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A Pyrenesulfonyl imidazolium derivative as selective cyanide ion sensor in aqueous media

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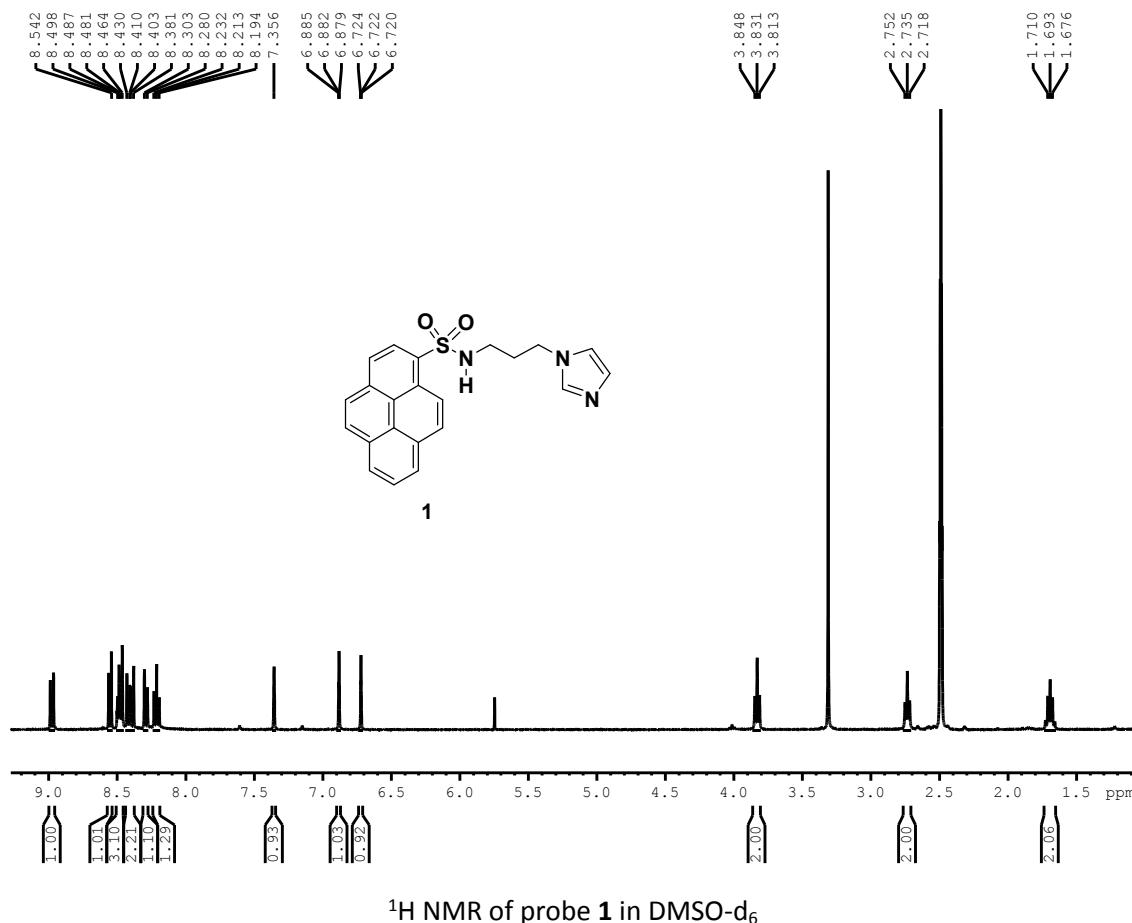
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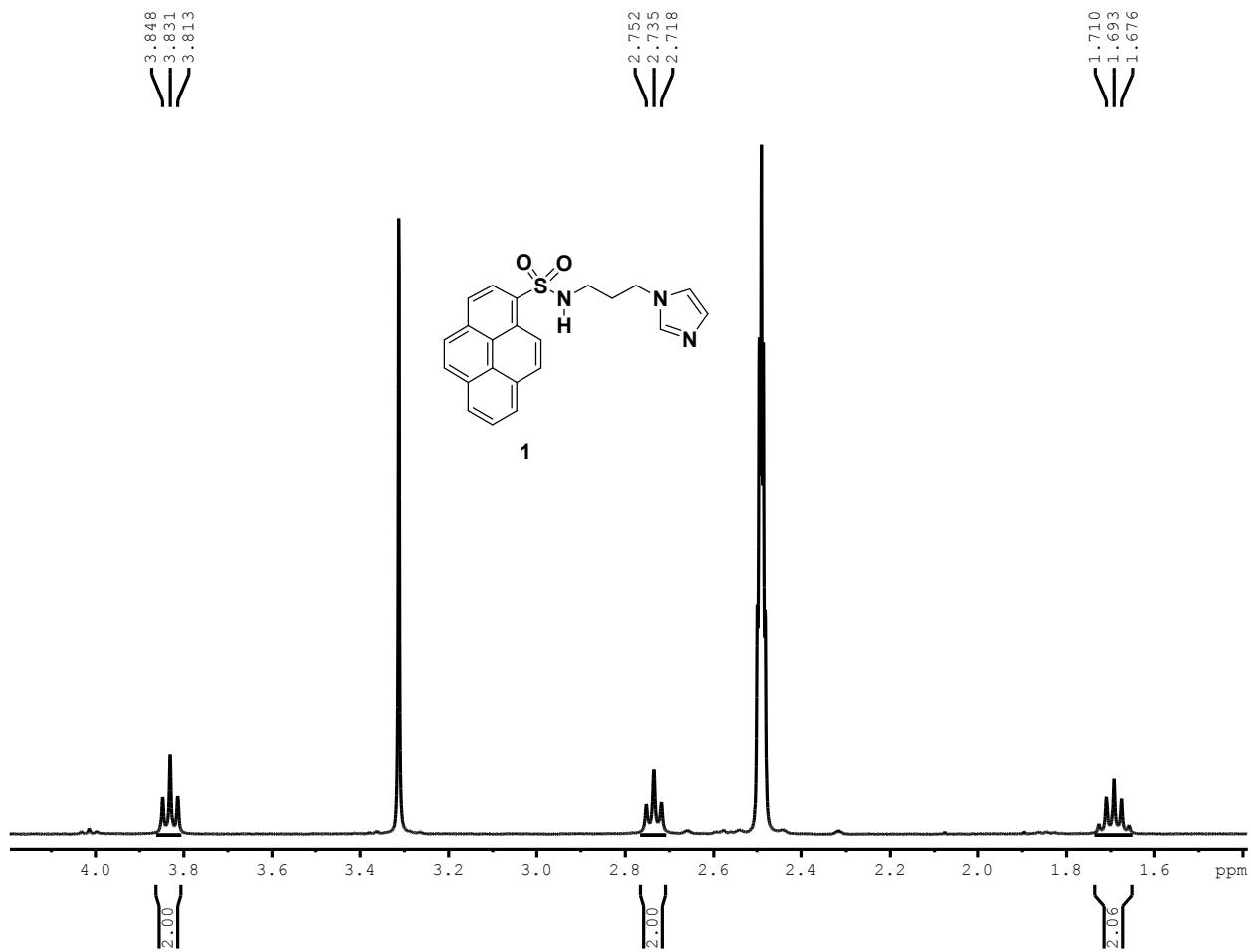
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complex and their energy differences."

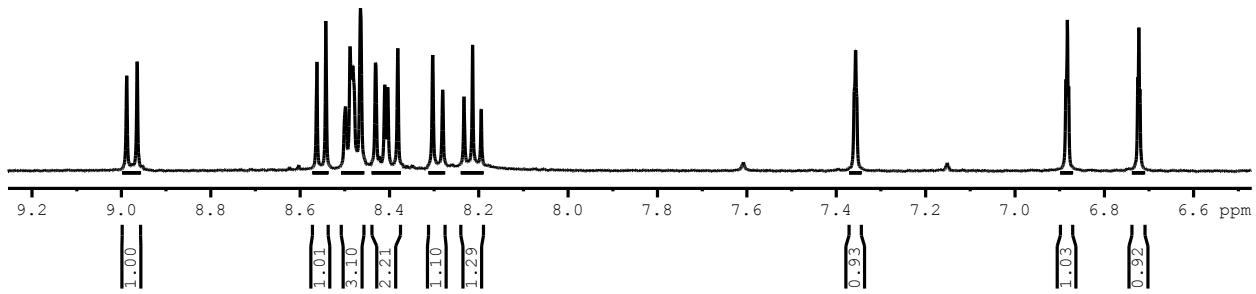
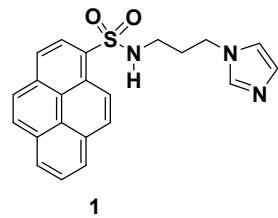
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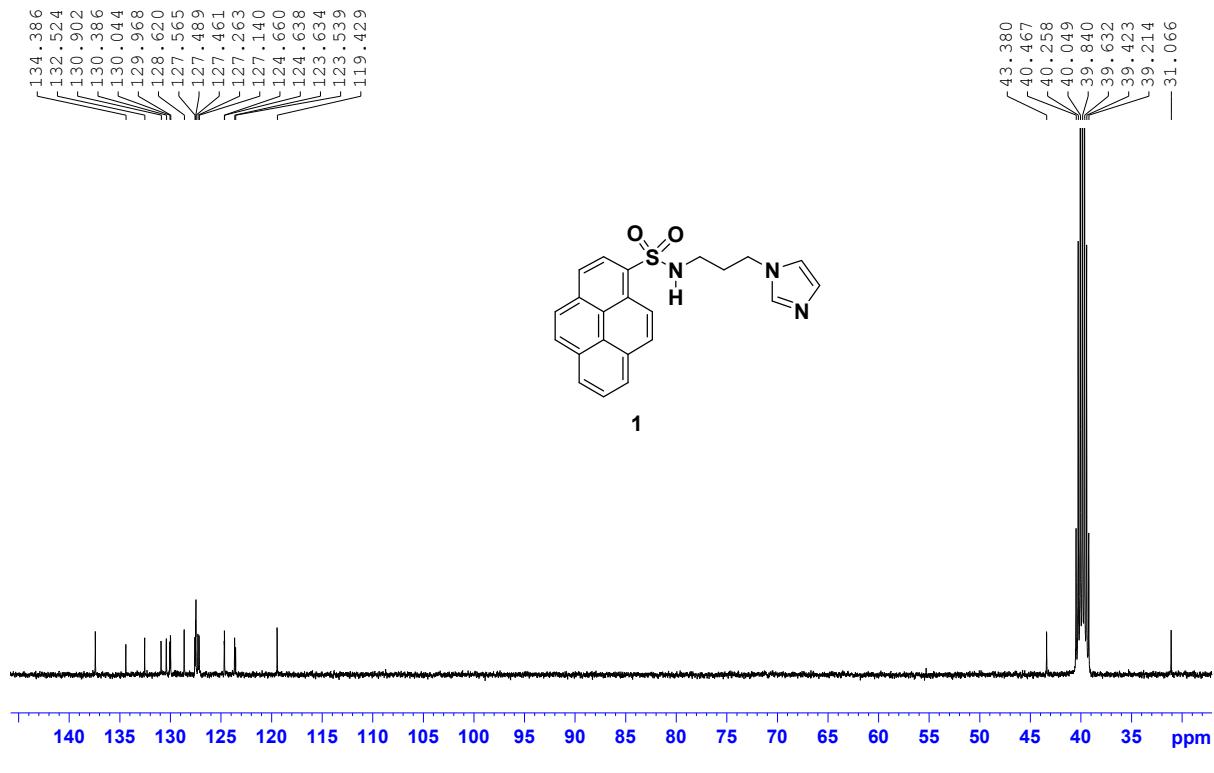




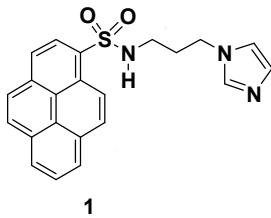
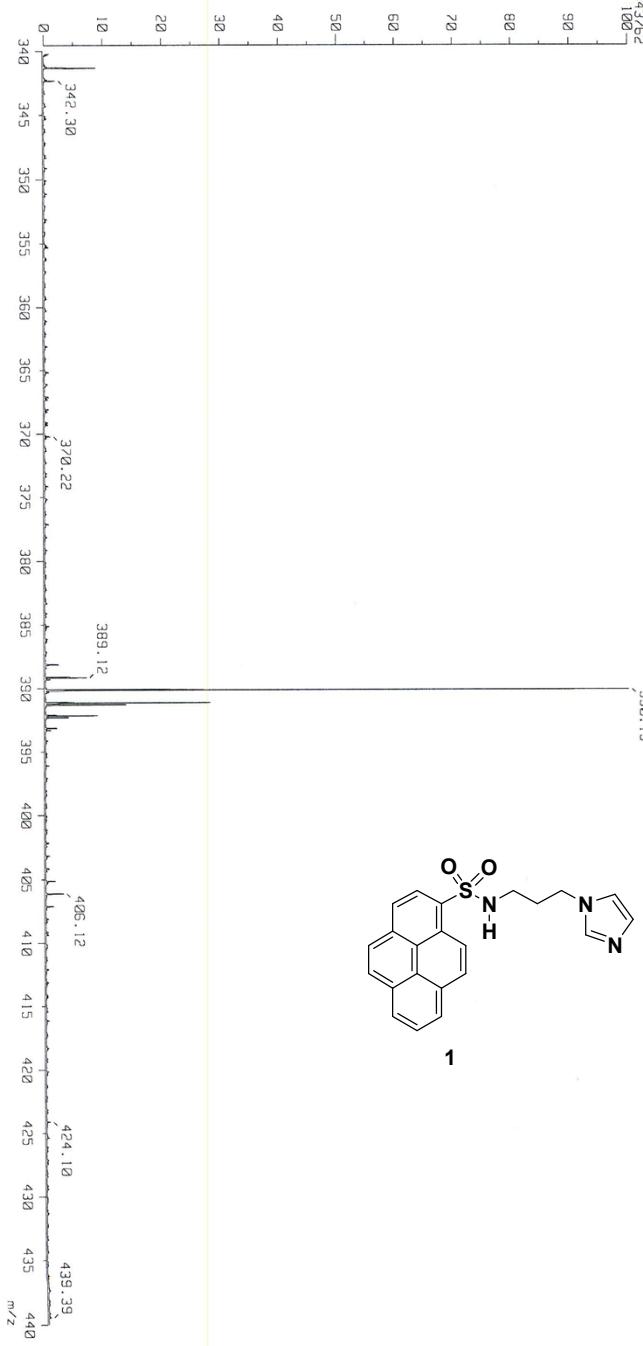
^1H NMR of probe **1** aliphatic region in DMSO-d_6



^1H NMR of probe **1** aromatic region in DMSO-d_6



[Mass Spectrum]
 Data : FR-2-C22H19N3O2S
 Sample : -
 Note : -
 Inlet : Direct
 Spectrum Type : Normal Ion [F⁻-, rear]
 RT : 0.28 min Scan# : (5,7)
 BP : m/z 390.1273 Int. : 40.23
 Output m/z range : 340.0000 to 440.0000
 Cut Level : 0.00 %

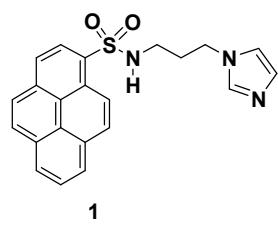


HRMS of probe **1**

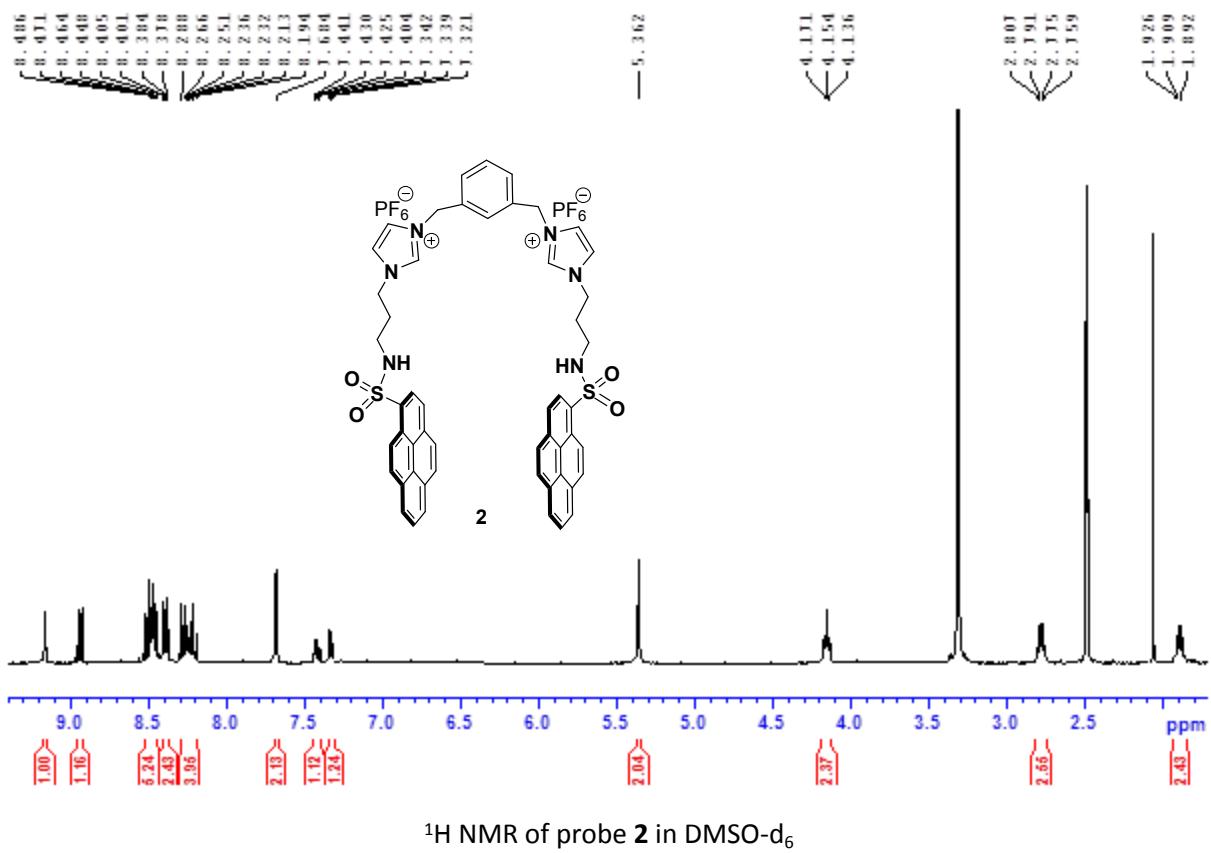
[Mass Spectrum]
 Data : RK-2-C2H19N3O2S
 Sample : -
 Note : -
 Inlet : Direct Ion [E-Linear]
 Spectrum type : Normal Scan# : (6,)
 RT : 0.28 min Int. : 40.23
 BP : m/z 390.1223 Cut Level : 0.00 %
 Output m/z range : 382.4332 to 399.0504
 880525

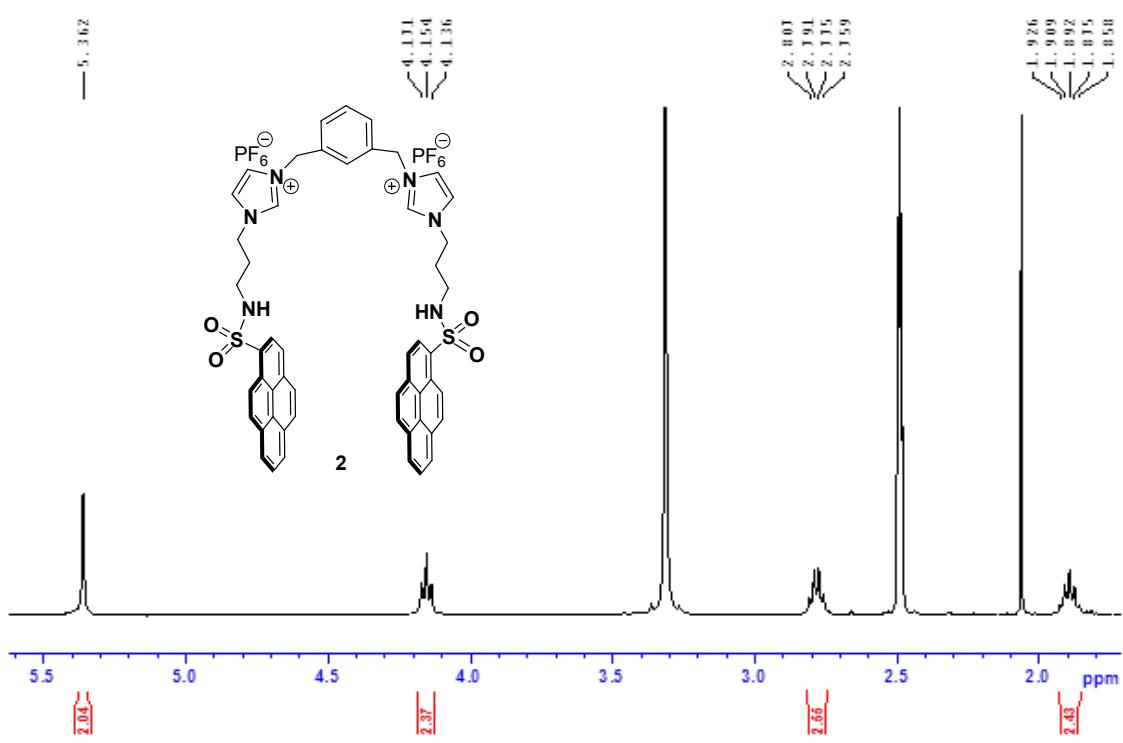
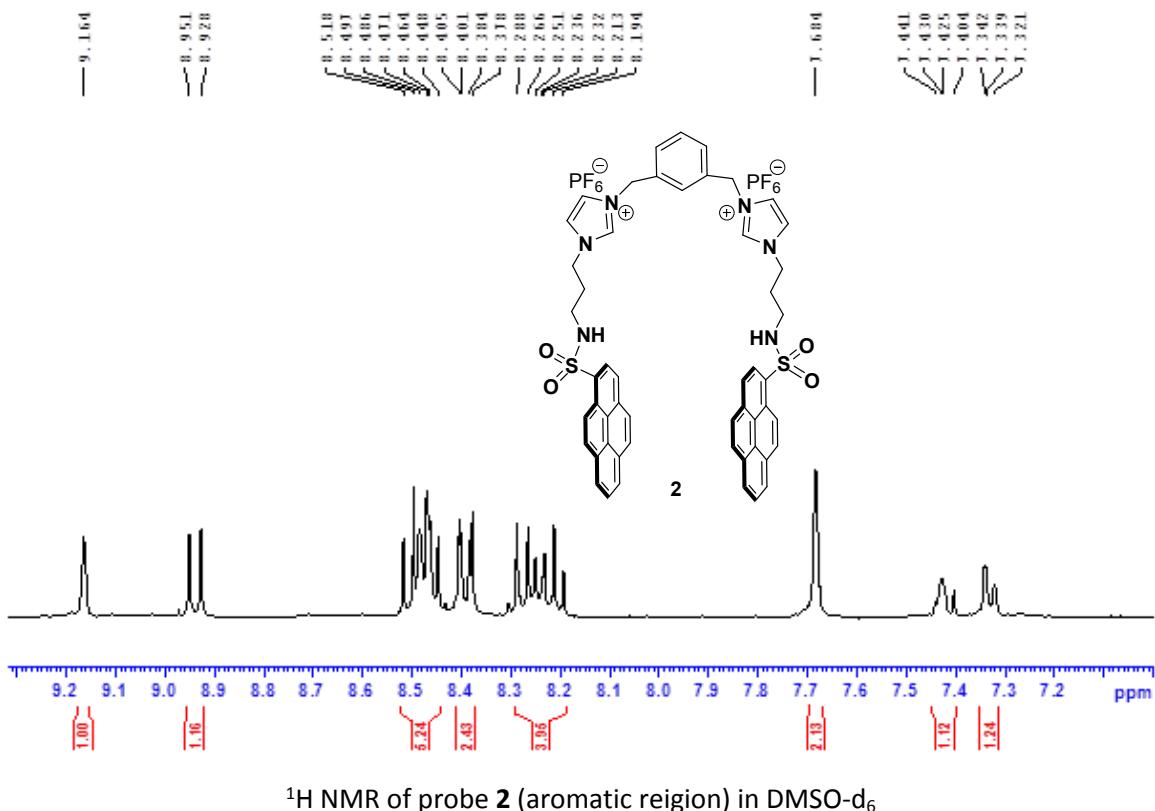


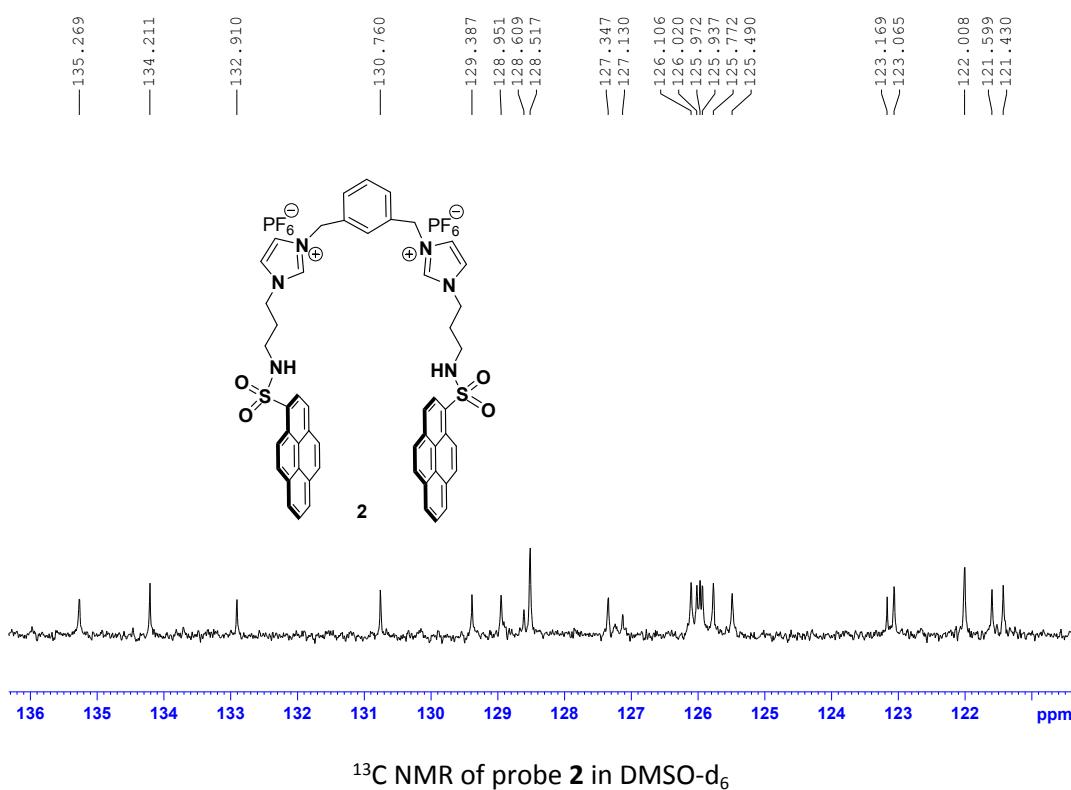
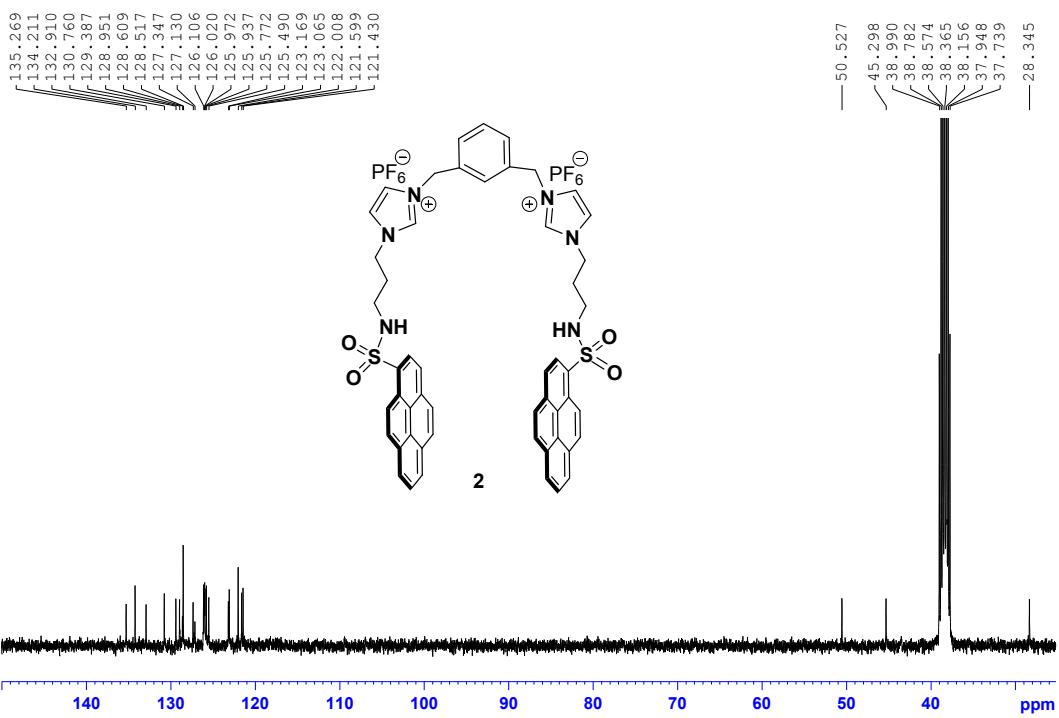
Date : 17-Mar-2014 14:37
 Ion Mode : FAB+
 Scan# : (6,)
 Int. : 40.23
 Cut Level : 0.00 %

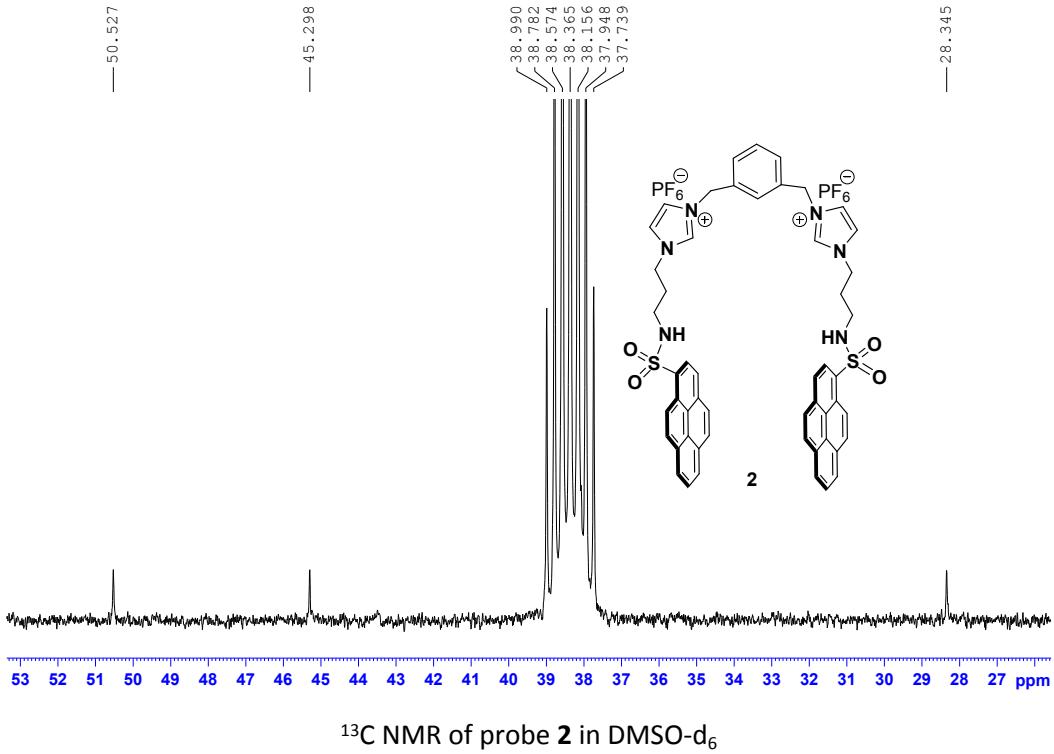


HRMS of probe 1

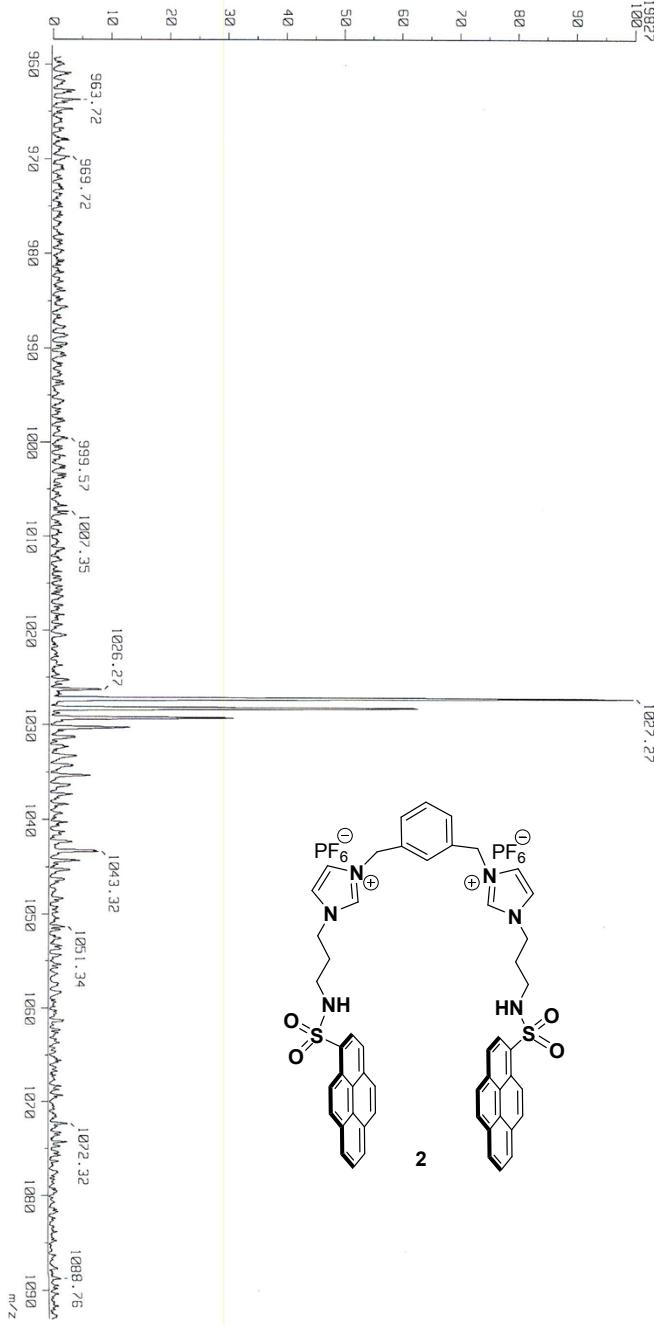








[Mass Spectrum]
 Data : RK-DSX-52H46T12NS04P2S2
 Sample : -
 Note : -
 Inlet : Direct
 Spectrum Type : Normal Ion [E/I-linear]
 RT : 0.63 min Scan# : (13,14)
 BP : m/z 1027.2667 Int. : 29.56
 Output m/z range : 958.0000 to 1093.0000 Cut Level : 0.00 %
 619827
 1027.27



HRMS of probe 2

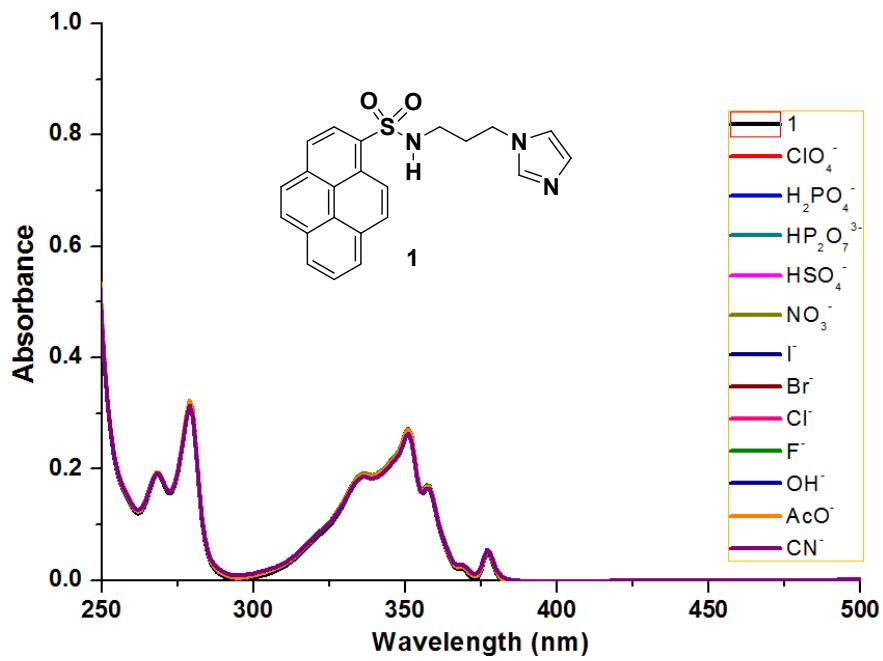


Fig. SI 1: UV-vis study of probe **1** (10 μ M, PBS -EtOH (5:95), pH = 7.4) on addition of different anions viz. F^- , Cl^- , Br^- , I^- , NO_3^- , ClO_4^- , HSO_4^- , H_2PO_4^- , $\text{HP}_2\text{O}_7^{3-}$, AcO^- , CN^- .

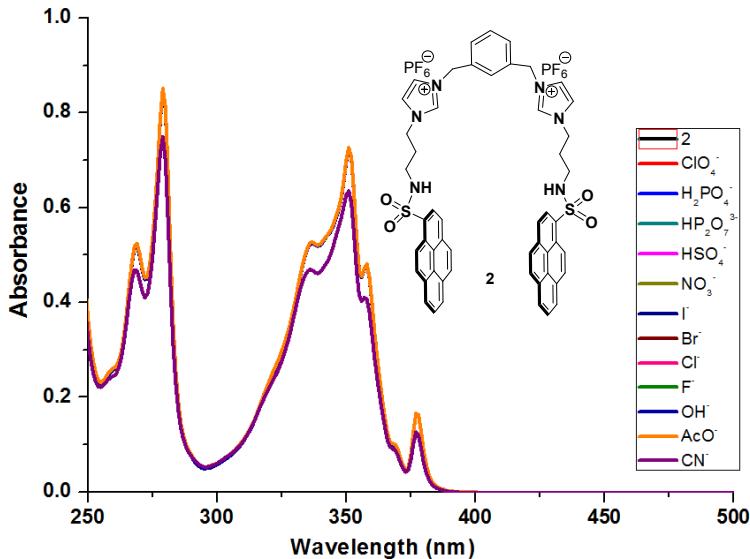


Fig. SI 2: UV-vis study of probe **2** (10 μ M, PBS -EtOH (5:95), pH = 7.4) on addition of different anions viz. F^- , Cl^- , Br^- , I^- , NO_3^- , ClO_4^- , HSO_4^- , H_2PO_4^- , $\text{HP}_2\text{O}_7^{3-}$, AcO^- , CN^- .

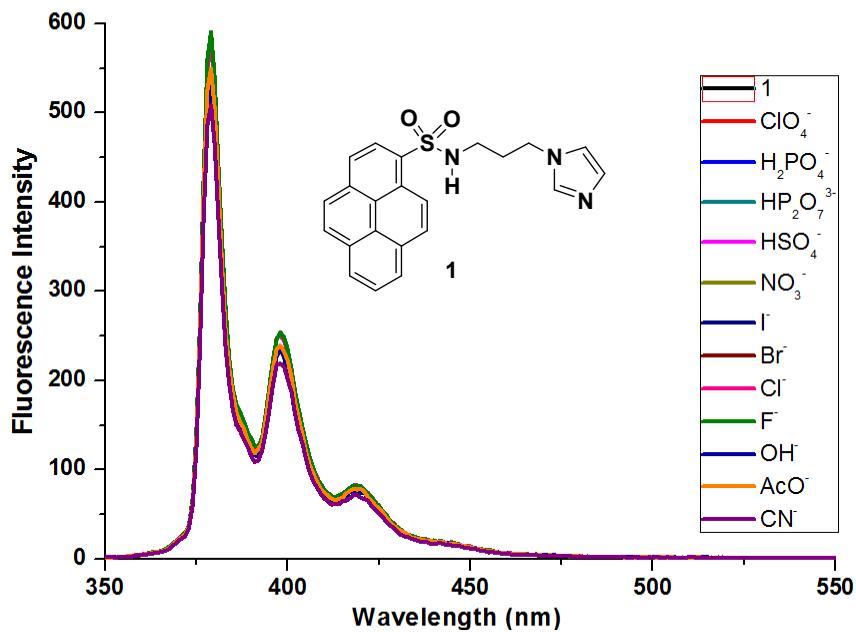


Fig. SI 3: Fluorescence study of probe **1** (1 μM, PBS -EtOH (5:95), pH = 7.4) on addition of different anions viz. F^- , Cl^- , Br^- , I^- , NO_3^- , ClO_4^- , HSO_4^- , H_2PO_4^- , $\text{HP}_2\text{O}_7^{3-}$, AcO^- , CN^- -anions $\lambda_{ex} = 336 \text{ nm}$, slit width 3, 3.

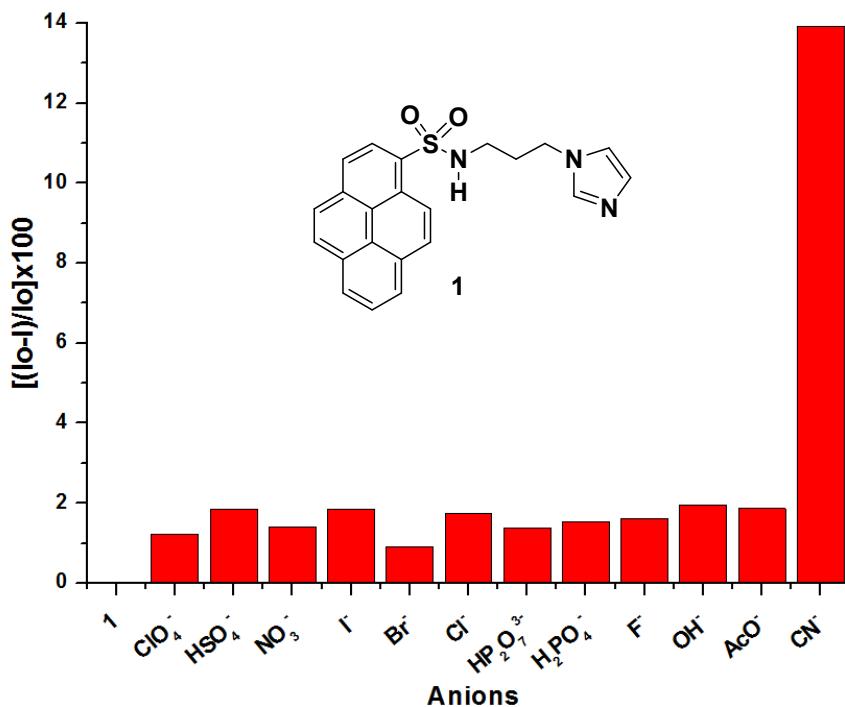


Fig. SI 4: Fluorescence relative intensity bar diagram of probe **1** (1 μM, PBS -EtOH (5:95), pH = 7.4) on addition of different anions viz. F^- , Cl^- , Br^- , I^- , NO_3^- , ClO_4^- , HSO_4^- , H_2PO_4^- , $\text{HP}_2\text{O}_7^{3-}$, AcO^- , CN^- -anions $\lambda_{ex} = 336 \text{ nm}$, $\lambda_{em} = 379 \text{ nm}$, slit width 3, 3.

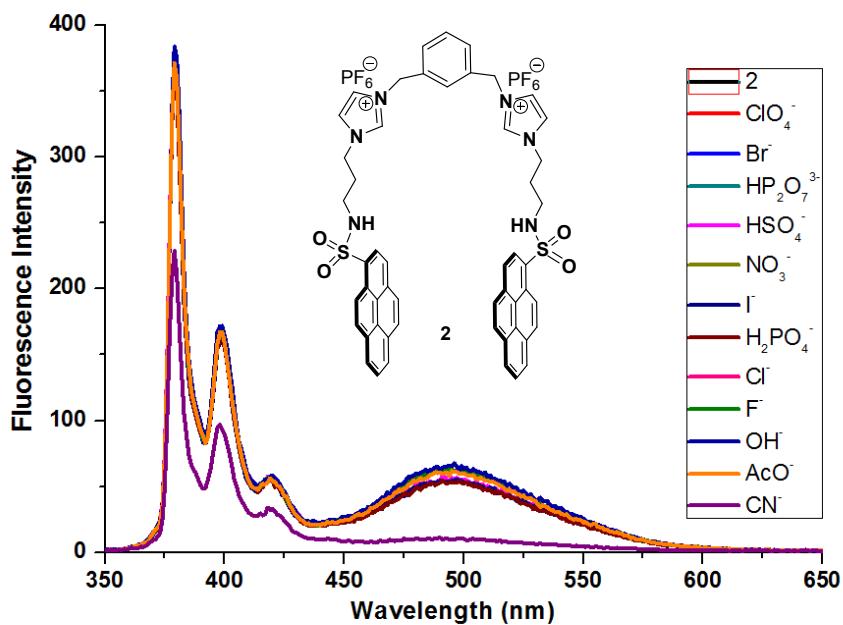


Fig. SI 5: Fluorescence study of probe **2** (1 μM, PBS -EtOH (5:95), pH = 7.4) on addition of different anions viz. F^- , Cl^- , Br^- , I^- , NO_3^- , ClO_4^- , HSO_4^- , H_2PO_4^- , $\text{HP}_2\text{O}_7^{3-}$, AcO^- , CN^- -anions $\lambda_{ex} = 336$ nm, slit width 3.3.

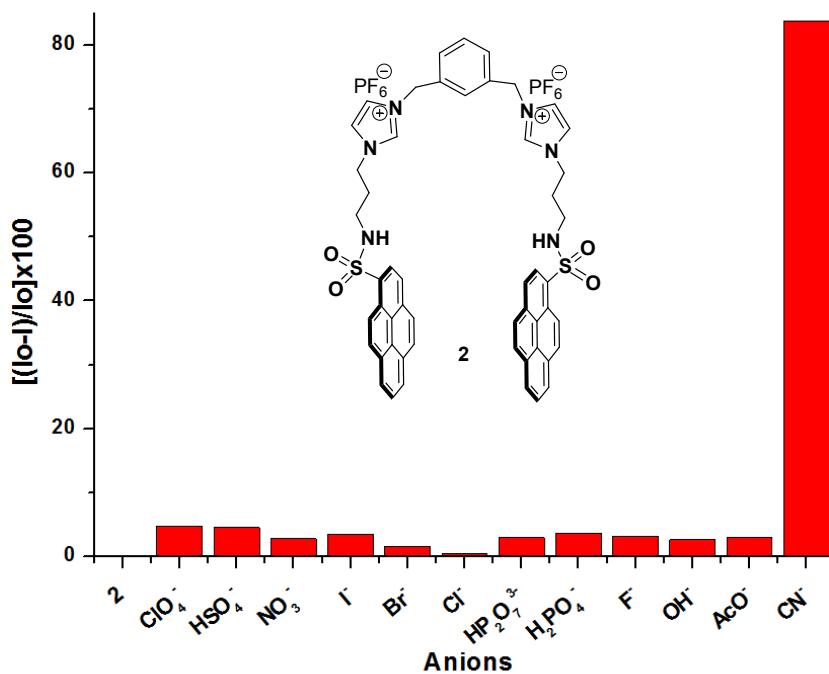


Fig. SI 6: Fluorescence relative intensity bar diagram of probe **2** (1 μM, PBS -EtOH (5:95), pH = 7.4) on addition of different anions viz. F^- , Cl^- , Br^- , I^- , NO_3^- , ClO_4^- , HSO_4^- , H_2PO_4^- , $\text{HP}_2\text{O}_7^{3-}$, AcO^- , CN^- -anions $\lambda_{ex} = 336$ nm, $\lambda_{em} = 494$ nm, slit width 3.3.

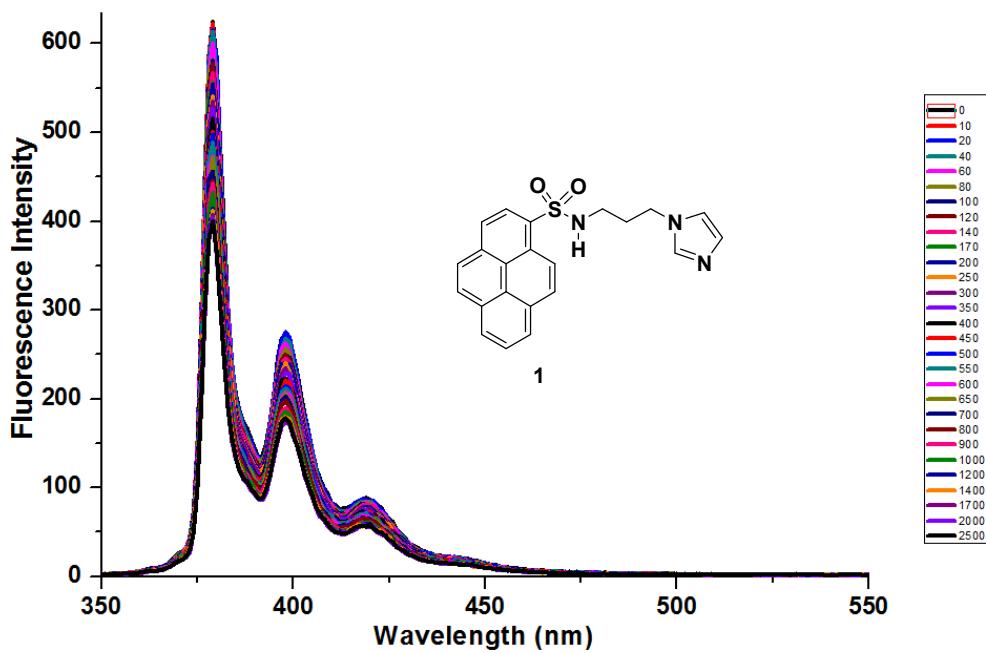


Fig. SI 7: Fluorescence titration of probe **1** (1 μM , PBS -EtOH (5:95), pH = 7.4) with CN^- ion, $\lambda_{\text{ex}} = 336 \text{ nm}$, slit width 3, 3.

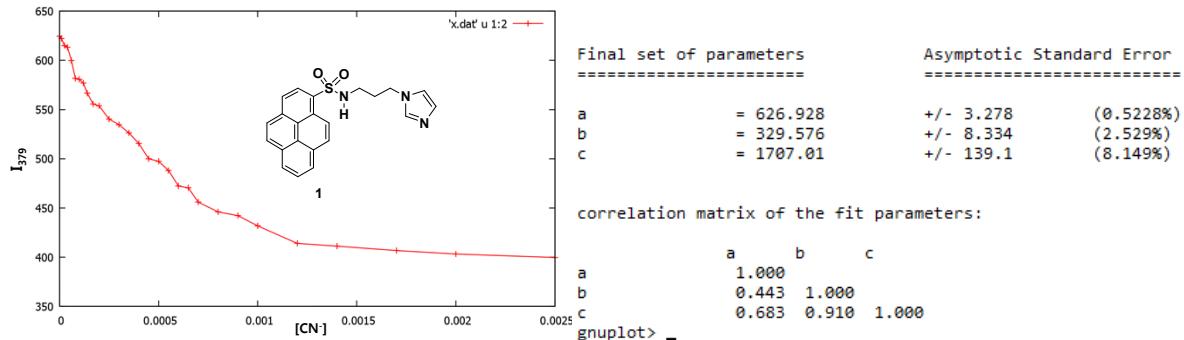


Fig. SI 8: The spectral fitting of the fluorescence titration data of probe **1** (1 μM , PBS -EtOH (5:95), pH = 7.4) with CN^- ion, $\lambda_{\text{ex}} = 336 \text{ nm}$, slit width 3, 3.

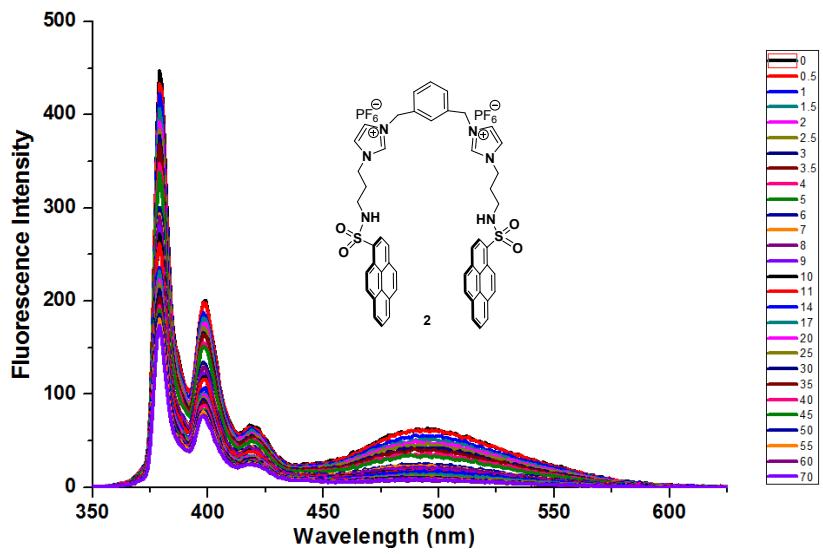


Fig. SI 9: Fluorescence titration of probe **2** (1 μ M, PBS -EtOH (5:95), pH = 7.4) with CN^- ion, $\lambda_{\text{ex}} = 336 \text{ nm}$, slit width 3, 3.

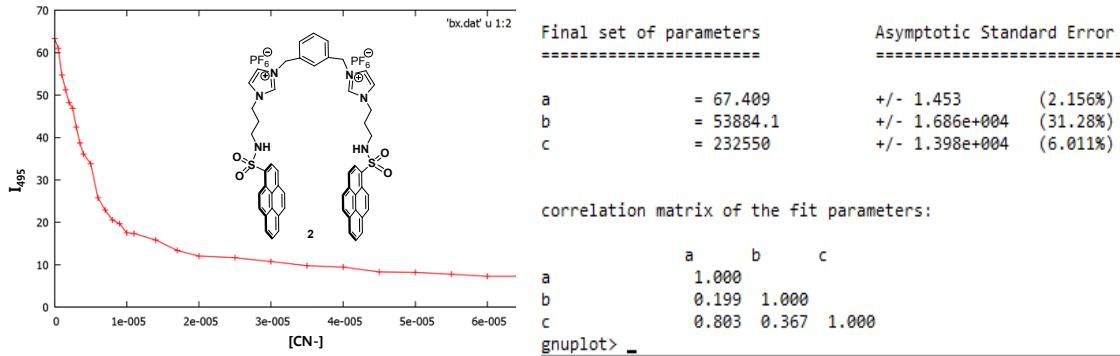


Fig. SI 10: The spectral fitting of the fluorescence titration data of probe **2** (1 μ M, PBS -EtOH (5:95), pH = 7.4) with CN^- ion, $\lambda_{\text{ex}} = 336 \text{ nm}$, $\lambda_{\text{em}} = 495 \text{ nm}$, slit width 3, 3.

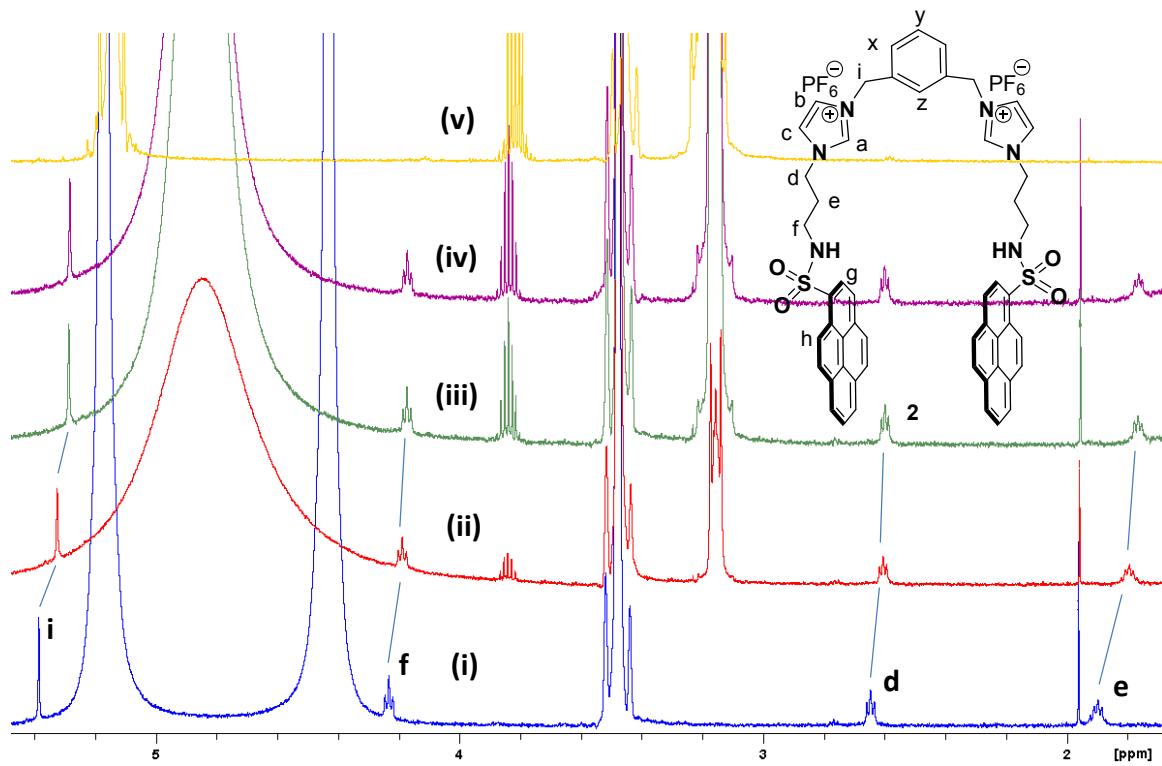


Fig. SI 11: (i) Partial ¹H NMR spectra of probe **2**; and (ii) upon addition of 1 eq. of TBACN; (iii) 2 eq. of TBACN; (iv) 3 eq. of TBACN; and (v) only TBACN in $D_2O-CD_3CD_2OD$ (1:6).

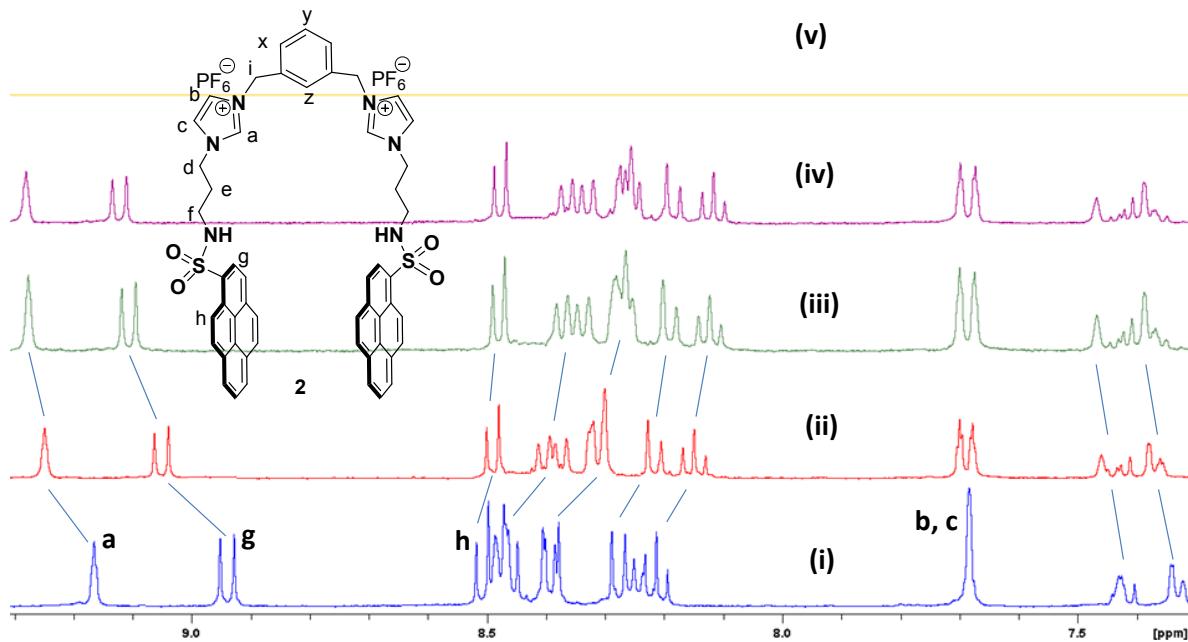


Fig. SI 12: (i) Partial ¹H NMR spectra of probe **2**; and (ii) upon addition of 1 eq. of TBACN; (iii) 2 eq. of TBACN; (iv) 3 eq. of TBACN; and (v) only TBACN in $DMSO-d_6$.

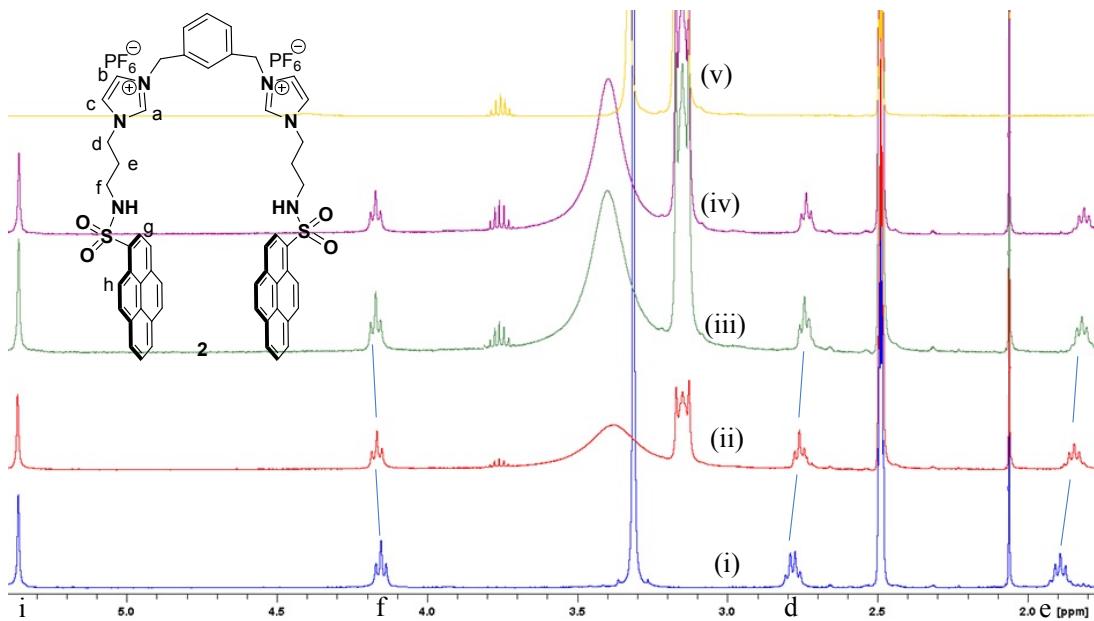


Fig. SI 13: (i) Partial ¹H NMR spectra of probe **2**; and (ii) upon addition of 1 eq. of TBACN; (iii) 2 eq. of TBACN; (iv) 3 eq. of TBACN; and (v) only TBACN in DMSO-d₆.

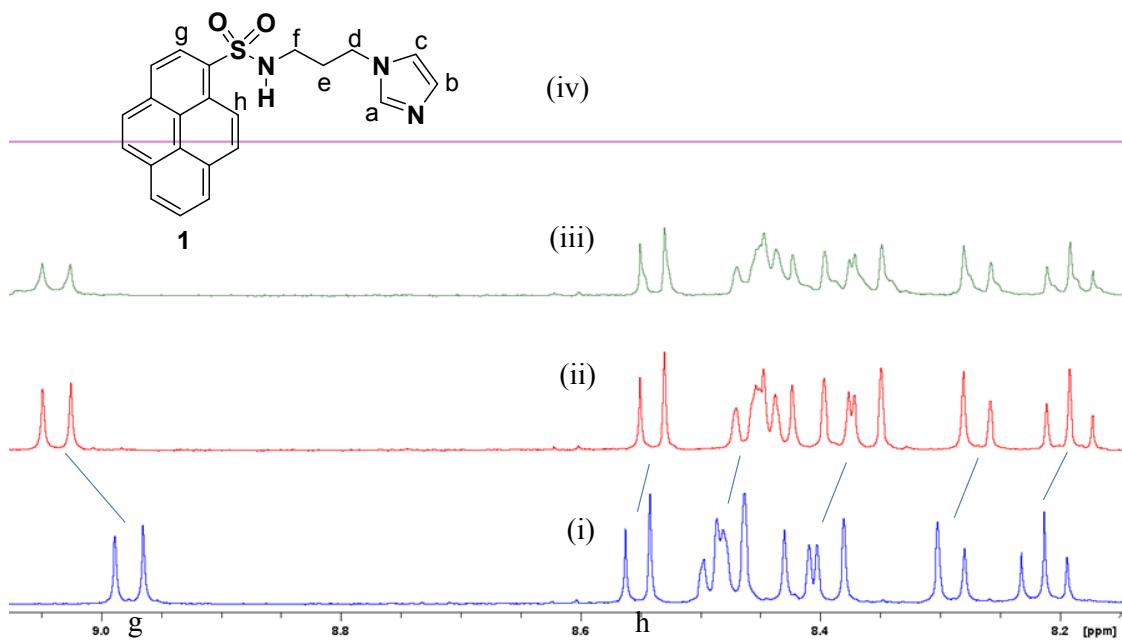


Fig. SI 14: (i) Partial ¹H NMR spectra of probe **1**; and (ii) upon addition of 1 eq. of TBACN; (iii) 2 eq. of TBACN; and (iv) only TBACN in DMSO-d₆.

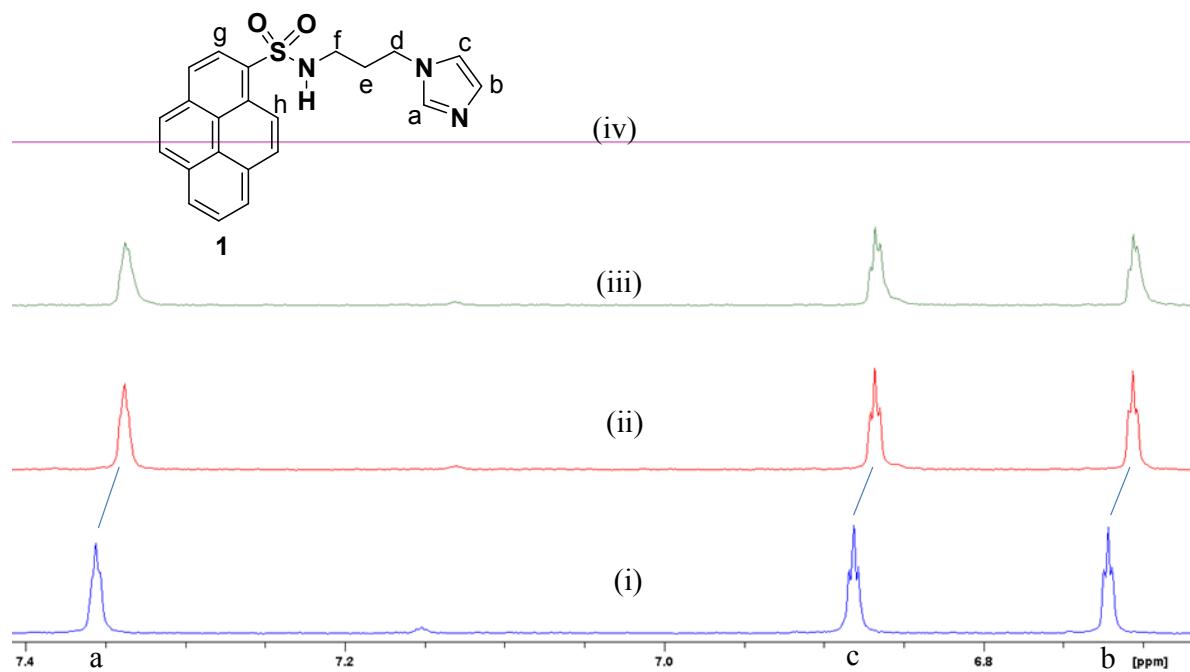


Fig. SI 15: (i) Partial ¹H NMR spectra of probe **1**; and (ii) upon addition of 1 eq. of TBACN; (iii) 2 eq. of TBACN; and (iv) only TBACN in DMSO-d₆.

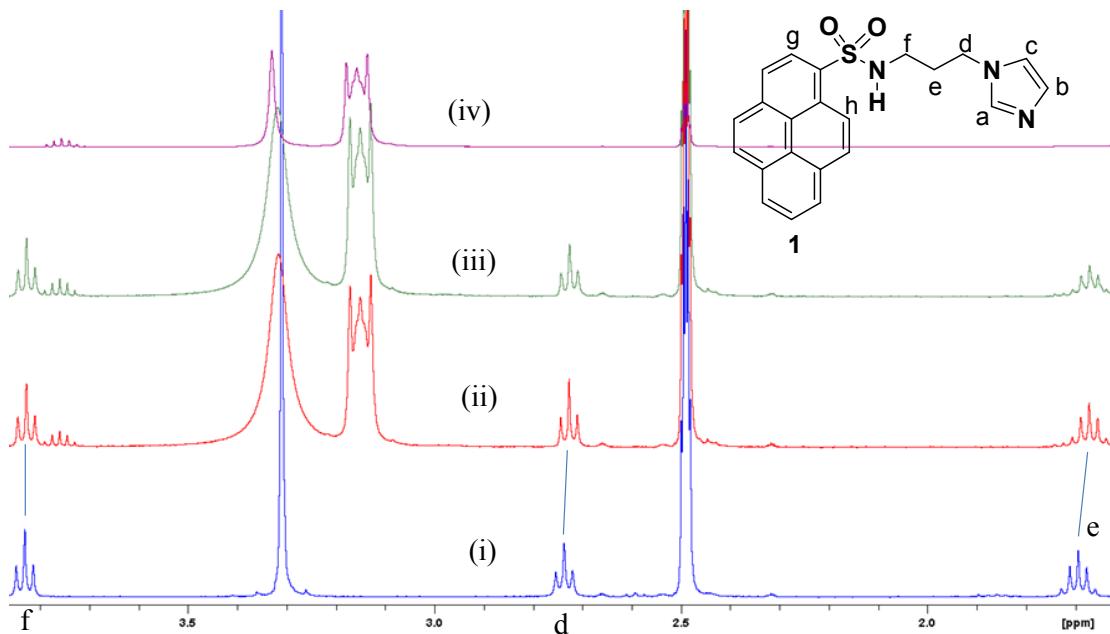


Fig. SI 16: (i) Partial ¹H NMR spectra of probe **1**; and (ii) upon addition of 1 eq. of TBACN; (iii) 2 eq. of TBACN; and (iv) only TBACN in DMSO-d₆.

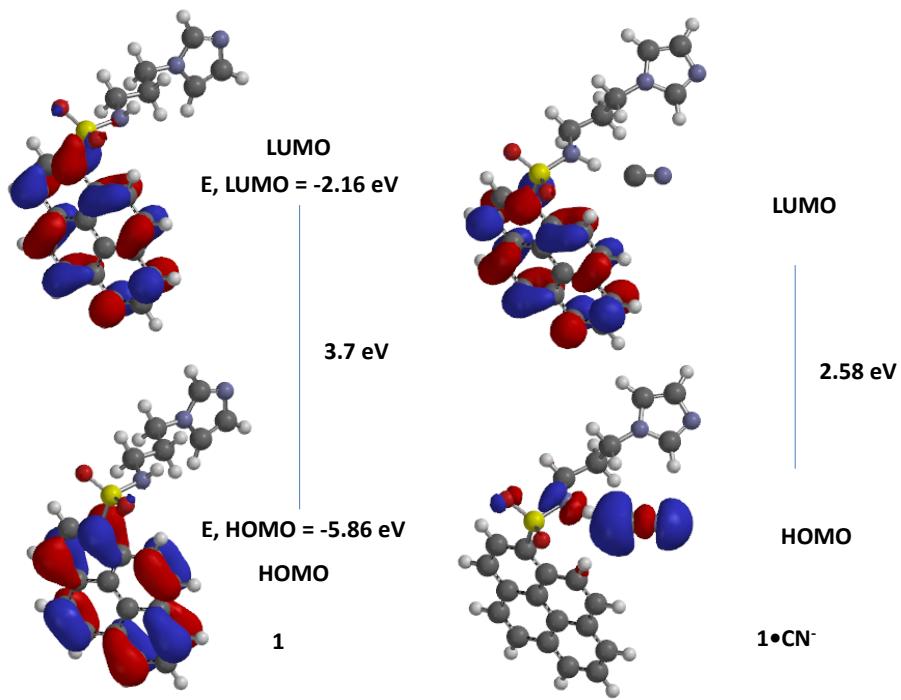


Fig. SI 17: “B3LYP/6-31G* calculated molecular orbitals of probe **1** and **1**• CN^- complex and their energy differences.”

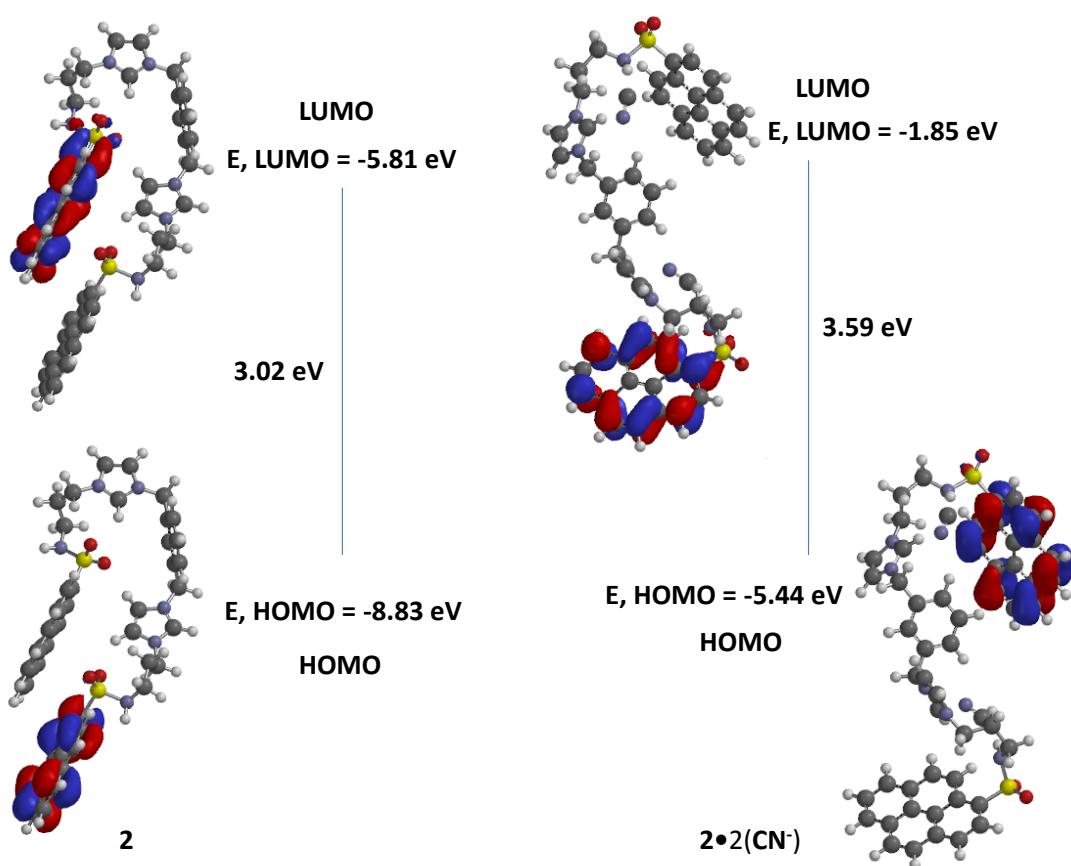


Fig. SI 18: “B3LYP/6-31G* calculated molecular orbitals of probe **2** and **2**•**2**(CN⁻) complex and their energy differences.”

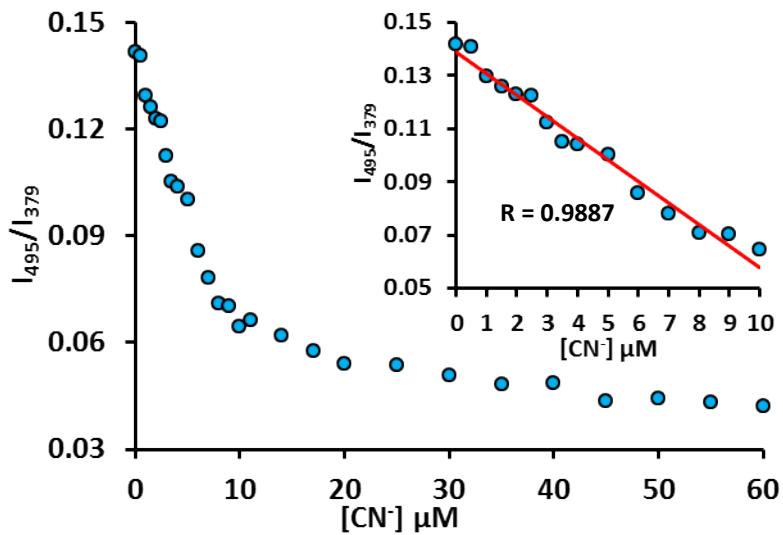


Fig. SI 19: Fluorescence ratiometric response (I_{495}/I_{379}) of probe 2 (1 μM , PBS -EtOH (5:95), pH = 7.4) with TBACN toward $[\text{CN}^-]$.

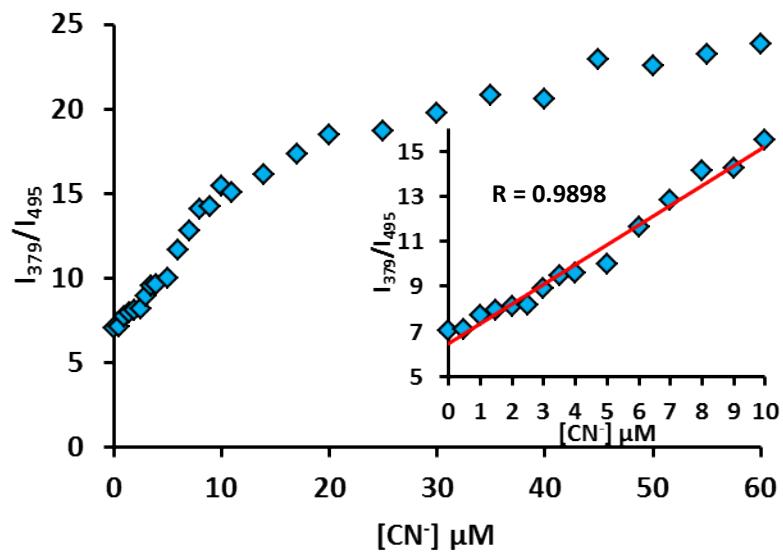


Fig. SI 20: Fluorescence ratiometric response (I_{379}/I_{495}) of probe 2 (1 μM , PBS -EtOH (5:95), pH = 7.4) with TBACN toward $[\text{CN}^-]$.