*compounds*

MDPI

*Article*

# A Novel Quinoxaline-Rhodamine Conjugate for a Simple and Efficient Detection of Hydrogen Sulphate Ion

**Sutapa Sahu [1], Yeasin Sikdar [1], Riya Bag [1], Dilip K. Maiti [1], José P. Cerón-Carrasco [2,*] and Sanchita Goswami [1,*]**

[1] Department of Chemistry, University of Calcutta, 92, A.P.C. Road, Kolkata- 700009, India; sutapa.sahu11@gmail.com (S.S.); y.sikdar@gmail.com (Y.S.); riyabag.chem@gmail.com (R.B.); maitidk@yahoo.com (D.K.M.)

[2] Reconocimiento y Encapsulación Molecular, Universidad Católica San Antonio de Murcia (UCAM), 30107 Murcia, Spain

* Correspondence: jpceron@ucam.edu (J.P.C.-C.); sgchem@caluniv.ac.in (S.G.); Tel.: +34-968-278-819 (J.P.C.-C.); +91-033-2350-8386 (S.G.)

**Contents of the Supporting Information**

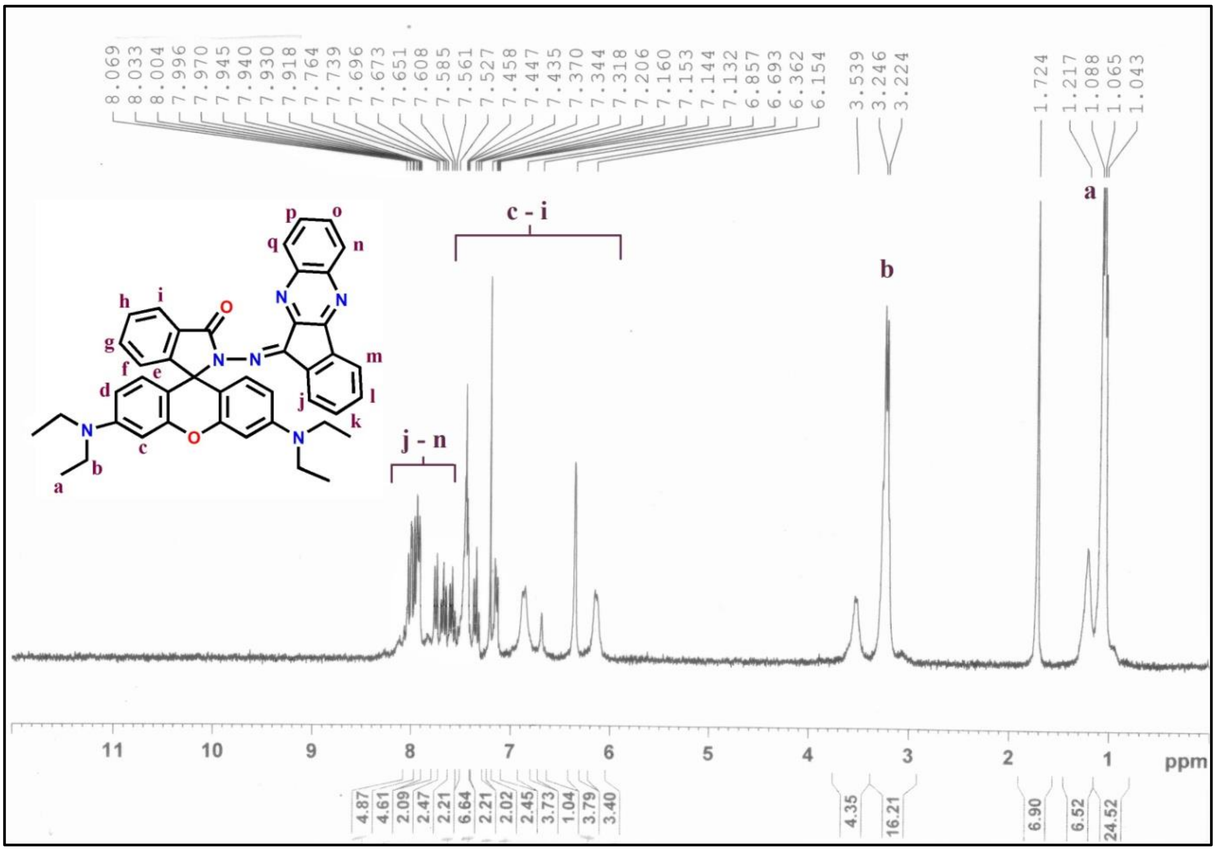


**Figure S1.** $^{1}H$ NMR spectrum of **QRH** in $CDCl_3$.

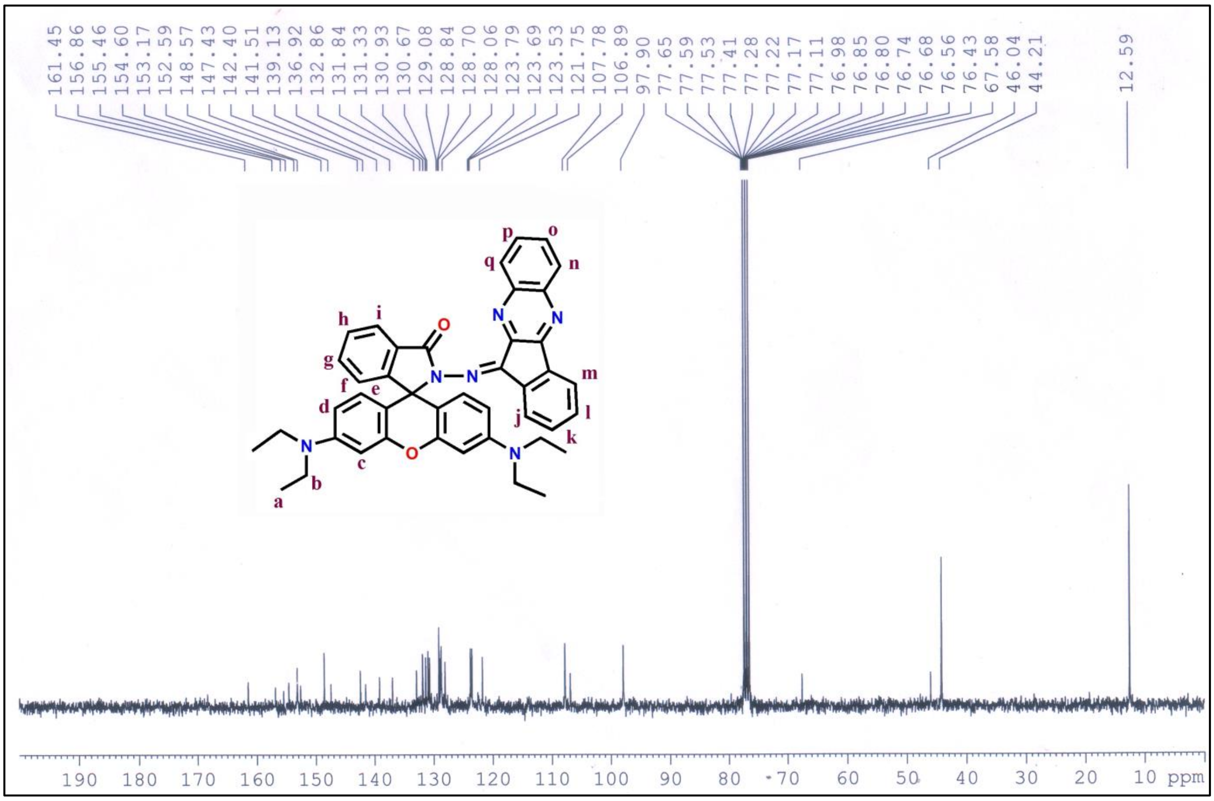


**Figure S2.** $^{13}C$ NMR spectrum of **QRH** in $CDCl_3$.

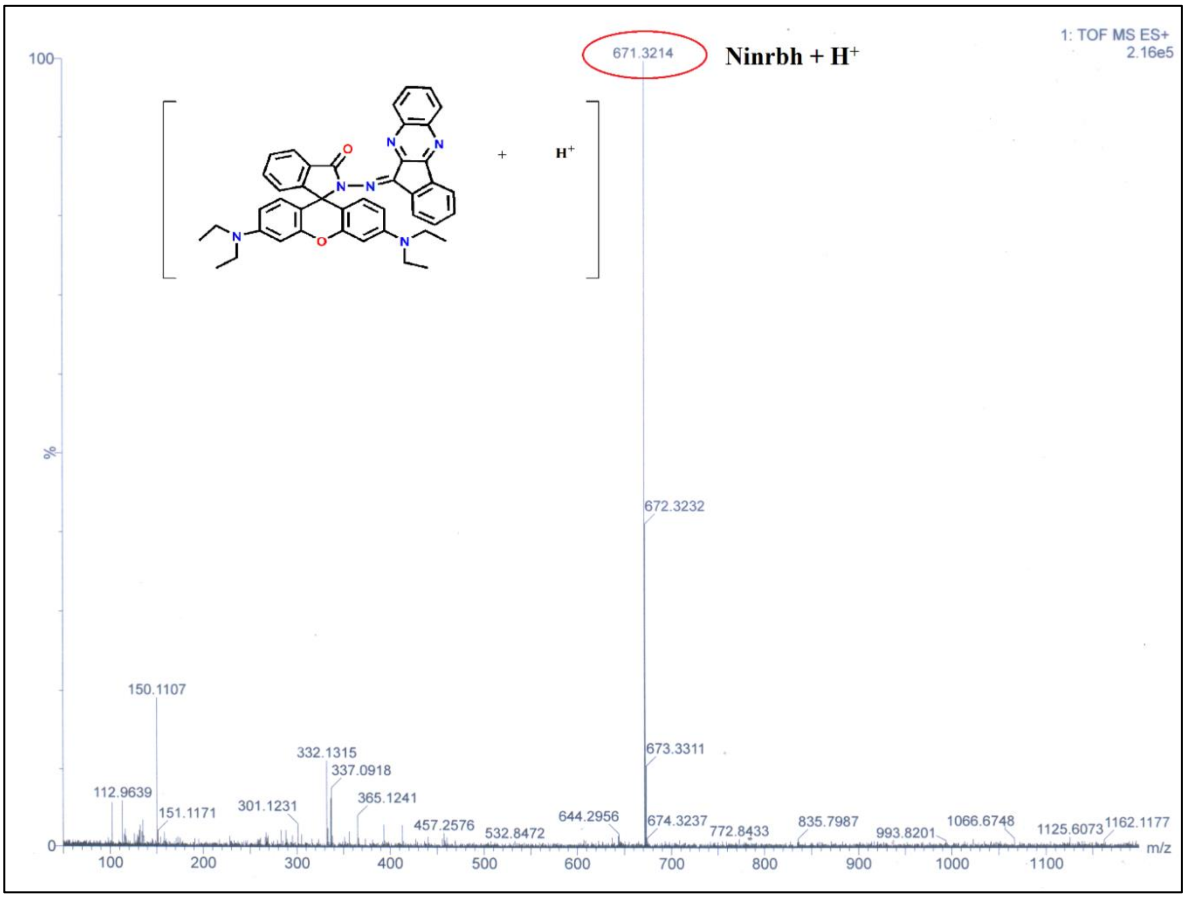



**Figure S3.** ESI–MS Spectrum of **QRH**.

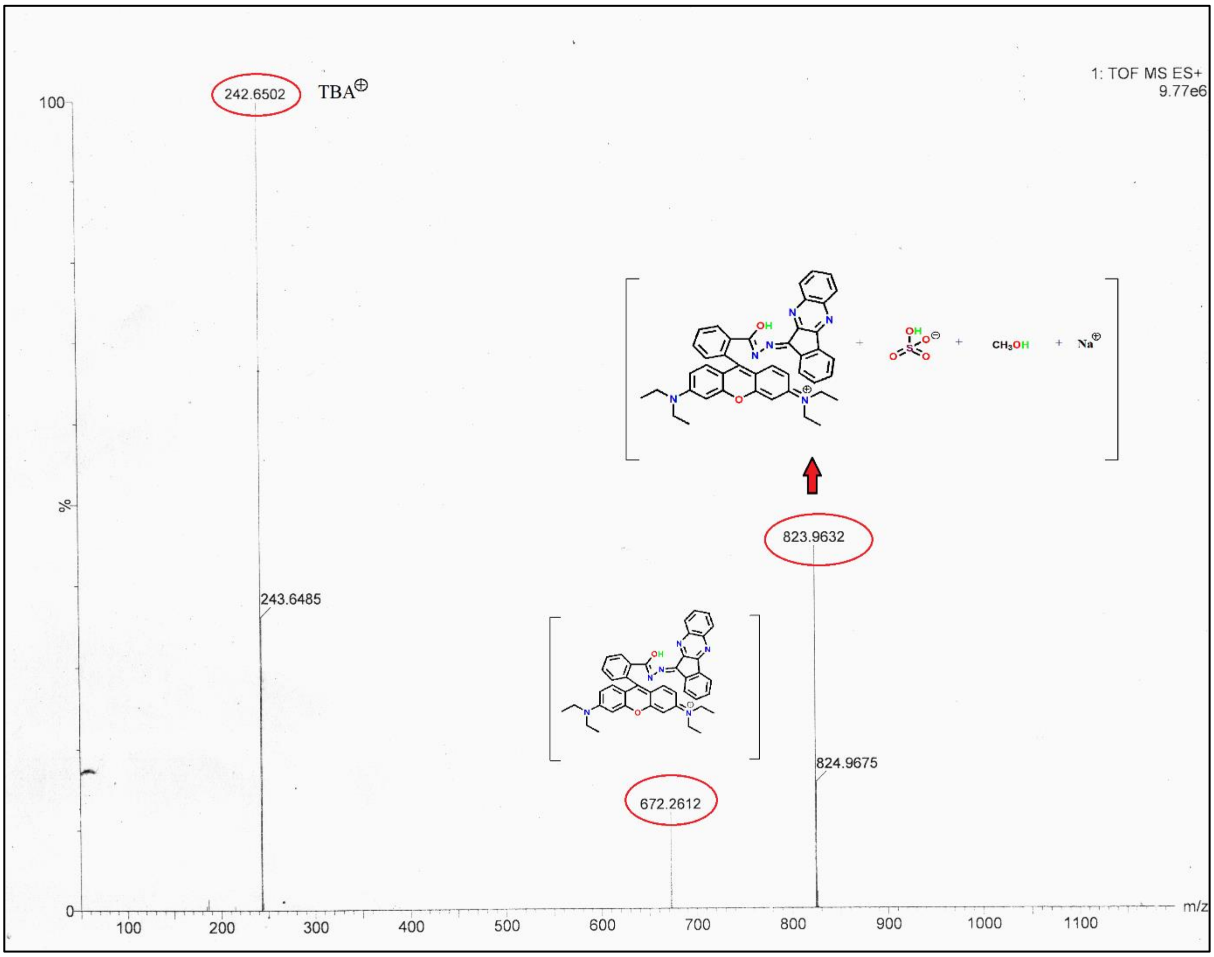



**Figure S4.** ESI–MS Spectrum of **QRH +** TBAHS. (TBA+: Tetrabutyl ammonium ion).

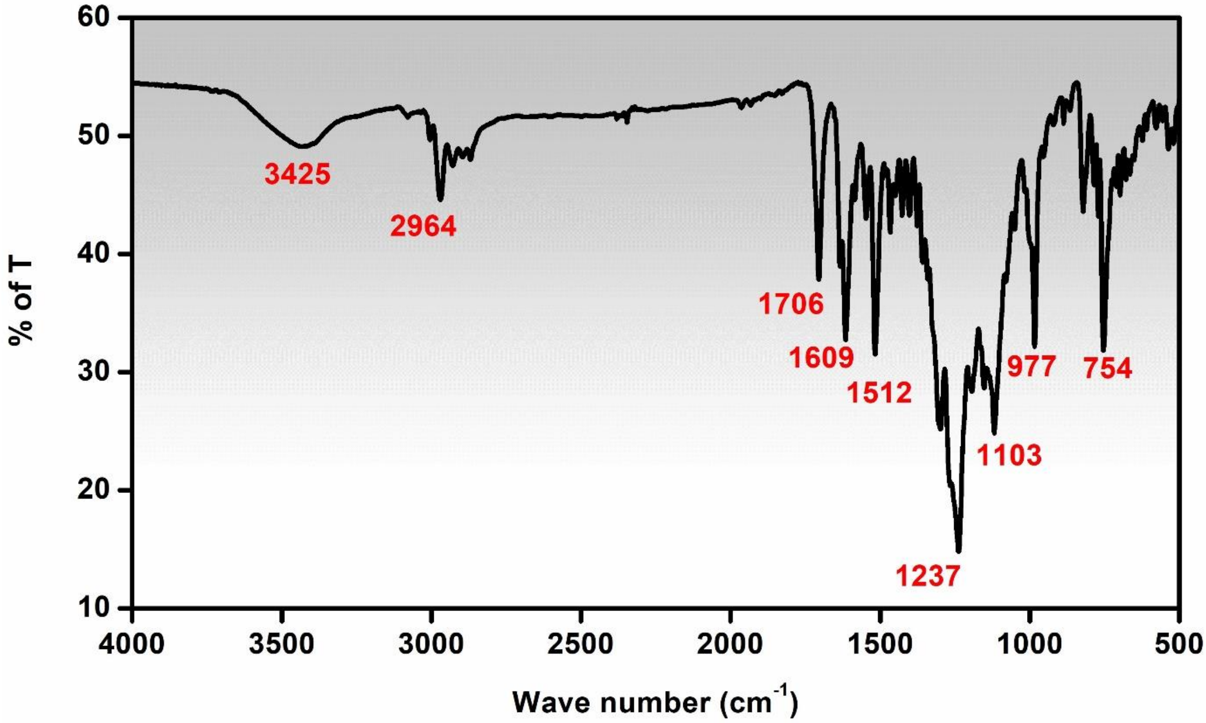



**Figure S5.** FT–IR Spectrum of **QRH**.

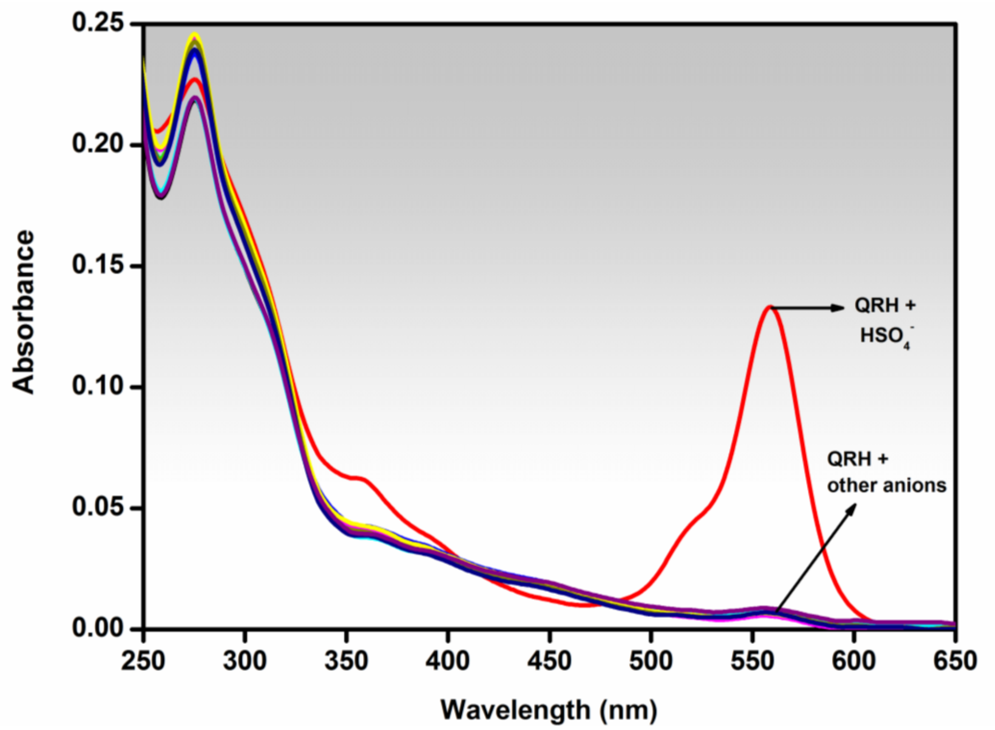



**Figure S6.** Absorbance spectra of **QRH** ($10^{-6}$ M) in presence of 20 equiv. of various anions ($F^-$, $OAc^-$, $Cl^-$, $Br^-$,$I^-$,$ClO_4^-$, $HSO_4^-$, $PF_6^-$, $SCN^-$) in methanol.

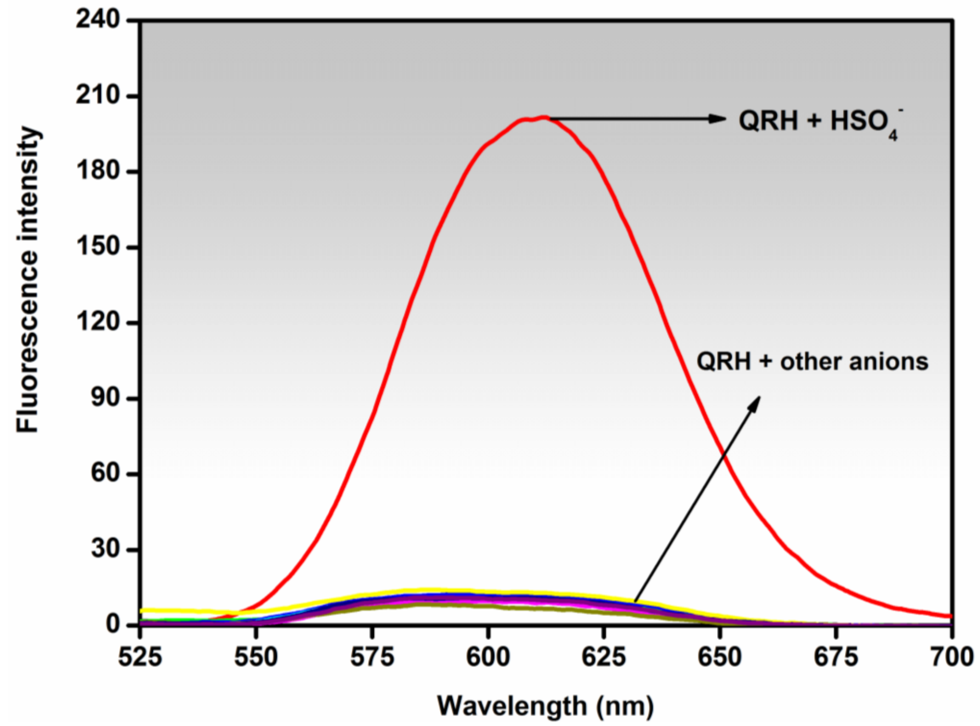



**Figure S7.** Emission spectra of **QRH** ($10^{-5}$ M) in presence of 6 equiv. of various anions ($F^-$, $OAc^-$, $Cl^-$, $Br^-$,$I^-$,$ClO_4^-$, $HSO_4^-$, $PF_6^-$, $SCN^-$) in methanol.

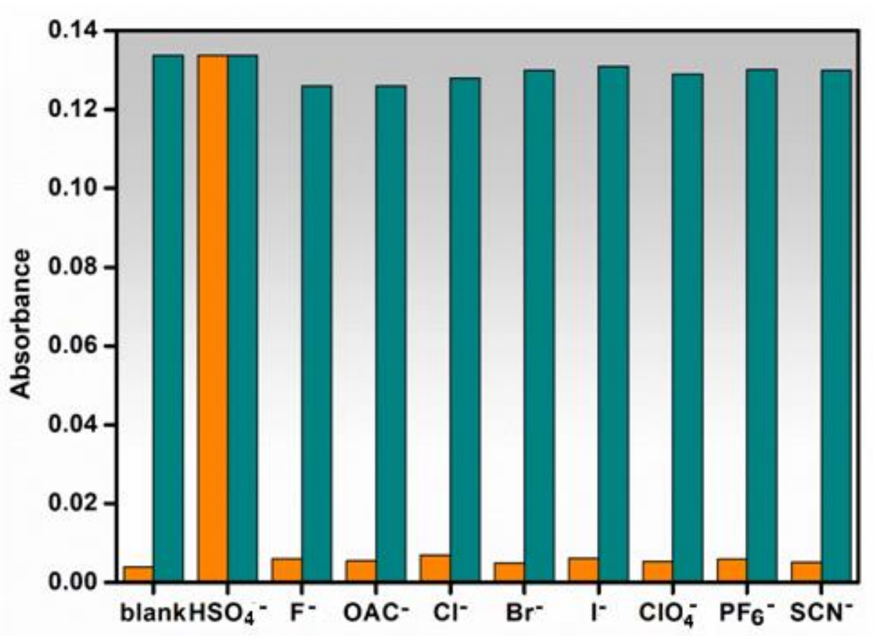



**Figure S8.** Absorption intensity of **QRH** ($10^{-6}$ M) in the presence of 20 equiv. of different anion in absence of same equiv. of TBAHS in solution [the orange bar portion]. Absorption intensity of a mixture of **QRH** ($10^{-6}$ M) with 20 equiv. of other anions followed by addition of 20 equiv. of $HSO_4^-$, to the solution ($\lambda_{abs}$ = 558 nm) [the green bar portion].

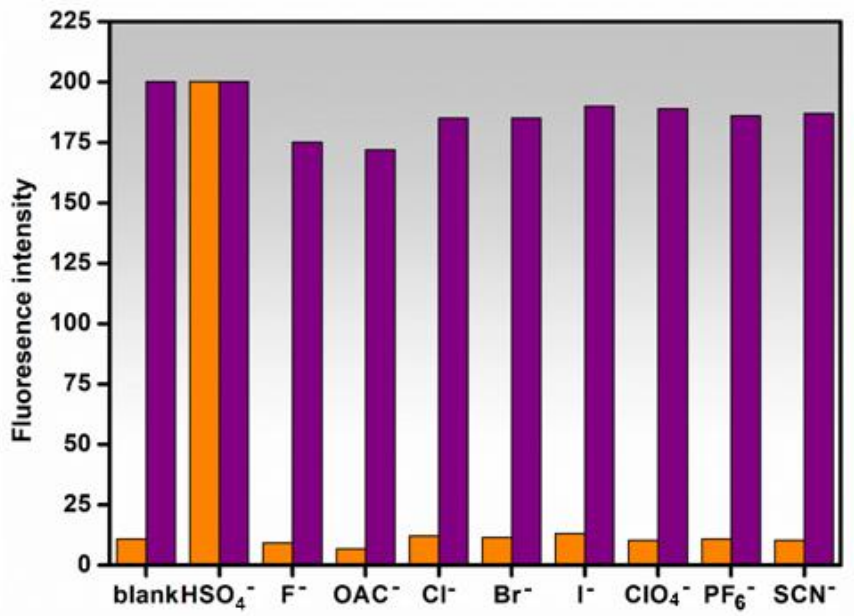



**Figure S9.** Emission intensity of **QRH** ($10^{-5}$ M) in the presence of 6 equiv. of different anion in absence of same equiv. of TBAHS in solution [the orange bar portion]. Emission intensity of a mixture of **QRH** ($10^{-5}$ M) with 6 equiv. of other anions followed by addition of 6 equiv. of $HSO_4^-$ to the solution ($\lambda_{ex}$ = 357 nm,$\lambda_{em}$ = 609 nm) [the purple bar portion].

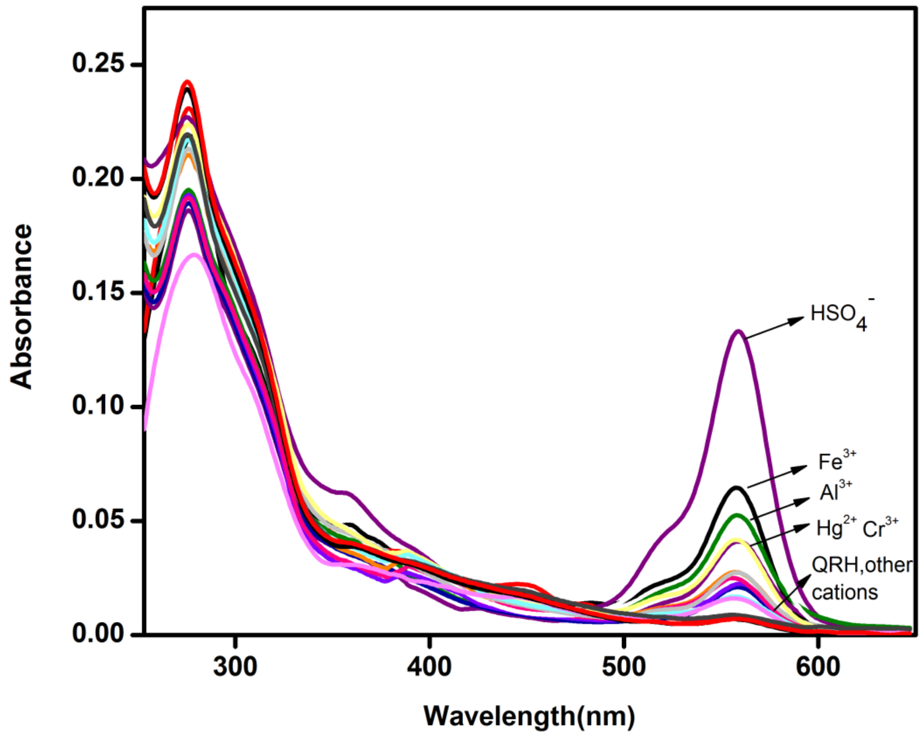



**Figure S10.** Absorbance spectra of **QRH** ($10^{-6}$ M) in presence of various cations versus $HSO_4^-$ in methanol.

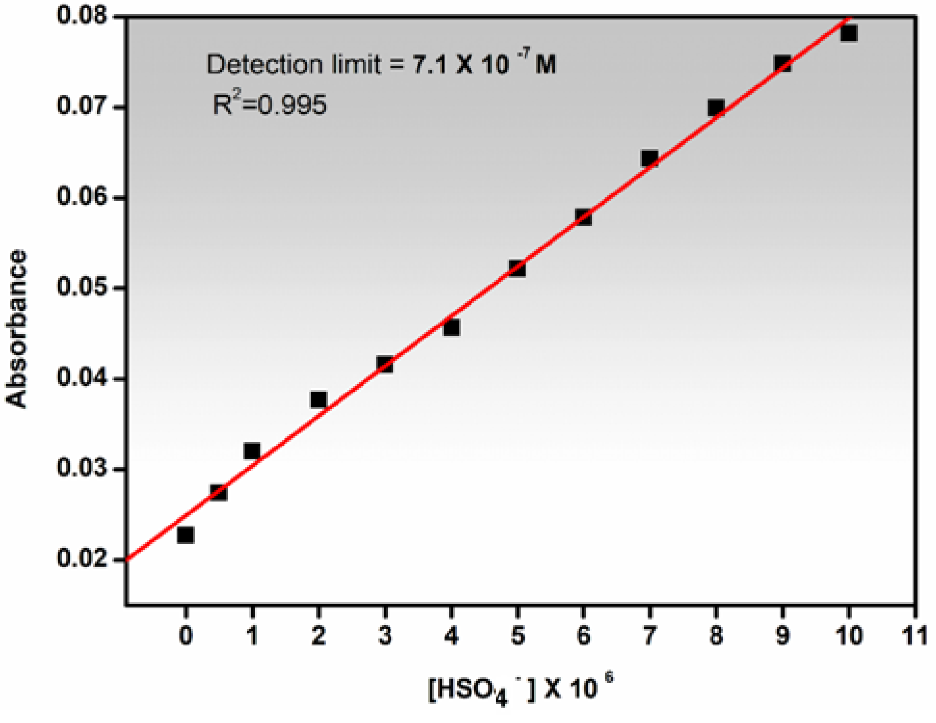



**Figure S11.** Determination of the detection limit for absorption of $HSO_4^-$ in methanol at 558 nm.

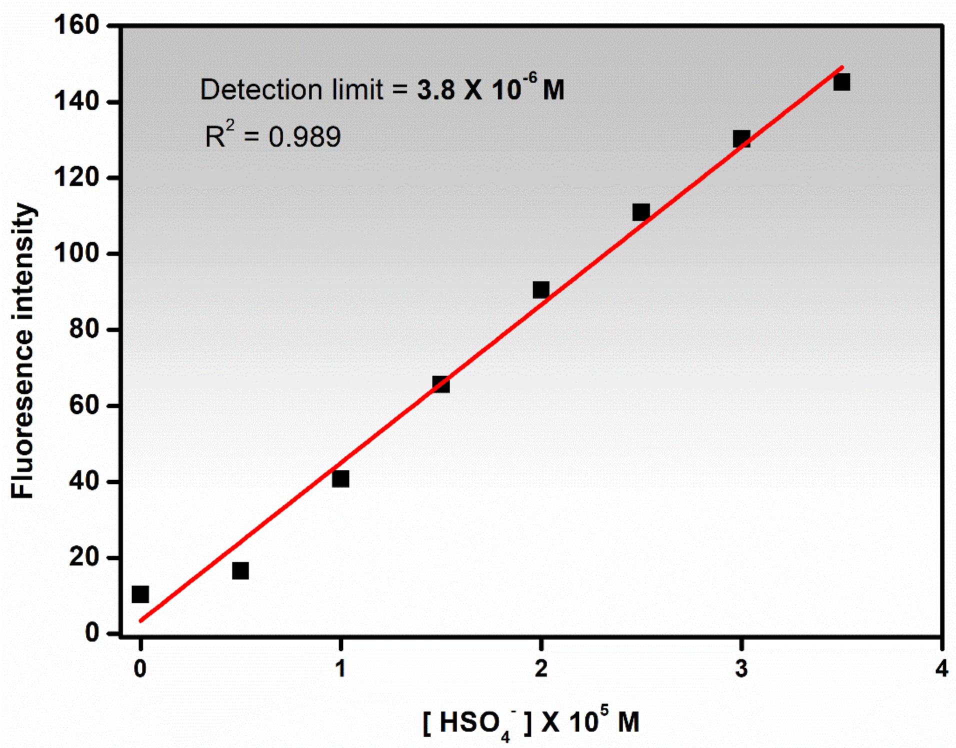



**Figure S12.** Determination of the detection limit for emission of $HSO_4^-$ in methanol at 609 nm.

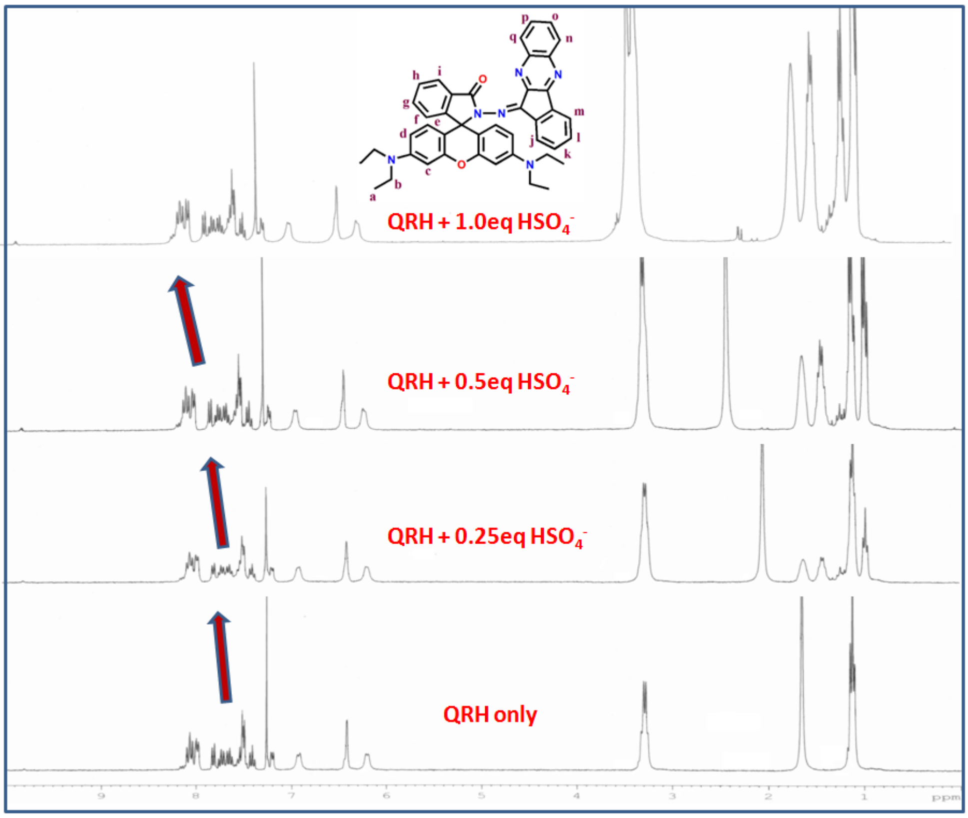



**Figure S13.** [1]H NMR titration of **QRH** in presence of TBAHS(Tetrabutyl ammonium hydrogen sulphate) in $CDCl_3$.

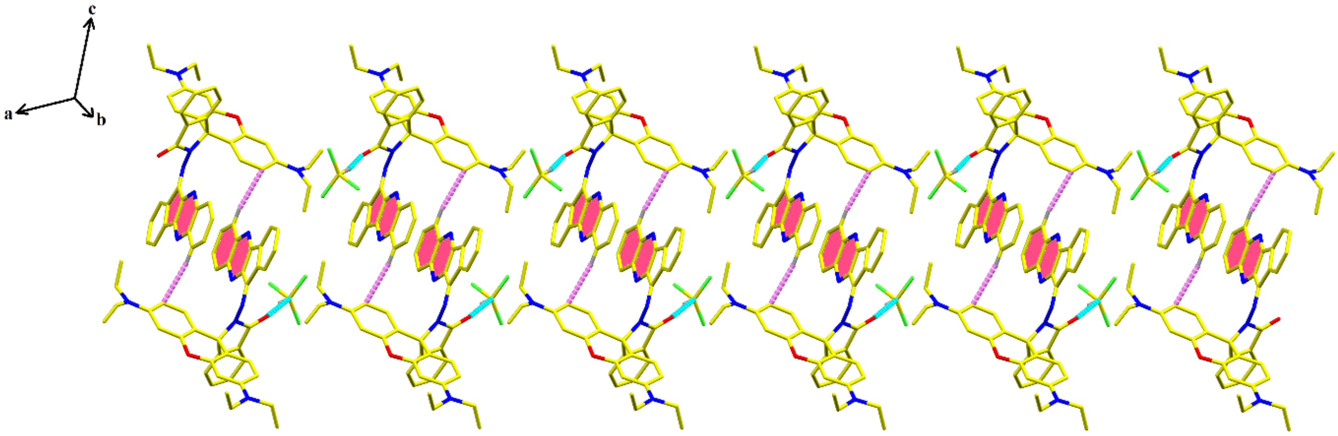
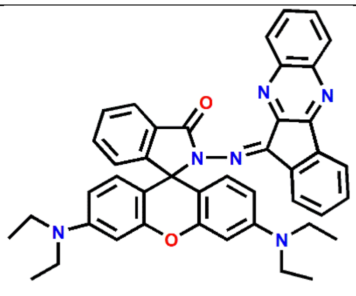
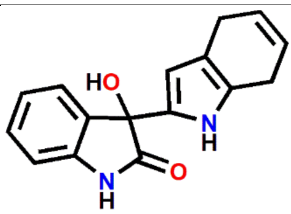
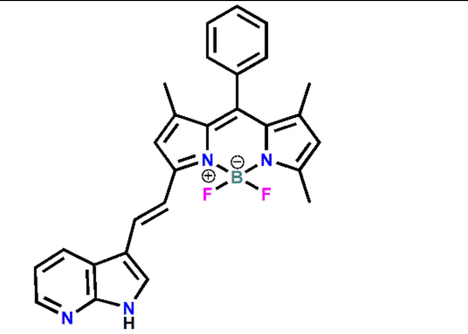
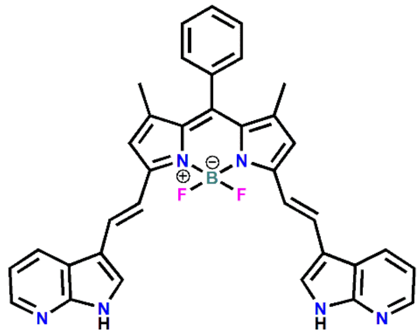
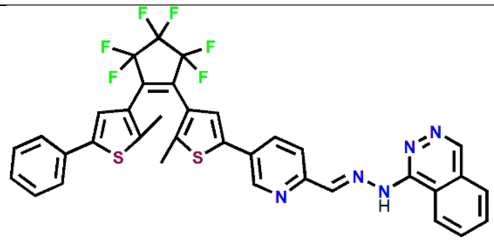
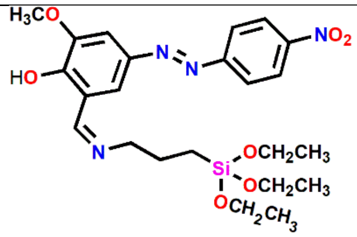
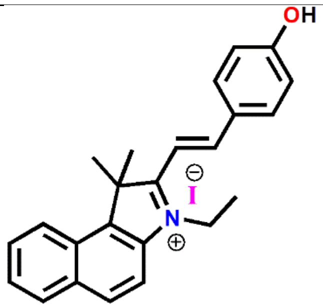



**Figure S14.** The supramolecular 2D packing diagram of the **QRH** showing the stacking interaction and C–H···π interaction.

**Table S1.** $HSO_4^-$ sensing receptors found in the literature.

| Ligand Structure | Solvent | Detection limit | | Reference |
|---|---|---|---|---|
| | | **Absorption** | **Emission** | |
|  | $CH_3OH$ | 0.71 μM | 3.8 μM | This work |
|  | $CH_3CN/H_2O$ (v/v : 7/3) | 9.2 μM | 8.9 μM | [1] |

| | | | | |
|---|---|---|---|---|
|  | $CH_3CN$ | – | 75.6 μM | [2] |
|  | | – | 44.2 μM | |
|  | THF | – | 13 μM | [3] |
|  | Solid phase | – | – | [4] |
|  | EtOH/$H_2O$ (v/v: 8/2) | – | 1.39 nM | [5] |

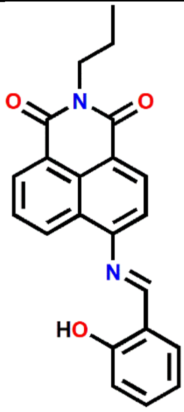
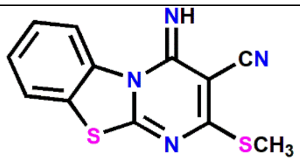
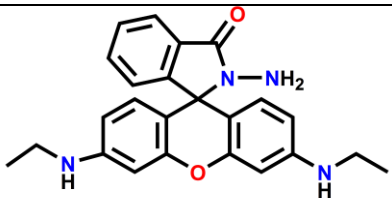
| | | | | |
|---|---|---|---|---|
|  | $CH_3OH$ | 2 μM | 0.05 μM | [6] |
|  | $CH_3CN/H_2O$ (v/v: 1/2) | 0.16 μM | – | [7] |
|  | $CH_3OH$ | 16.70 μM | 3.72 μM | [8] |

**Table S2.** The crystallographic data for **QRH**.

| CCDC No | 1957625 |
|---|---|
| Chem. Formula | C44 H39 Cl3 N6 O2 |
| Formula weight | 790.16 |
| Crystal color, habit | red, rectangular |
| Temp (K) | 296 |
| $\lambda^a$/ Å | 0.71073 |
| Crystal system | Triclinic |
| Space group | *P –1* |
| Unit cell dimensions | |
| *a* (Å) | 11.567(4) |
| *b*(Å) | 11.953(4) |
| *c*(Å) | 16.207(9) |
| *α*(deg) | 102.192(7) |
| *β* (deg) | 106.219(7) |
| *γ* (deg) | 103.127(5) |
| Volume (Å$^3$), Z | 2003.1(15) |
| Density (mg m$^{-3}$) | 1.310 |
| AbsorptionCoeff(mm$^{-1}$) | 0.274 |
| F(000) | 824 |
| Crystal size (mm) | 0.24 × 0.20 × 0.16 |
| θ range (deg) | 1.4–25.0 |
| | $-13 \le h \le 13$ |
| Limiting indices | $-13 \le k \le 14$ |
| | $-19 \le l \le 19$ |

| | |
|---|---|
| Reflections collected | 13887 |
| Unique reflections [$R_{int}$] | 6885 (0.099) |
| Completeness to θ | 97.4%(25.0) |
| Data/restraints/parameters | 6885/2/518 |
| GOOF on $F^2$ | 0.934 |
| $R_1^a$, $wR_2^b$values [I > 2σ(I)] | 0.0750, 0.1982 |
| $R_1^a$,$wR_2^b$ values (all data) | 0.1467, 0.2417 |
| Maximum, minimum residual peaks (e·Å$^{-3}$) | 0.402–0.335 |

[a]Graphitemonochromator [b]$R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [c]$wR_2 = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2]/\Sigma[w(|F_o|^2)^2]\}^{1/2}$

## References

1. Bayindir, S.; Lafzi, F. A simple oxindole-based colorimetric $HSO_4^-$ sensor: Naked-eye detection and spectroscopic analysis. *J. Photochem. Photobiol. A Chem.* 2**019**, *376*, 146–154.
2. Keşan, G.; Topaloğlu, B.; Özcan, E.; Kazan, H.H.; Eçik, E.T.; Şenkuytu, E.; Sengul, I.F.; Kandemir, H.; Çoşut, B. Azaindole-BODIPYs: Synthesis, fluorescent recognition of hydrogen sulfate anion and biological evaluation. *Spectrochim. Acta A Mol. Biomol. Spectrosc*. **2019**, *213*, 73–82.
3. Cui, S.; Qiu, S.; Lu, R.; Pu, S. A multi-functional fluorescent sensor for $Zn^{2+}$ and $HSO_4^-$ based on a new diarylethene derivative. *Tetrahedron Lett.* **2018**, *59*, 3365−3372.
4. Hezaveh, S.M.; Khanmohammadi, H.; Zendehdel, M. Rapid detection of $HSO_4^-$ in water: Novel immobilized azo-azomethine colorimetric anion receptors on solid supports. *Spectrochim. Acta A Mol. Biomol. Spectrosc.* **2018**, *199*, 21−31.
5. Yu, T.; Yin, G.; Niu, T.; Yin, P.; Li, H.; Zhang, Y.; Chen, H.; Zeng, Y.; Yao, S. A novel colorimetric and fluorescent probe for simultaneous detection of $SO_3^{2-}$/$HSO_3^-$ and $HSO_4^-$ by different emission channels and its bioimaging in living cells. *Talanta* **2018**, *176*, 1–7.
6. Goel, R.; Sharma, S.; Paul, K.; Luxami, V. Naphthalimide based chromofluorescent sensor and DNA intercalator: Triggered by $Hg^{2+}$/$HSO_4^-$ cleavage reaction. *Sens. Actuator B Chem.* **2017**, *246*, 776–782.
7. Padghan, S.D.; Bhosale, R.S.; Ghule, N.V.; Puyad, A.L.; Bhosale, S.V. Hydrogen sulfate ion sensing in aqueous media based on a fused pyrimido benzothiazole derivative. *RSC Adv.* **2016**, *6*, 34376–34380.
8. Upadhyay, Y.; Bothra, S.; Kumar, R.; Choi, H.; Sahoo, S.K. Optical sensing of hydrogen sulphate using rhodamine 6G hydrazide from aqueous medium. *Spectrochim. Acta A Mol. Biomol. Spectrosc.* **2017**, *180*, 44–50.