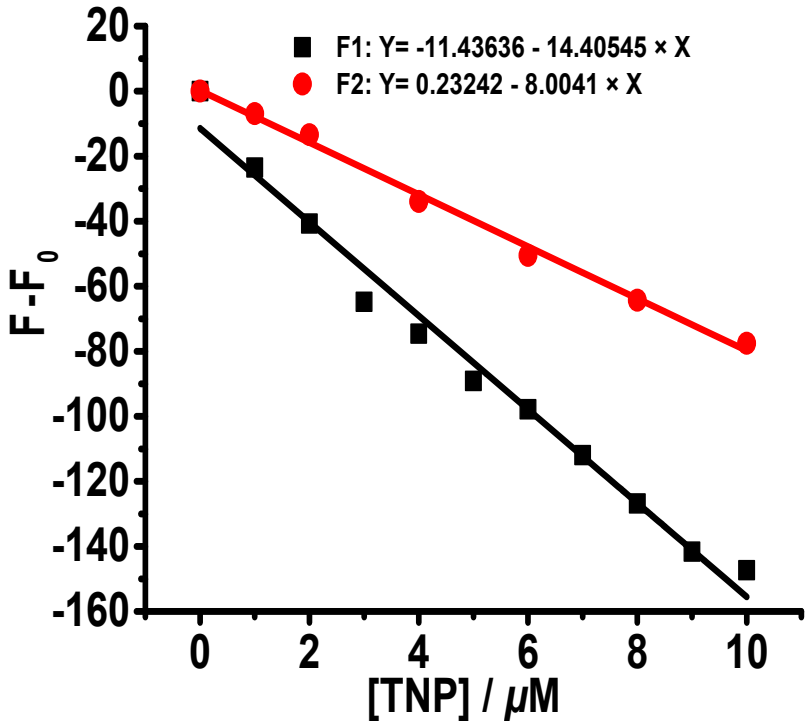



**Figure S28.** Plot of the intensity a mixture of chemosensors and TNP in HEPES buffer (pH = 7.0).

**Table S4.** The Stern-Volmer quenching constants and detection limits in HEPES buffer (pH = 7.0).

| | **F1** | **F2** |
|---|---|---|
| | TNP | TNP |
| LOD/ $\mu$M | 0.57 | 0.93 |
| $K_{sv}$ /$M^{-1}$ | $3.94\times10^4$ | $2.1\times10^4$ |

**21. Optimized structures, cartesian coordinates and computed total energies of F1, F1+TNP, F2 and F2+TNP.**

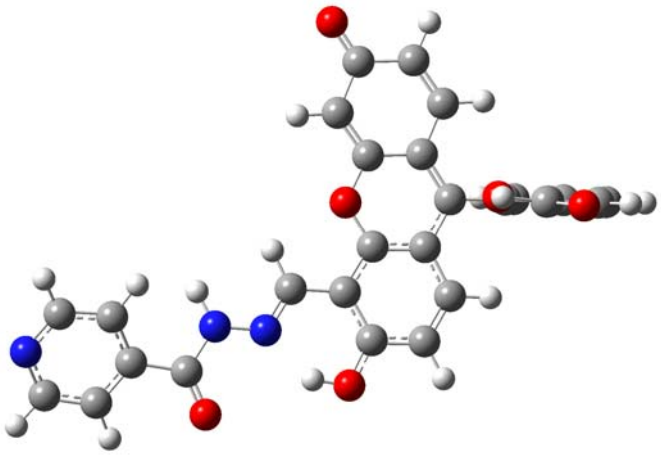


**Figure S29**. Optimized structure of **F1**.

B3LYP/6-31G(d) in gas phase, E = –1654.6897019 a.u.

charge = 0 Multiplicity = 1

| | | | |
|---|---|---|---|
| O | 2.085330087 | 5.5547045071 | -0.1064262301 |
| O | 0.3387702364 | 1.1844536977 | -0.1553870583 |
| O | -1.6609356449 | -3.1425208947 | -0.2432275419 |
| H | -2.4906651369 | -2.6015434234 | -0.1713007968 |
| O | 5.3195509389 | -1.6375590798 | 2.8479825886 |
| O | -5.4609931534 | -2.2314038754 | -0.1715707789 |
| N | -3.0801773736 | -0.9371089169 | -0.0500432237 |
| N | -4.2696634125 | -0.2911153889 | 0.041672068 |
| H | -4.2861781951 | 0.7240528898 | -0.0116392294 |
| N | -9.1328163765 | 1.2077393496 | 0.2046395561 |
| C | 1.4239429112 | 2.0343776146 | -0.1904448768 |
| C | 1.177803487 | 3.3671175384 | -0.1310768762 |
| H | 0.1632275706 | 3.743834889 | -0.0617275686 |
| C | 2.2718541023 | 4.3346146245 | -0.1563543502 |
| C | 3.6292496972 | 3.7588770435 | -0.2429203311 |
| H | 4.4503340214 | 4.4695071489 | -0.2533364401 |
| C | 3.8484581834 | 2.4251905006 | -0.3025639331 |
| H | 4.859569143 | 2.0350792144 | -0.3617855565 |
| C | 2.7581327122 | 1.4721410225 | -0.2876998676 |
| C | 2.9200441951 | 0.1051620966 | -0.3393660652 |
| C | 1.7584118314 | -0.7539482957 | -0.3194581581 |
| C | 1.8128712669 | -2.165661056 | -0.3938765194 |
| H | 2.7810647376 | -2.647799513 | -0.4756747449 |
| C | 0.6710763134 | -2.937651603 | -0.366503156 |
| H | 0.7162738907 | -4.0196306756 | -0.4233153363 |

| | | | |
|---|---|---|---|
| C | -0.5983156947 | -2.3343628229 | -0.2637051916 |
| C | -0.7069001992 | -0.9180233983 | -0.1909323092 |
| C | 0.4851330935 | -0.1645048249 | -0.2223792031 |
| C | 4.6610805062 | -1.0954406905 | 1.982908225 |
| C | 5.0497173426 | -1.0628101884 | 0.5389055774 |
| C | 6.2988477873 | -1.6335745619 | 0.2477033648 |
| H | 6.8667132864 | -2.050496386 | 1.0722225824 |
| C | 6.7948117674 | -1.6603947563 | -1.0506379533 |
| H | 7.7645612495 | -2.105214572 | -1.2532291456 |
| C | 6.0382461834 | -1.1096138667 | -2.0852412523 |
| H | 6.4113729486 | -1.1198291009 | -3.1055165319 |
| C | 4.7948353975 | -0.541924192 | -1.810803731 |
| H | 4.2052741523 | -0.1163728895 | -2.6175117459 |
| C | 4.2773282377 | -0.5057713993 | -0.5069208661 |
| C | -1.991360867 | -0.2471319338 | -0.0937204349 |
| H | -1.9979781413 | 0.8455757741 | -0.0614152288 |
| C | -5.4470707045 | -1.0213611066 | -0.0286867185 |
| C | -6.7007973339 | -0.2004015868 | 0.0742399428 |
| C | -6.7798689142 | 1.0459418453 | 0.7067206037 |
| H | -5.92291916 | 1.496301837 | 1.1998454573 |
| C | -8.012433588 | 1.7004075585 | 0.7435679456 |
| H | -8.1016424279 | 2.6669933594 | 1.2361564325 |
| C | -9.0487219852 | 0.0082454703 | -0.3872982897 |
| H | -9.9720985843 | -0.3791700895 | -0.813505975 |
| C | -7.8721210069 | -0.733139383 | -0.4730476653 |
| H | -7.8477696985 | -1.7070951644 | -0.9494805629 |
| O | 3.5024951294 | -0.4571621459 | 2.2637449142 |
| H | 3.3743221909 | -0.5540072002 | 3.2265731859 |

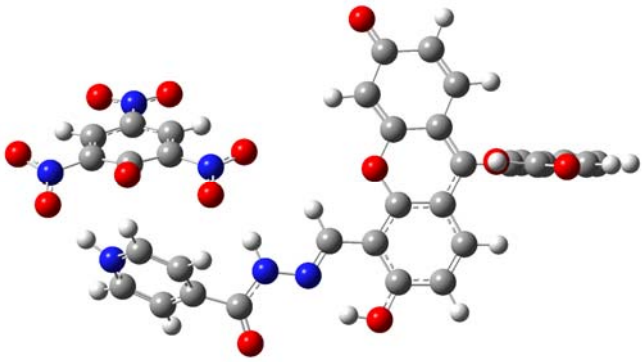


**Figure S30**. Optimized structure of **F1+TNP**.

B3LYP/6-31G(d) in gas phase, E = –2575.6494594 a.u.

charge = 0 Multiplicity = 1

| | | | |
|---|---|---|---|
| C | -3.9039997178 | -3.1953220797 | 1.5240868847 |
| H | -3.1760964409 | -3.2966748921 | 2.3200926151 |
| C | -5.1280263779 | -2.6099011069 | 1.7924174015 |
| H | -5.4067509744 | -2.2189731622 | 2.7602909344 |
| C | -5.7702184524 | -2.8217562004 | -0.471593132 |
| H | -6.5470604009 | -2.605746353 | -1.1952718239 |
| C | -4.5637296857 | -3.4153705977 | -0.790617504 |
| H | -4.3516764109 | -3.7194893408 | -1.8092014413 |
| C | -3.5824683737 | -3.5255210842 | 0.2044802867 |
| C | -2.1738471742 | -3.9078189116 | -0.1944953924 |
| C | 0.7678504187 | -1.9887075682 | -0.0417791167 |
| H | 0.3480057687 | -1.0397788598 | 0.3003654516 |
| N | -1.2849559963 | -2.9286594779 | 0.1684490322 |
| H | -1.6341018282 | -2.0178124173 | 0.496083329 |
| N | 0.0334244332 | -3.045599443 | -0.1739909797 |
| N | -6.0062586938 | -2.4143334558 | 0.7925480141 |
| H | -6.7765271705 | -1.7352177988 | 0.9448258618 |
| O | -1.9173750024 | -4.9367989398 | -0.7948165135 |
| C | -4.0108698471 | 1.273620054 | 0.1412934988 |
| C | -3.9598033703 | 2.3273721552 | -0.7563805801 |
| H | -3.0068871686 | 2.6771765752 | -1.1331125297 |
| C | -5.1419270196 | 2.9152427068 | -1.2012488111 |
| C | -6.3881649836 | 2.4291918425 | -0.7970933651 |
| H | -7.2942829807 | 2.8665444471 | -1.1974333565 |
| C | -6.4491485733 | 1.3712559095 | 0.0873404967 |
| C | -5.2670373621 | 0.7941442118 | 0.7431318312 |
| N | -2.7622119979 | 0.6128684711 | 0.4356158153 |
| N | -5.0805468595 | 4.0076569151 | -2.1596660067 |
| N | -7.7678284874 | 0.8485192211 | 0.3869611877 |
| O | -5.3433184655 | 0.0324078137 | 1.7169678041 |

| | | | |
|---|---|---|---|
| O | -2.8079554265 | -0.5315584874 | 0.9313534616 |
| O | -1.6985596376 | 1.1633596652 | 0.1392917201 |
| O | -3.9662372324 | 4.3914908071 | -2.5217454 |
| O | -6.1485009812 | 4.4831168017 | -2.5541158584 |
| O | -8.7334369231 | 1.5982850649 | 0.2813066402 |
| O | -7.9022411725 | -0.3585544 | 0.6902379684 |
| O | 8.3665343193 | -1.0194656961 | 2.2587765263 |
| O | 2.2711003946 | 4.7351599761 | 1.5941391867 |
| O | 2.3364507908 | 0.220280532 | 0.2658526677 |
| O | 2.146716751 | -4.3567081804 | -1.042139016 |
| H | 1.1927175613 | -4.2268884109 | -0.8009160345 |
| C | 7.4426168164 | -0.5923586058 | 1.5953138142 |
| C | 7.5970594112 | -0.0300468564 | 0.2180139431 |
| C | 8.9201413593 | 0.049522893 | -0.2447005202 |
| H | 9.7060892382 | -0.3022045321 | 0.4145820601 |
| C | 9.2154919832 | 0.5653779461 | -1.50129931 |
| H | 10.2463422391 | 0.6192520149 | -1.8385901527 |
| C | 8.1781905774 | 1.0142022568 | -2.31908727 |
| H | 8.3905604338 | 1.4231416728 | -3.3029455311 |
| C | 6.8594398813 | 0.939151145 | -1.8731122404 |
| H | 6.0526583169 | 1.2865756614 | -2.5117793444 |
| C | 6.5412142117 | 0.4211984565 | -0.6082236209 |
| C | 5.087636667 | 0.3662979892 | -0.2511762594 |
| C | 4.4230299338 | 1.4831092766 | 0.202768662 |
| C | 5.0547750139 | 2.7609362002 | 0.4601311448 |
| H | 6.121829949 | 2.8430951143 | 0.2791990218 |
| C | 4.3503019738 | 3.822487301 | 0.9140356411 |
| H | 4.8272481305 | 4.7785223565 | 1.1087014178 |
| C | 2.8974958948 | 3.7559294386 | 1.1781595111 |
| C | 2.266026404 | 2.4633911355 | 0.9199535275 |
| C | 2.9976336828 | 1.4135920973 | 0.471988533 |
| C | 2.9781671646 | -0.8825614326 | -0.1895387553 |
| C | 2.1809418896 | -2.0360171136 | -0.3602408303 |
| C | 2.8124600031 | -3.2149388544 | -0.8435066445 |
| C | 4.1899349532 | -3.2056527104 | -1.13537456 |
| H | 4.639312441 | -4.1205225476 | -1.5054681368 |
| C | 4.9346733375 | -2.0588480172 | -0.9519273956 |
| H | 5.994594374 | -2.0695714839 | -1.1826058064 |
| C | 4.355408851 | -0.8618239735 | -0.4705313669 |
| H | 1.1999856669 | 2.3633978607 | 1.0938231819 |
| H | 6.2204433104 | -0.9689747595 | 2.9588029903 |
| O | 6.1738446422 | -0.584986236 | 2.062609542 |

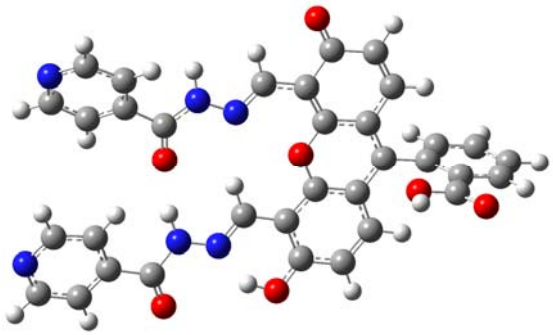


**Figure S31**. Optimized structure of **F2**.

B3LYP/6-31G(d) in gas phase, E = –2163.921766 a.u.

charge = 0 Multiplicity = 1

| | | | |
|---|---|---|---|
| O | -6.8181430195 | -0.7738262328 | -2.6971447473 |
| O | -1.9538569322 | 5.0482417718 | 0.4315923339 |
| O | -1.2301534898 | 0.3841108378 | 0.3099839307 |
| O | -0.251445666 | -4.2661963279 | 0.2117141803 |
| H | 0.6827813431 | -3.9107263648 | 0.1401960801 |
| O | 3.2637270128 | 0.7570466465 | 0.038850523 |
| O | 3.4899777672 | -4.3590792974 | -0.0148012291 |
| N | 0.8643400197 | 2.1586614337 | 0.1405786229 |
| N | 2.1093679661 | 2.7347624786 | 0.0499938201 |
| H | 2.1869327934 | 3.7481081887 | 0.1208214945 |
| N | 6.9563919481 | 4.1784258917 | -0.2737774512 |
| N | 1.6086068309 | -2.4587667297 | 0.072657438 |
| N | 2.9229094971 | -2.1468533782 | -0.0267275178 |
| H | 3.1940300602 | -1.1629690942 | 0.0051568405 |
| N | 8.0249601587 | -2.2418590526 | -0.4980391711 |
| C | -6.0086087531 | -0.5653274261 | -1.8162413383 |
| C | -6.3396264075 | -0.5966505934 | -0.3576860934 |
| C | -7.6842651256 | -0.8670942017 | -0.0586311187 |
| H | -8.3614646459 | -1.0304560828 | -0.889758388 |
| C | -8.1339882496 | -0.9230904365 | 1.2555327702 |
| H | -9.1785910762 | -1.133869157 | 1.4642419015 |
| C | -7.2335750435 | -0.7055014574 | 2.2987128076 |
| H | -7.567998581 | -0.7443998958 | 3.3315711462 |
| C | -5.8951797158 | -0.4353700255 | 2.0167866085 |
| H | -5.195064313 | -0.2670299425 | 2.8298881207 |
| C | -5.4241933046 | -0.3748867363 | 0.6965998262 |
| C | -3.9635638032 | -0.0924189251 | 0.5178215814 |
| C | -3.4887976059 | 1.2108118927 | 0.5075525981 |
| C | -4.34169787 | 2.3753143256 | 0.5868929615 |
| H | -5.4119036465 | 2.2156214387 | 0.6680102819 |

| | | | |
|---|---|---|---|
| C | -3.8349459128 | 3.6284667226 | 0.5619740301 |
| H | -4.4741370883 | 4.5037559013 | 0.6212710488 |
| C | -2.3949691186 | 3.8920278415 | 0.4507888571 |
| C | -1.5090874091 | 2.7101189586 | 0.3624198798 |
| C | -2.071944605 | 1.4465268324 | 0.3924979775 |
| C | -1.6684539866 | -0.9018725103 | 0.337735951 |
| C | -0.6725135802 | -1.8892303639 | 0.257110987 |
| C | -1.1001633298 | -3.2453603408 | 0.2820802462 |
| C | -2.4776112189 | -3.5544278526 | 0.3874736279 |
| H | -2.7579698712 | -4.6020212126 | 0.4042251584 |
| C | -3.4201329203 | -2.5564266115 | 0.4659777533 |
| H | -4.4709845535 | -2.8114466789 | 0.5483742211 |
| C | -3.0444238603 | -1.1887694754 | 0.4431489059 |
| C | -0.0998276486 | 3.0133682542 | 0.2516106651 |
| H | 0.0962854498 | 4.0926803182 | 0.2671571665 |
| C | 3.247201707 | 1.9886959514 | -0.0075497629 |
| C | 4.5152728046 | 2.7873613844 | -0.1145343207 |
| C | 5.6791818289 | 2.2700703313 | 0.4641331578 |
| H | 5.6531884255 | 1.317392156 | 0.981788847 |
| C | 6.8604888672 | 3.0031349988 | 0.3628232496 |
| H | 7.7767534106 | 2.628566153 | 0.8151502269 |
| C | 5.8429414644 | 4.6565715096 | -0.8395911699 |
| H | 5.9414332925 | 5.6035635194 | -1.3670957544 |
| C | 4.6062799005 | 4.0106391616 | -0.7889990675 |
| H | 3.7522781328 | 4.4450777809 | -1.3009986925 |
| C | 0.7326276095 | -1.5135584559 | 0.1545781056 |
| H | 1.0020209482 | -0.4556359072 | 0.1496065352 |
| C | 3.831299474 | -3.1873138707 | -0.0831145823 |
| C | 5.2745526023 | -2.7892712687 | -0.2315586186 |
| C | 6.2353345743 | -3.7793177887 | -0.0004632057 |
| H | 5.9158489515 | -4.7771372592 | 0.2787781549 |
| C | 7.5828268353 | -3.4557764647 | -0.141004096 |
| H | 8.3482405436 | -4.2083231648 | 0.0401544627 |
| C | 7.0974882802 | -1.3054972877 | -0.7289338342 |
| H | 7.469593085 | -0.3268926814 | -1.0284238767 |
| C | 5.7225349624 | -1.5183814101 | -0.6116133505 |
| H | 5.039967691 | -0.7017922478 | -0.821128439 |
| O | -4.7147043349 | -0.2807438763 | -2.0872959122 |
| H | -4.6373535512 | -0.294887594 | -3.0603323457 |

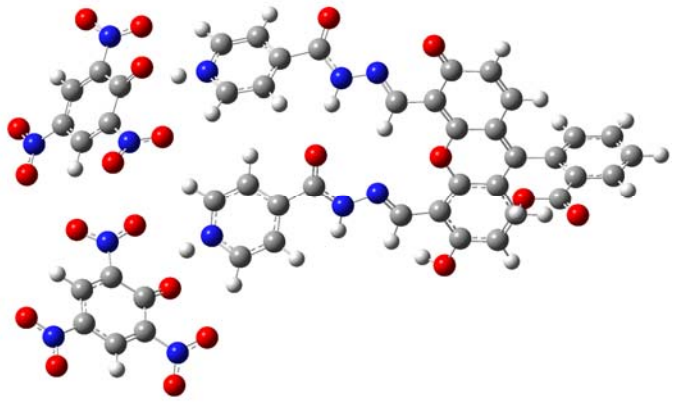


**Figure S32**. Optimized structure of **F2+TNP**.

B3LYP/6-31G(d) in gas phase, E = –4005.8135635 a.u.

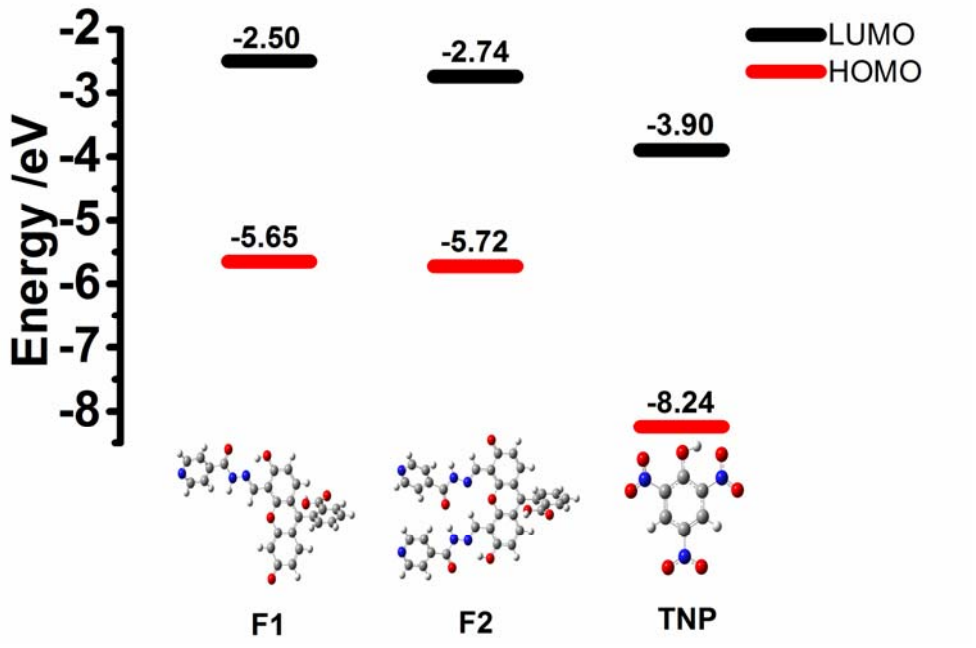
charge = 0 Multiplicity = 1

| | | | |
|---|---|---|---|
| O | 10.9515423038 | 3.3460182515 | -1.8825476229 |
| O | 6.338567952 | -3.5103034646 | -2.8574445184 |
| C | 6.0422343095 | -1.8246536469 | -1.1815493955 |
| C | 4.1098024059 | 1.7216488385 | 1.7373158239 |
| C | 5.5552415464 | 1.7057394994 | 1.8913761561 |
| C | 6.4541400198 | 0.9267177702 | 1.117153171 |
| C | 4.5983970826 | -1.9807897064 | -1.0499494256 |
| C | 6.6930076234 | -0.8405879277 | -0.4789540569 |
| C | 1.1145537484 | 0.513513868 | 0.3579256968 |
| C | 8.894742578 | -1.4950616061 | -1.3768246352 |
| C | 7.8471074973 | 1.1331985561 | 1.1569839492 |
| C | 10.8975633158 | 1.503844871 | -0.3542909638 |
| C | 8.3483334496 | 2.114976773 | 2.0341870399 |
| C | 6.8384128865 | -2.6780706689 | -2.1077761774 |
| C | 8.6917230814 | 0.3325663166 | 0.2954752145 |
| C | 8.1261573589 | -0.6348590694 | -0.5009142104 |
| C | 10.1766887144 | 0.5169400861 | 0.3583591564 |
| C | 10.3062561852 | 2.4947385145 | -1.3060268538 |
| C | 6.1305550985 | 2.6281135913 | 2.8061248238 |
| C | 7.5097946001 | 2.8420927943 | 2.8578250323 |
| C | -0.5943875245 | 2.417918661 | 0.5759469942 |
| C | -0.2925343719 | 1.0515292984 | 0.481020885 |
| C | -1.3416733888 | 0.1244946698 | 0.4582081152 |
| C | -0.2028168636 | -2.9815957489 | -1.8212532853 |
| C | 8.2970756803 | -2.448598967 | -2.1186931819 |
| C | 1.9559749776 | -4.2660895774 | -1.2832575861 |
| C | -2.6504527361 | 0.5693481789 | 0.5747949503 |
| C | 10.8855987859 | -0.3475691338 | 1.2062975933 |
| C | -1.9199914299 | 2.8114549857 | 0.6925460011 |

| | | | |
|---|---|---|---|
| C | 0.4514329758 | -4.0914563101 | -1.266929997 |
| C | 12.268906529 | -0.2497292414 | 1.3528786563 |
| C | 12.2897463748 | 1.5903669309 | -0.1965578552 |
| C | -1.5881230108 | -2.9343132322 | -1.8033860244 |
| C | 12.9755615996 | 0.7251360621 | 0.6484857981 |
| C | -1.6970627112 | -5.0276531996 | -0.7251897341 |
| C | -0.3160075423 | -5.137602469 | -0.7376760453 |
| O | -9.8478043527 | 4.7880606333 | -2.1695684679 |
| O | -3.4199572997 | 5.8112691337 | 0.2496445182 |
| C | -7.7956535213 | 3.6823224043 | -0.7709664071 |
| O | -8.9131918057 | 6.7617381295 | -2.1614319374 |
| C | -6.7162689919 | 3.1696230277 | -0.0667334 |
| C | -7.8128824794 | 5.0297751843 | -1.1142632618 |
| O | -4.8166165628 | 7.4774067225 | 0.2571059484 |
| C | -5.678954735 | 5.3642140005 | -0.0779385179 |
| C | -6.7560465101 | 5.8764367173 | -0.7710032961 |
| O | -7.8300632057 | 1.1652394527 | 0.1557004484 |
| O | -5.6918316284 | 1.1717145979 | 0.5384436356 |
| O | -4.6812744707 | 3.586931932 | 1.1410158378 |
| C | -5.6012644716 | 3.9882052969 | 0.3810543312 |
| O | -9.7930093306 | -3.5392243256 | 2.6398376898 |
| O | -4.7176169837 | -4.4764052268 | -0.8573710537 |
| O | -6.0910341647 | -0.8518557859 | -1.6359056317 |
| C | -8.0219539364 | -3.1508639068 | 1.2174039945 |
| C | -6.1754984496 | -2.676943586 | -0.2242784843 |
| C | -7.5650146303 | -4.4589597634 | 1.3972988863 |
| C | -5.659067362 | -4.0326102087 | -0.1466808854 |
| C | -6.412296557 | -4.8732230357 | 0.7614338973 |
| O | -4.2089951764 | -1.7411736313 | -0.9992416706 |
| C | -7.3343466146 | -2.2509973629 | 0.4063934364 |
| O | -6.7830190861 | -7.0641283714 | 1.3836259158 |
| H | 4.5749758281 | 2.9147583091 | 3.9205357704 |
| H | 1.7416196129 | 2.0461097676 | 1.5818282573 |
| H | 2.1876028265 | -2.2261787987 | -0.9106396663 |
| H | 3.6173756397 | 2.5625556257 | 2.246628691 |
| H | -3.8837500617 | 2.2869272356 | 0.8408424075 |
| H | 4.0357002736 | -1.117598413 | -0.6815692403 |
| H | 9.9688595821 | -1.349384157 | -1.4172690275 |
| H | 9.4189093463 | 2.2801454475 | 2.0790787454 |
| H | 7.8944252783 | 3.5677476303 | 3.5653626778 |
| H | 0.1739995765 | 3.1819791563 | 0.5276943901 |
| H | -1.1320651587 | -0.9319484887 | 0.3491148424 |
| H | 0.3517107905 | -2.1649655965 | -2.2666814483 |
| H | -3.3676882379 | -3.9104921566 | -1.1772066792 |

| | | | |
|---|---|---|---|
| H | 8.8618206773 | -3.0927340241 | -2.7853974048 |
| H | -3.5117313416 | -0.086861696 | 0.54245681 |
| H | 10.3375514401 | -1.1079105874 | 1.755208306 |
| H | -2.2640902656 | 3.8399195909 | 0.761832234 |
| H | 12.7891190646 | -0.9362140726 | 2.0147703106 |
| H | 12.8139982402 | 2.3544992935 | -0.7598749079 |
| H | -2.1756374253 | -2.1160553968 | -2.2016567553 |
| H | 14.0529415068 | 0.8090686543 | 0.7542688471 |
| H | -2.3749270656 | -5.7637807645 | -0.3050408523 |
| H | 0.1789662353 | -6.0180992149 | -0.345096536 |
| H | -8.6158014039 | 3.0361793485 | -1.0561035539 |
| H | -6.7765357425 | 6.9190457668 | -1.0613029709 |
| H | -8.1056678368 | -5.1398262453 | 2.0421174247 |
| H | -7.6721714007 | -1.2247222809 | 0.3031628902 |
| O | -4.729230942 | -6.4523493838 | 0.9977648678 |
| O | -9.5971146202 | -1.5548749562 | 1.7498195863 |
| N | -5.9404974245 | -6.2267082855 | 1.0535190265 |
| N | -9.2224293728 | -2.7162798503 | 1.9182191039 |
| N | -5.460639143 | -1.6989039865 | -1.014463383 |
| N | -6.7491421502 | 1.7494511217 | 0.2342876298 |
| N | -8.9386404465 | 5.5637307277 | -1.868789186 |
| N | -4.5639724939 | 6.2747650269 | 0.174957877 |
| N | 3.3834580045 | 0.9240499364 | 1.0290783109 |
| N | 4.0159038611 | -3.097614205 | -1.3248657233 |
| N | 2.6561155688 | -3.0882136608 | -1.1979312609 |
| N | 2.0528627985 | 1.256953795 | 1.016674043 |
| N | -2.8919073013 | 1.8832121619 | 0.706364533 |
| N | -2.2877513102 | -3.9369352897 | -1.2485933428 |
| O | 5.9184251932 | -0.0221082443 | 0.3219230829 |
| O | 5.3811469372 | 3.3845099223 | 3.6601295058 |
| O | 1.3436144933 | -0.5130355799 | -0.2693105565 |
| O | 2.4367873758 | -5.3819673125 | -1.3700825776 |
| H | 8.7261283548 | 3.063551231 | -2.1276850828 |
| O | 8.9697978642 | 2.3705063226 | -1.4845530297 |

**22. HOMO and LUMO energy-level diagram of F1, F2 and TNP.**




**Firgue S33.** HOMO and LUMO energy-level diagram of **F1**, **F2** and TNP.

**23. The images of paper sensors absorbed different concentration of F1 and F2 under visible light and UV light.**

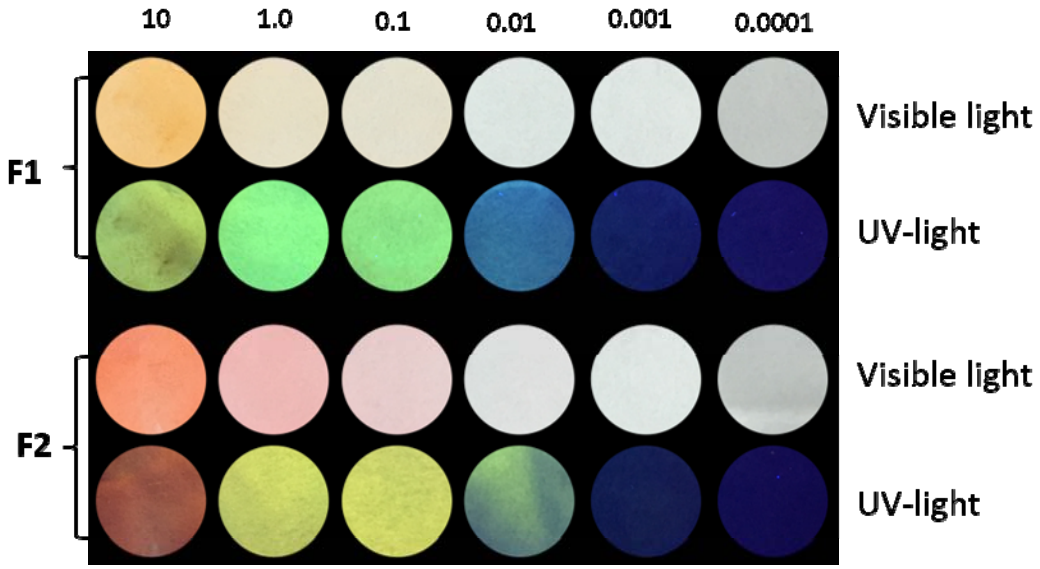



**Figure S34.** The images of paper sensors absorbed different concentration of **F1** and **F2** under visible light and UV light (365 nm). [TNP]= 10.0 mM, 1.0 mM, $1.0\times10^{-1}$ mM, $1.0\times10^{-2}$ mM, $1.0\times10^{-3}$ mM, $1.0\times10^{-4}$ mM。