# ELECTRONIC SUPPLEMENTARY INFORMATION

# (ESI)

## A tryptophan-containing fluorescent intramolecular complex as designer peptidic proton sensor

V. Haridas,[*a] Anita Yadav,[a] Sakshi Sharma[a] and Siddharth Pandey[*a]

[a] *Department of Chemistry, Indian Institute of Technology Delhi, Hauz Khas, New Delhi - 110016, India.*

[*] To whom correspondence should be addressed.

E-mail: sipandey@chemistry.iitd.ac.in, haridasv@chemistry.iitd.ac.in

---

## Table of Contents


| | **Page No.** |
|---|---|
| Data of Compounds **1**, **2**, and **3** | 3 - 4 |
| $^{1}$H NMR, $^{13}$C NMR, and HRMS of Compound **1**, **2**, and **3** | 5 - 9 |
| Table S1 | 10 |
| Figure S1 – Figure S8 | 11 - 18 |

**Data of Compound 1**

Yield: 36 %. Mp: 148 °C.

$^1$H NMR (DMSO $d_6$, 400 MHz): δ 1.19 (s, 9H), 1.30-1.42 (m, 1H), 1.48-1.58 (m, 1H), 1.61 (br s, 1H), 1.70 (br s, 1H), 1.80-1.90 (m, 1H), 2.18-2.30 (m, 2H), 2.50-2.60 (m, 1H), 2.73-2.84 (m, 3H), 2.86-2.96 (m, 3H), 3.88-4.08 (m, 1H), 4.44-4.56 (m, 1H), 4.77-4.90 (m, 2H), 5.02-5.15 (m, 1H), 6.84-6.91 (m, 1H), 6.91-7.00 (m, 1H), 7.04 (s+s, 1H), 7.1-7.28 (m, 1H), 7.39 (d, 1H, $J$ = 8 Hz), 7.94-8.00 (m, 1H), 8.02-8.12 (m, 4H), 8.12-8.24 (m, 5H), 8.61 (d, 1H, $J$ = 8.4 Hz), 10.75 (s, 1H).

$^{13}$C NMR ($CDCl_3$, 75 MHz): δ 21.12, 24.97. 25.61, 28.09, 28.35, 28.78, 29.67, 29.82, 32.41, 33.97, 41.18, 46.16, 49.12, 49.96, 50.71, 58.12, 58.34, 60.47, 63.16, 79.60, 110.87, 111.04, 118.71, 119.45, 121.96, 122.52, 123.96, 124.79, 124.99, 125.25, 125.78, 127.08, 127.26, 127.47, 127.58, 127.71, 128.26, 129.05, 130.85, 130.91, 131.30, 132.75, 135.97, 155.06, 169.81, 172.59.

IR (KBr): 3422, 2926, 2855, 2364, 1628, 1512, 1453 cm$^{-1}$.

(HRMS): calcd for $C_{42}H_{45}N_5O_4H$ m/z 684.3544, found m/z 684.3578.

**Data of Compound 2**

Yield: 50.8 %. Mp: 142 °C.

$^1$H NMR ($CDCl_3$, 300 MHz): δ 0.70-1.00 (m, 6H), 1.48 (s, 9H), 1.55-1.81 (m, 4H), 1.91 (s, 2H), 1.93-2.16 (m, 1H), 2.31-2.60 (m, 2H), 2.64-2.84 (m, 2H), 3.05 (br s, 2H), 3.10-3.20 (m, 1H), 3.26-3.40 (m, 1H), 4.20-4.33 (m, 1H), 4.68-4.81 (m, 3H), 5.10-5.30 (m, 2H), 7.90-8.10 (s+m, 4H), 8.10-8.35 (m, 5H), 8.73 (d, 1H, $J$ = 9 Hz).

$^{13}$C NMR ($CDCl_3$, 75 MHz): δ 21.82, 22.79, 24.47, 28.07, 28.36, 28.79, 29.59, 29.93, 32.54, 41.02, 42.14, 46.18, 47.80, 48.67, 49.32, 50.61, 58.00, 58.21, 63.09, 79.45, 123.82, 124.13, 124.63, 124.83, 125.66, 126.96, 127.44, 127.60, 127.93, 128.25, 128.92, 129.14, 130.77, 131.20, 132.22, 132.65, 155.16, 169.63, 173.51.

IR (KBr): 3411, 3368, 2923, 2810, 2362, 2329, 1707, 1631, 1523, 1455, 848, 677, 540 cm$^{-1}$.

(HRMS): calcd for $C_{37}H_{46}N_4O_4Na$ m/z 633.3411, found m/z 633.3429.

**Data of Compound 3**

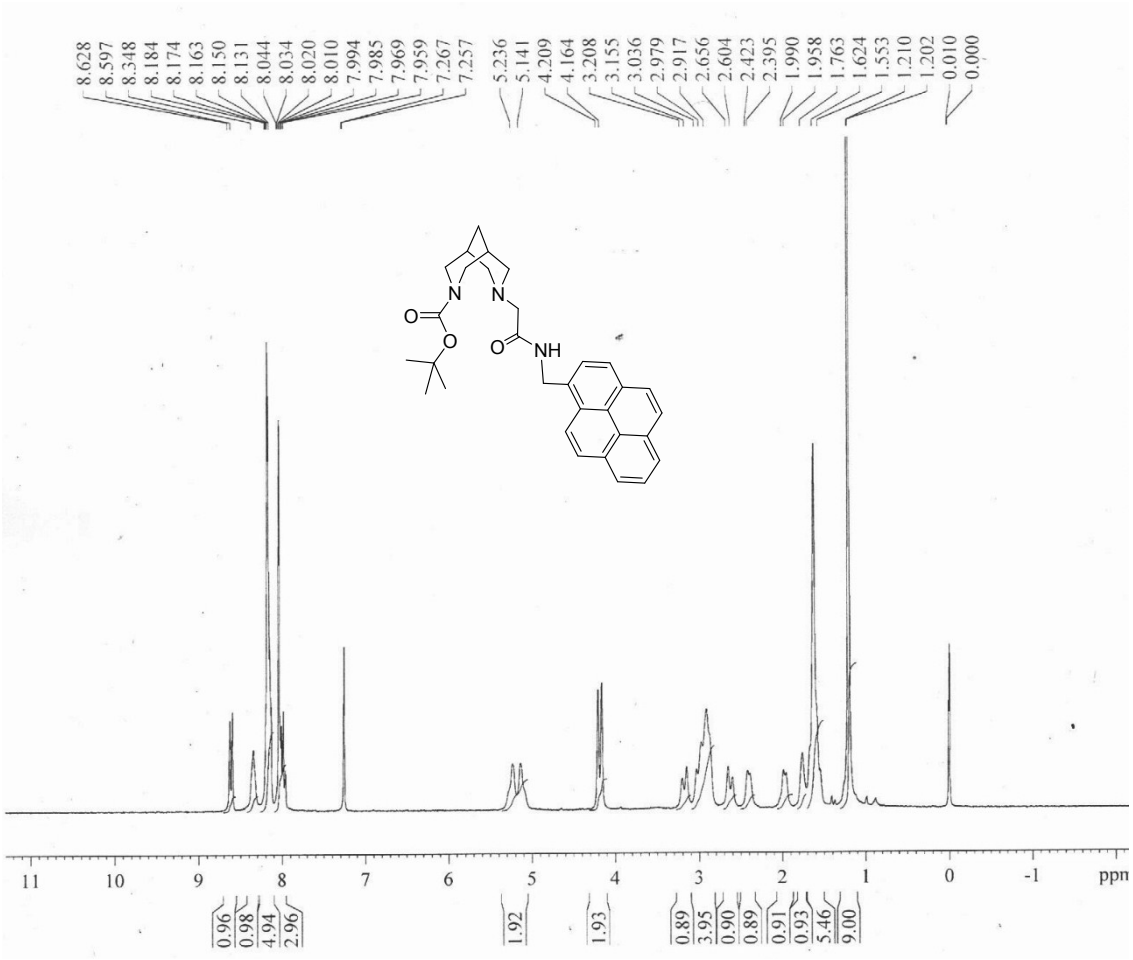
Yield: 55 %. Mp: 130 $^{o}$C.

$^{1}$H NMR ($CDCl_3$, 300 MHz): δ 1.21 (s, 9H), 1.50-1.70 (s+m, 3H), 1.76 (br s, 1H), 1.97 (d, 1H, *J* = 9.6 Hz), 2.41 (d, 1H, *J* = 8.4 Hz), 2.55-2.70 (m, 1H), 2.80-3.10 (m, 4H), 3.10-3.28 (m, 1H), 4.19 (d, 2H, *J* = 13.5 Hz), 5.05-5.36 (m, 2H), 7.95-8.10 (s+m, 3H), 8.10-8.27 (m, 5H), 8.35 (br s, 1H), 8.61 (d, 1H, *J* = 9.3 Hz).

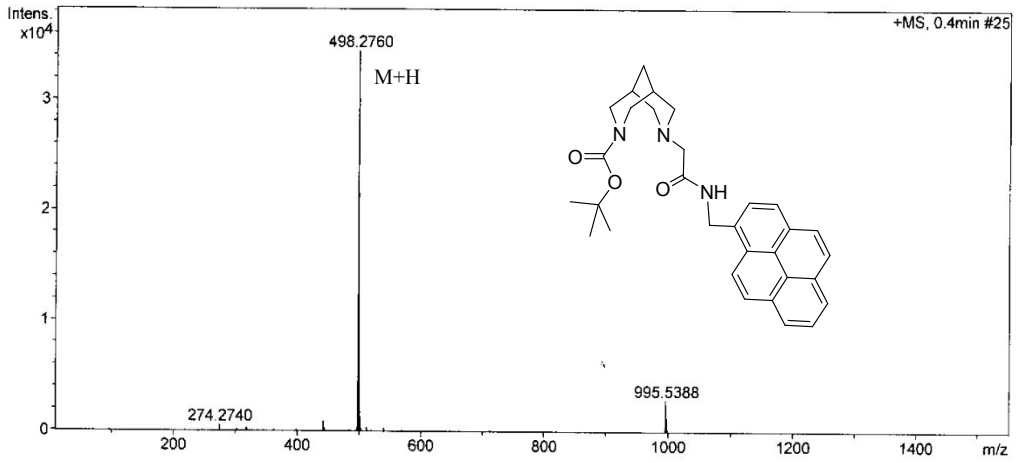
$^{13}$C NMR ($CDCl_3$, 75 MHz): 28.27, 28.42, 29.51, 32.07, 41.07, 47.02, 49.64, 58.47, 58.71, 63.17, 79.14, 123.76, 124.57, 124.68, 124.80, 124.83, 125.61, 126.87, 127.43, 127.46, 128.13, 128.87, 130.68, 130.74, 131.12, 132.25, 156.43, 169.61.

IR (KBr): 3448, 2973, 2919, 2860, 2805, 1670, 1519 cm$^{-1}$.

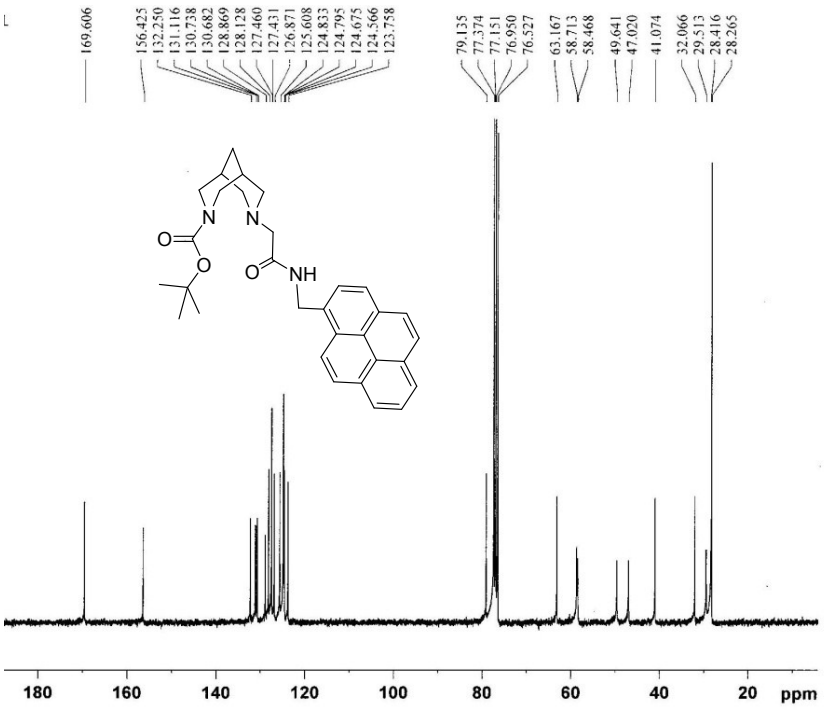
HRMS: Cald for $C_{31}H_{35}N_3O_3H$ m/z 498.2751, found m/z 498.2760.



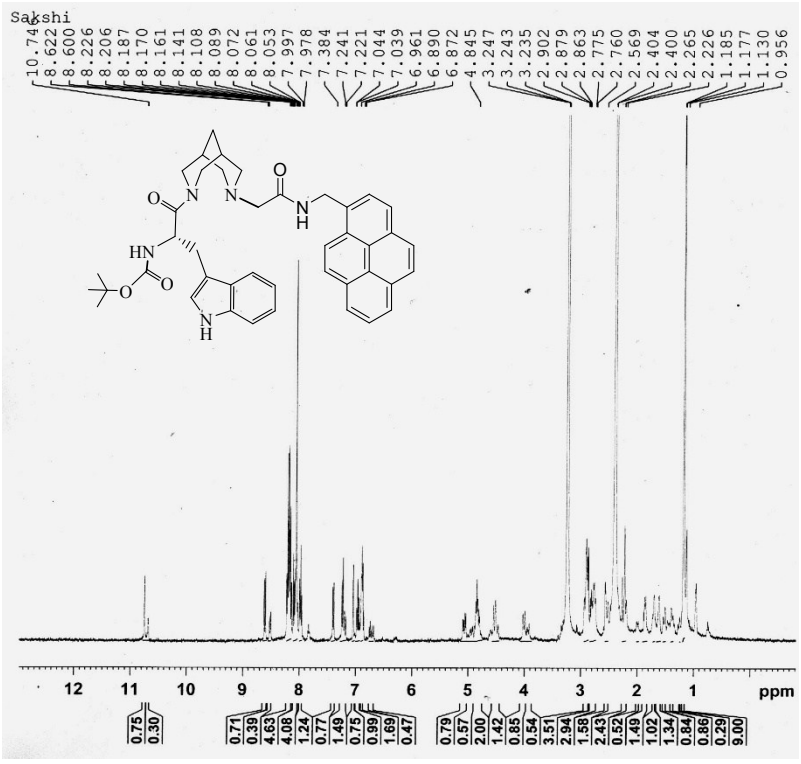

$^1$H NMR Spectrum of compound **3**, ($CDCl_3$, 300 MHz)



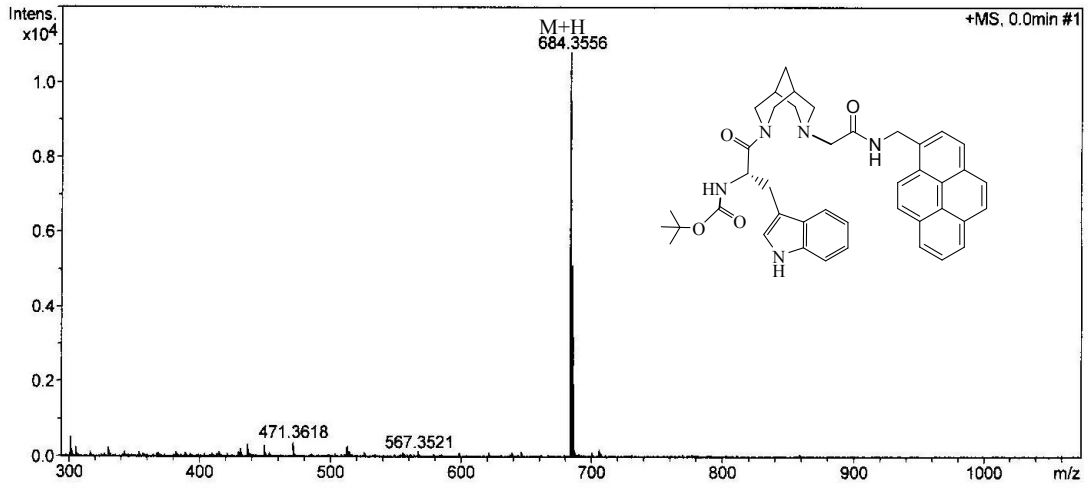

HRMS of compound **3**



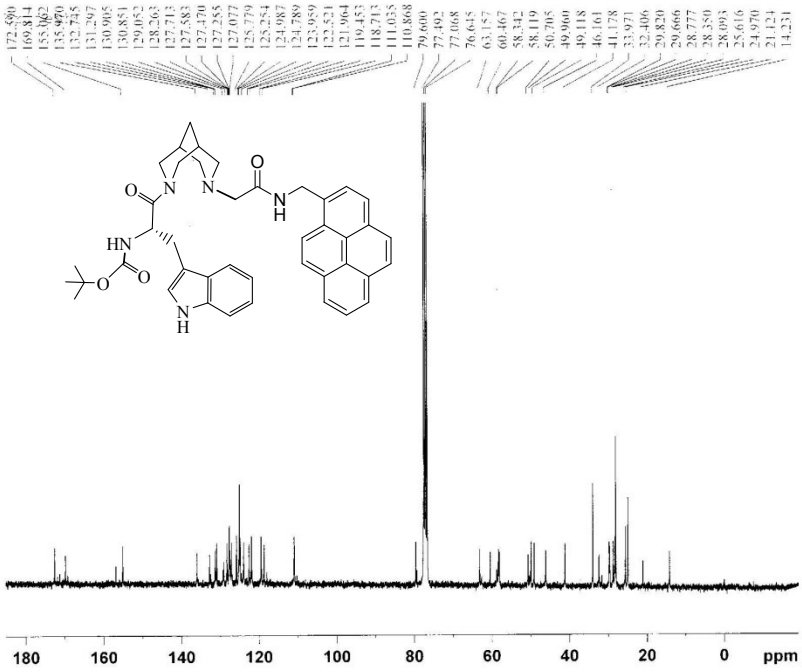

$^{13}$C NMR Spectrum of compound **3**, ($CDCl_3$, 75 MHz)



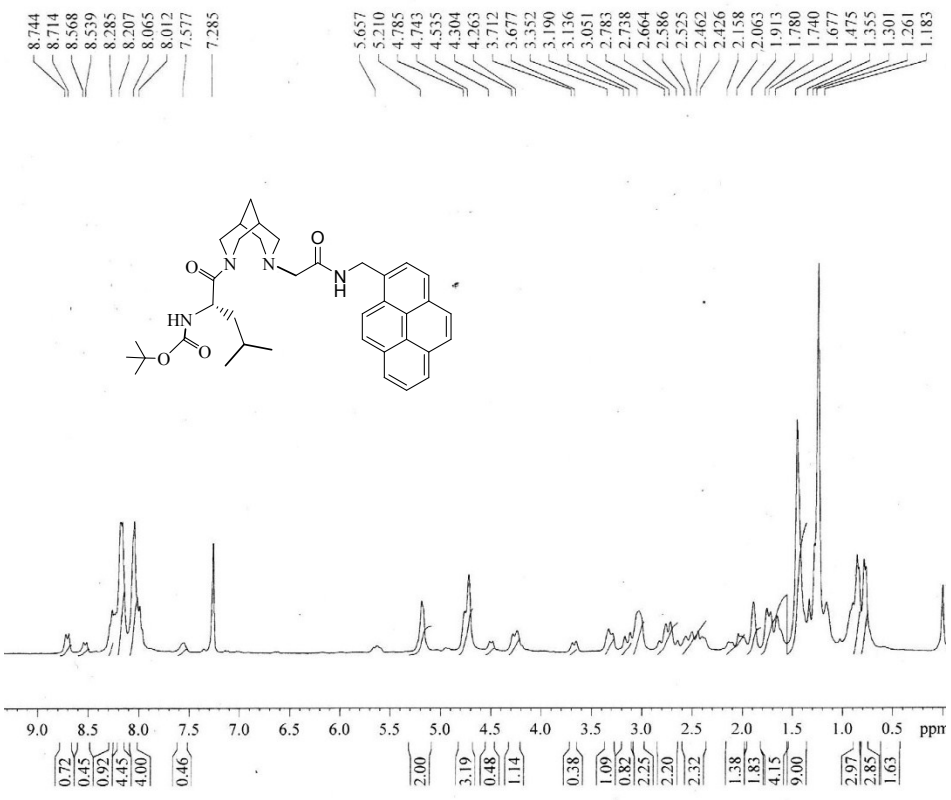

$^{1}$H NMR Spectrum of compound **1**, (DMSO-$d_6$, 400 MHz)



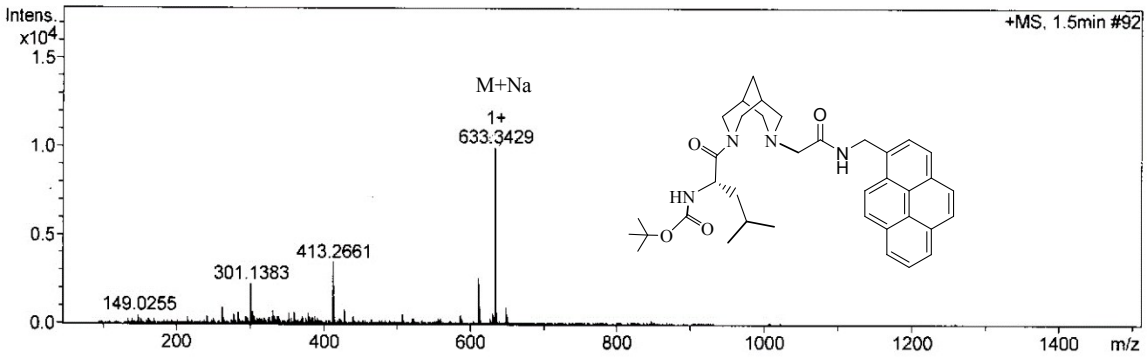

HRMS of compound **1**



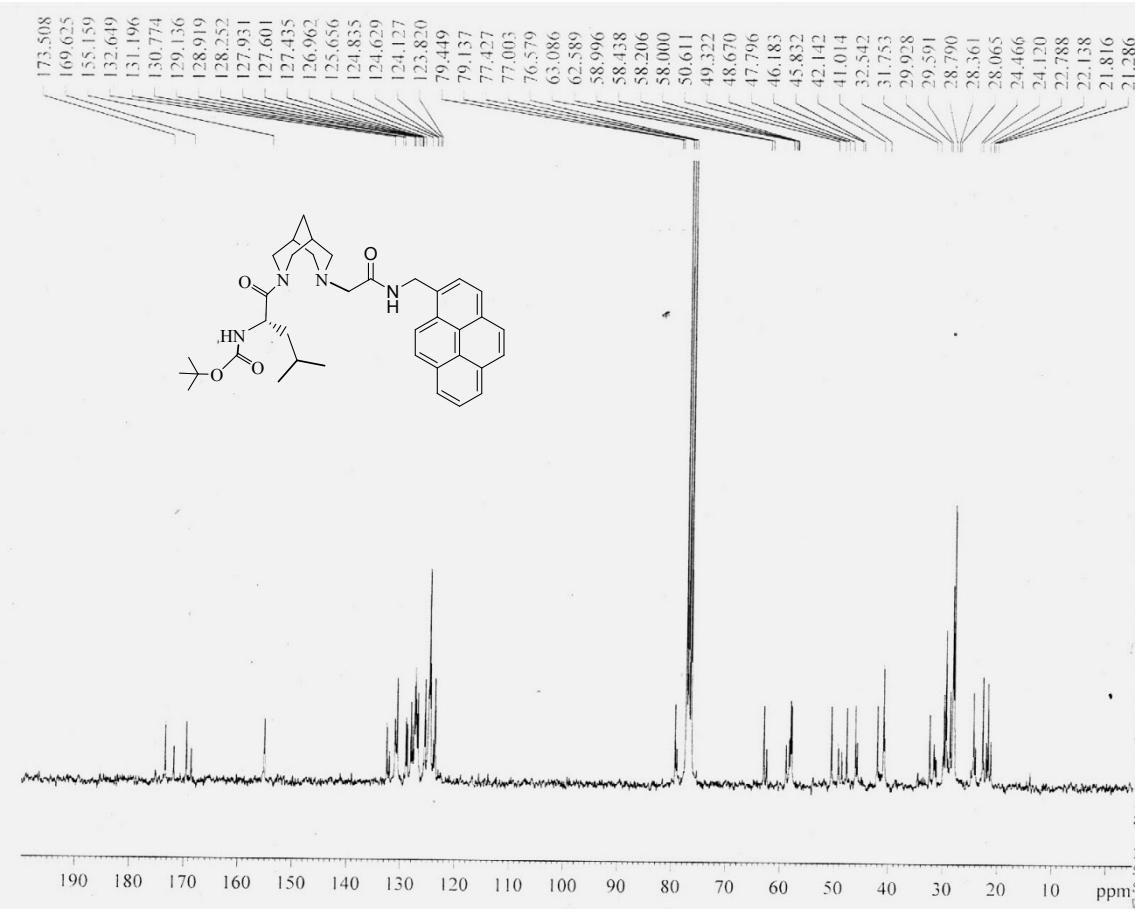

$^{13}C$ NMR spectrum of compound **1**, ($CDCl_3$, 75 MHz)




$^1$H NMR Spectrum of compound **2**, ($CDCl_3$, 300 MHz)




HRMS of compound **2**




$^{13}$C NMR spectrum of compound **2**, ($CDCl_3$, 75 MHz)

References:

1. (a) V. Haridas, S. Sadanandan, Y. K. Sharma, S. Chinthalapalli and A. Shandilya, *Tetrahedron Lett*., 2012, **53**, 623–626. (b) V. Haridas, S. Sadanandan, M. V. S. Gopalakrishna, M. B. Bijesh, R. P. Verma, S. Chinthalapalli and A. Shandilya, *Chem. Commun*., 2013, **49**, 10980. (c) S. Sharma, M. V. S. Gopalakrishna, P. Venugopalan, C. H. Suresh and V. Haridas, *Tetrahedron*, 2015, **71**, 8302-8306.

**Table S1:** Recovered intensity decay parameters for **1**, **2**, and **3** at 25° C. Excitation was carried out using a 340 nm LED. Errors associated to decay times as ≤5%.

| Compound | $\lambda_{em}$(nm) | $\tau_1$(ns) | $\tau_2$(ns) | $\tau_3$(ns) | $\alpha_1$ | $\alpha_2$ | $\alpha_3$ | $\chi^2$ | DW |
|---|---|---|---|---|---|---|---|---|---|
| | | | | **Acetonitrile** | | | | | |
| **1** | 376 | 5.6 | | | 1.00 | | | 11.7 | 0.19 |
| | | 1.8 | 12.6 | | 0.86 | 0.14 | | 1.13 | 1.63 |
| | 480 | 12.4 | | | 1.00 | | | 1.35 | 1.49 |
| | | 3.7 | 11.9 | | -0.13 | 0.87 | | 1.08 | 1.86 |
| **1** + $3.16\times10^{-3}$ M | 376 | 13.6 | | | 1.00 | | | 2.75 | 0.87 |
| $[H^+]$ | 1.7 | 14.6 | | 0.40 | 0.60 | | 1.59 | 1.46 | |
| | 480 | 9.4 | | | 1.00 | | | 7.53 | 0.32 |
| | | 1.8 | 12.8 | | 0.72 | 0.28 | | 1.34 | 1.58 |
| **2** | 376 | 17.2 | | | 1.00 | | | 1.56 | 1.49 |
| **3** | 376 | 17.5 | | | 1.00 | | | 1.41 | 1.52 |
| | | | | **Ethanol** | | | | | |
| **1** | 376 | 11.5 | | | 1.00 | | | 7.72 | 0.34 |
| | | 2.9 | 15.9 | | 0.64 | 0.36 | | 1.67 | 1.47 |
| | | 1.0 | 6.2 | 18.3 | 0.49 | 0.31 | 0.19 | 1.34 | 1.84 |
| | 480 | 18.7 | | | 1.00 | | | 2.60 | 0.89 |
| | | 13.8 | 14.1 | | -0.49 | 0.51 | | 1.94 | 1.19 |
| | | 0.8 | 8.1 | 15.9 | 0.26 | -0.24 | 0.49 | 1.18 | 1.80 |
| **1** + $3.16\times10^{-3}$ M | 376 | 23.8 | | | 1.00 | | | 4.35 | 0.48 |
| $[H^+]$ | | 2.0 | 25.9 | | 0.54 | 0.46 | | 1.13 | 1.71 |
| | | 1.2 | 6.5 | 26.7 | 0.51 | 0.11 | 0.38 | 1.06 | 1.84 |
| | 480 | 16.4 | | | 1.00 | | | 8.43 | 0.26 |
| | | 2.6 | 21.6 | | 0.72 | 0.28 | | 1.30 | 1.51 |
| | | 1.0 | 5.1 | 23.1 | 0.55 | 0.27 | 0.19 | 1.03 | 1.87 |
| **2** | 376 | 22.5 | | | 1.00 | | | 1.15 | 1.60 |
| **3** | 376 | 23.6 | | | 1.00 | | | 2.15 | 0.93 |

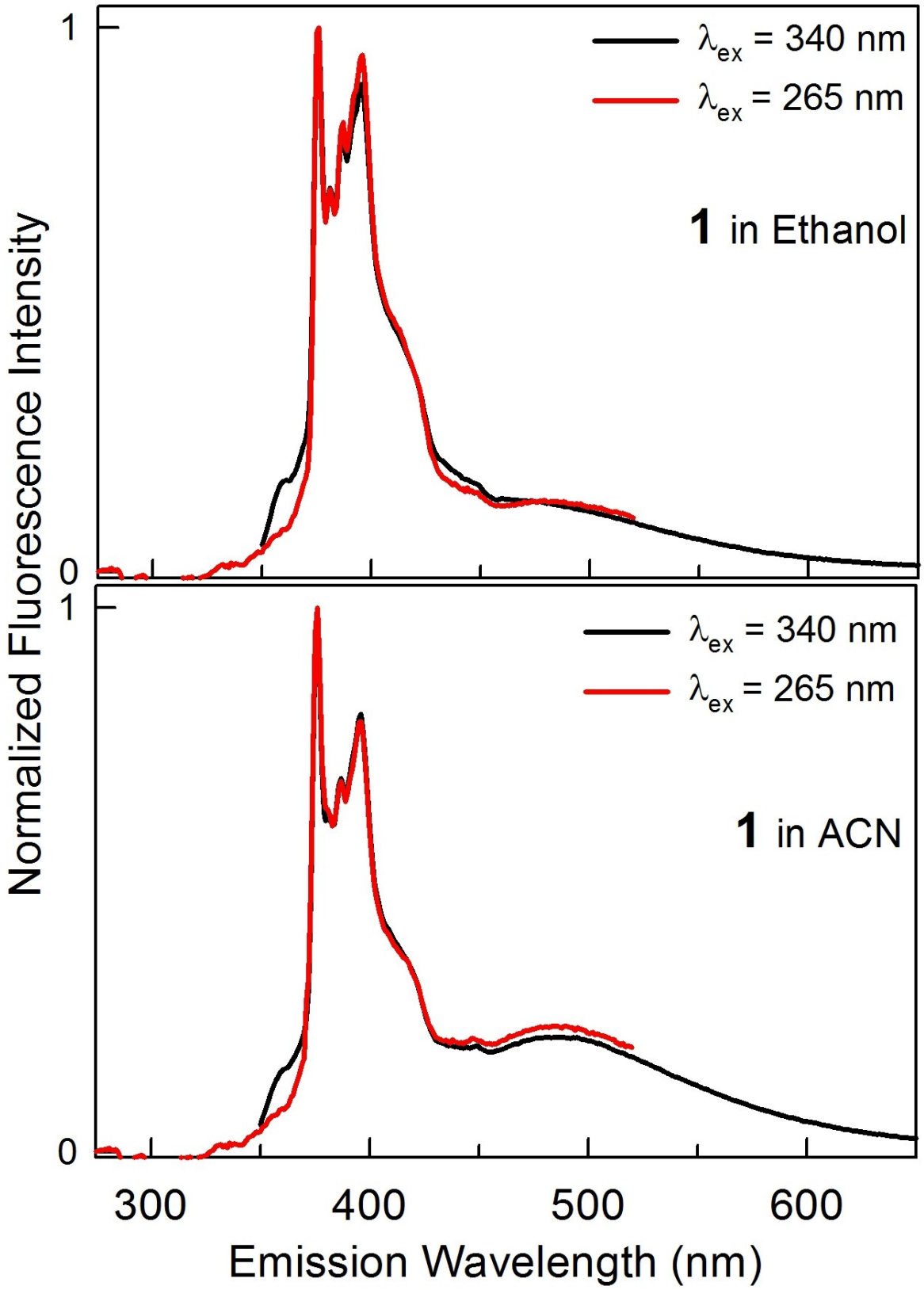



**Figure S1.** Normalized fluorescence emission spectra of **1** (10 μM) at 25°C.

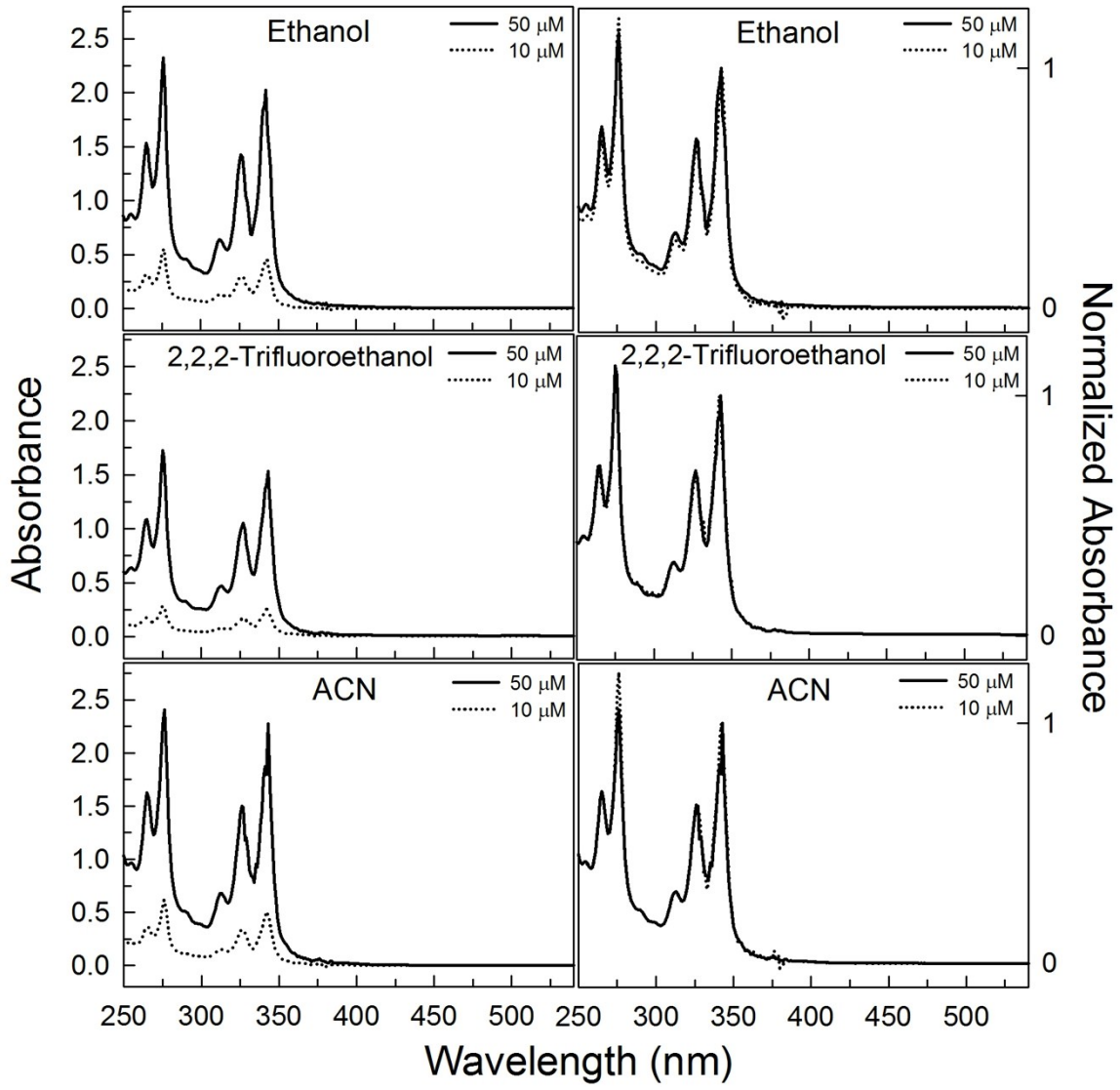



**Figure S2.** Absorbance spectra (left panels) of **1** at 10 μM and 50 μM, respectively, dissolved in ethanol (top panel), 2,2,2-trifluoroethanol (middle panel), and acetonitrile (lowest panel) at 25° C. Corresponding normalized absorbance spectra are presented in the right panels.

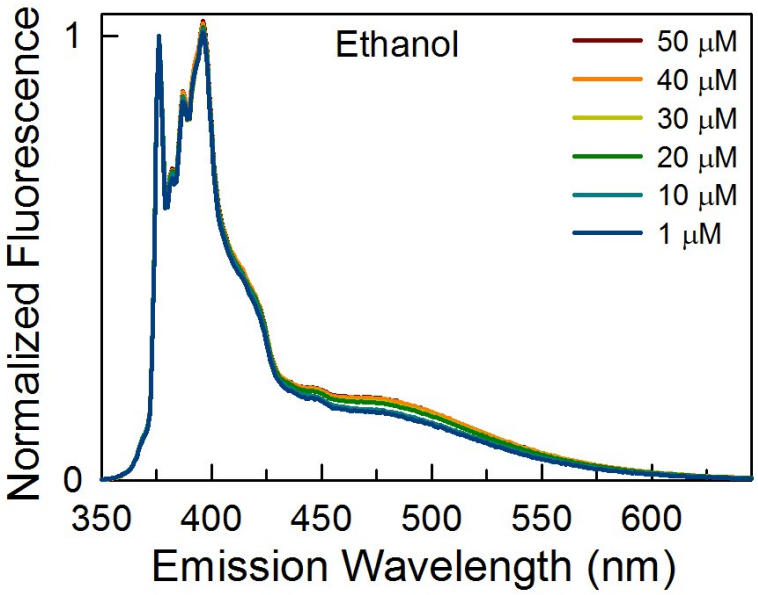



**Figure S3.** Normalized fluorescence emission spectra ($\lambda_{ex}$ = 340 nm) of **1** at different concentrations dissolved in ethanol at 25°C.

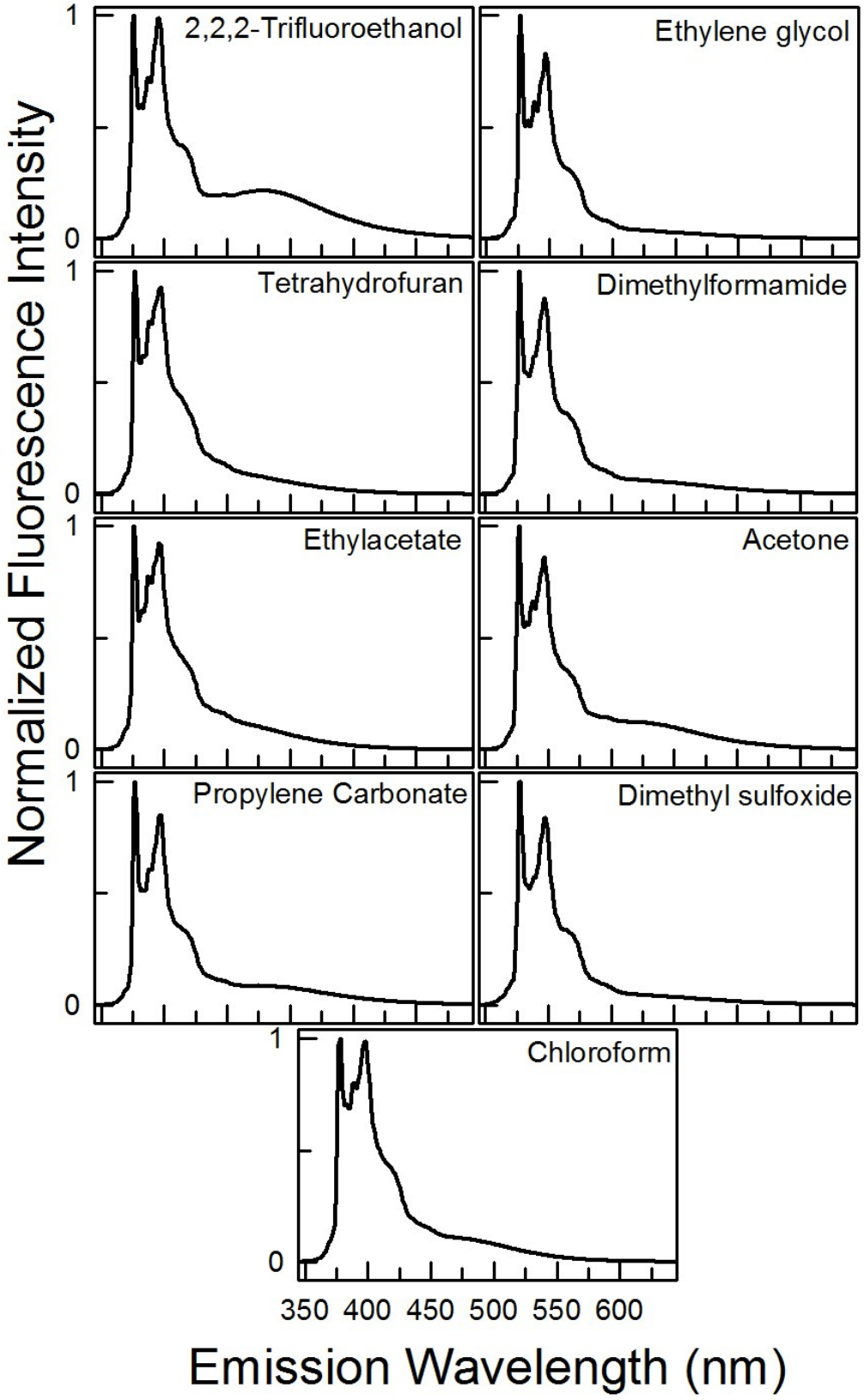



**Figure S4.** Normalized fluorescence emission spectra ($\lambda_{ex}$ = 340 nm) of **1** (10 μM) dissolved in various solvents at 25° C.

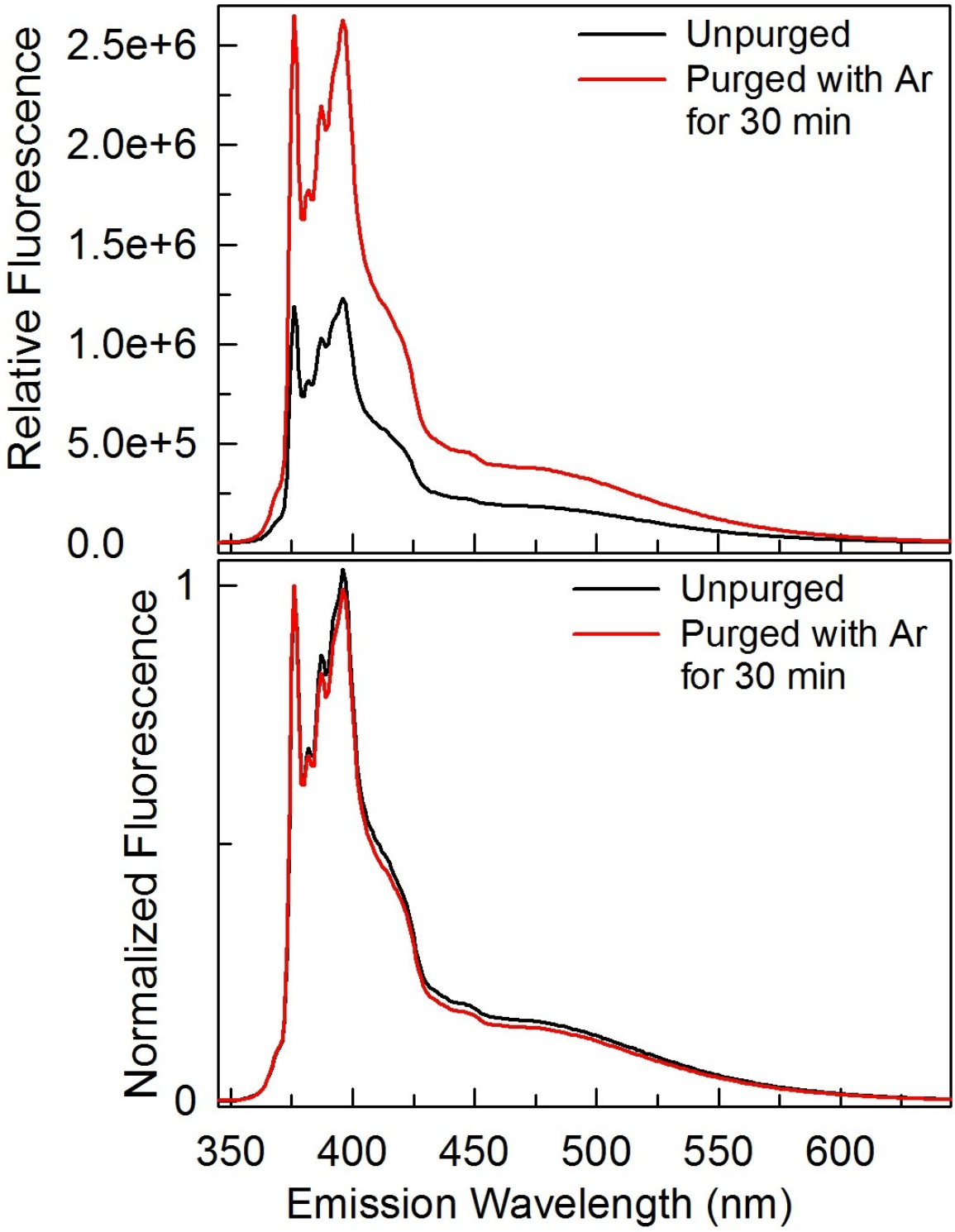



**Figure S5.** Relative and normalized fluorescence emission spectra ($\lambda_{ex}$ = 340 nm) of **1** (10 μM) dissolved in ethanol at 25° C.

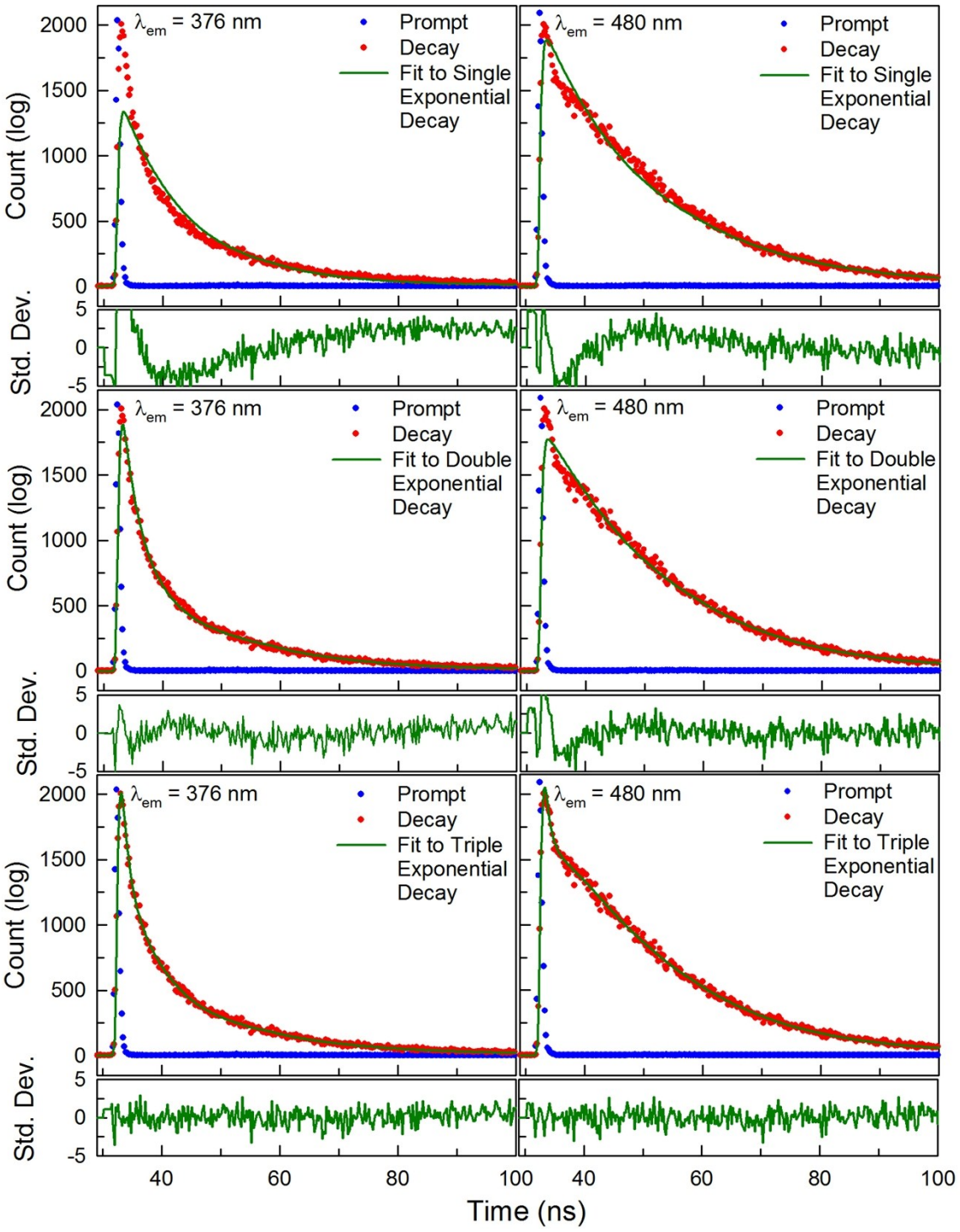



**Figure S6.** Fit of excited-state intensity decay data of **1** (10 μM) in ethanol at 25° C. Residuals are provided below each panel.

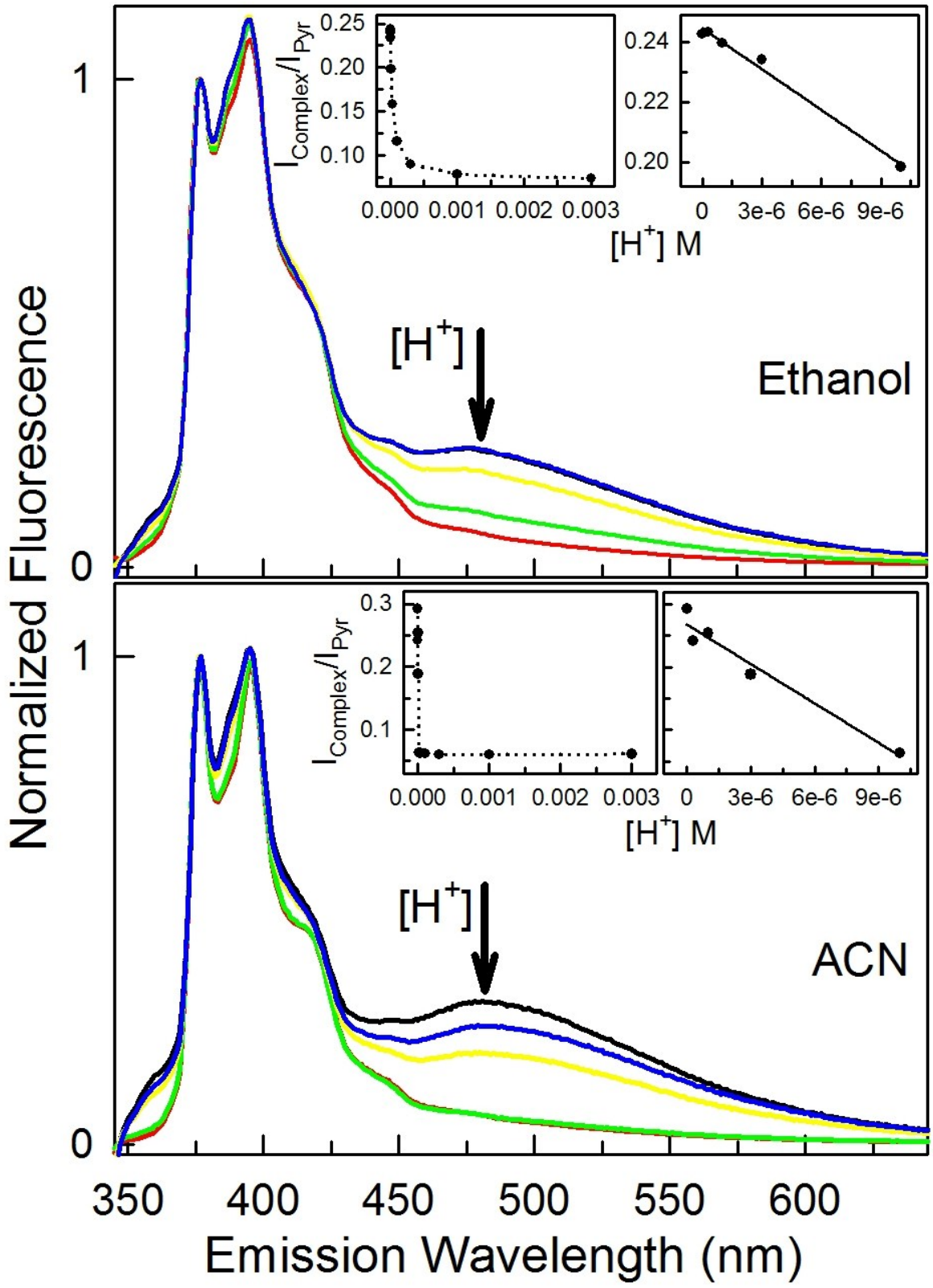



**Figure S7.** Normalized fluorescence emission spectra ($\lambda_{ex}$ = 340 nm) of **1** (10 μM) in the presence of varying [$H^+$] at 25° C. Corresponding $I_{complex}/I_{Pyr}$ as defined by $I_{475nm}/I_{376nm}$ versus [$H^+$] are provided in the insets.

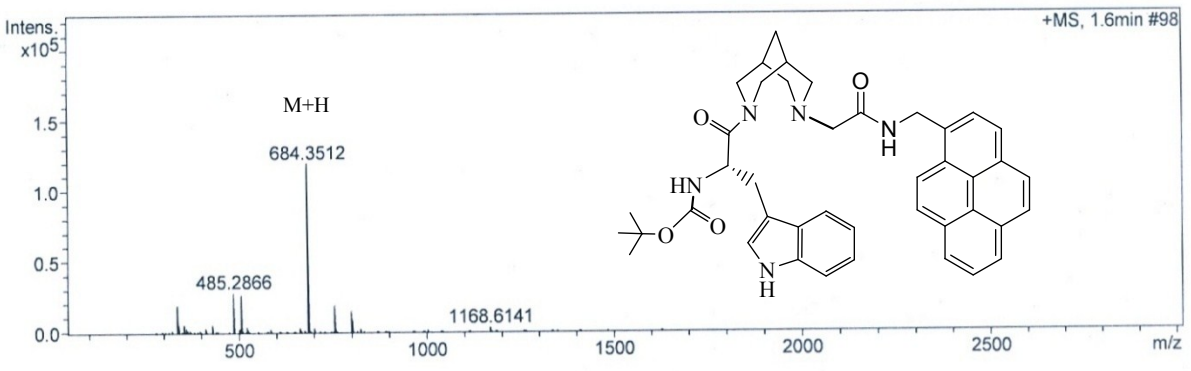



**Figure S8**: HRMS of compound **1** at pH 2.5 after keeping it overnight at room temperature.