Electronic Supplementary Material (ESI) for RSC Advances.

Dithieno[3,2-*a*:2',3'-*c*]phenazine-based Chemical Probe for Anions: A Spectroscopic Study of Binding

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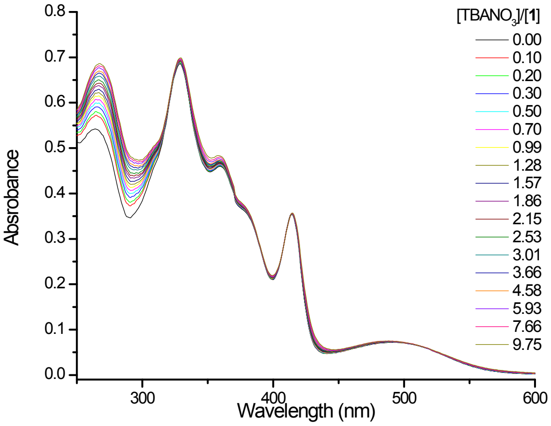
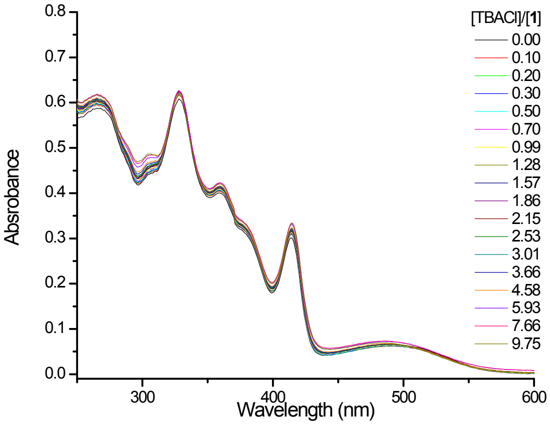
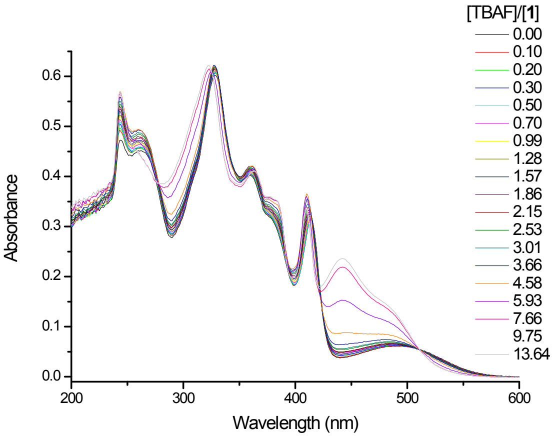
Supporting Information

Absorbance Titration Spectra







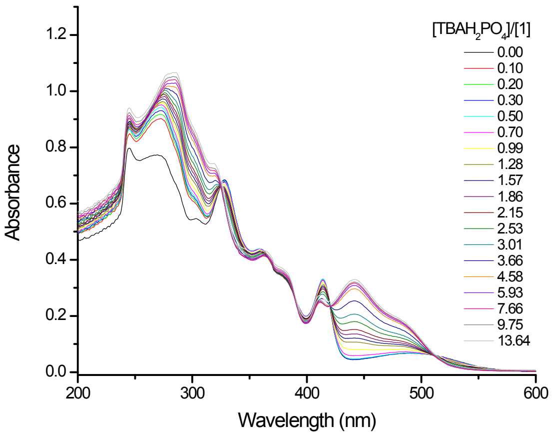


Figure SI-1. Absorbance spectra of **1** (10.0 μM in $CHCl_3$) upon titrating with tetrabutylammonium (TBA) anion solution (1.0 mM): (top left) TBA nitrate; (top right) TBA benzoate; (bottom left) TBA fluoride; (bottom right) TBA dihydrogen phosphate.

Emission Titration Spectra

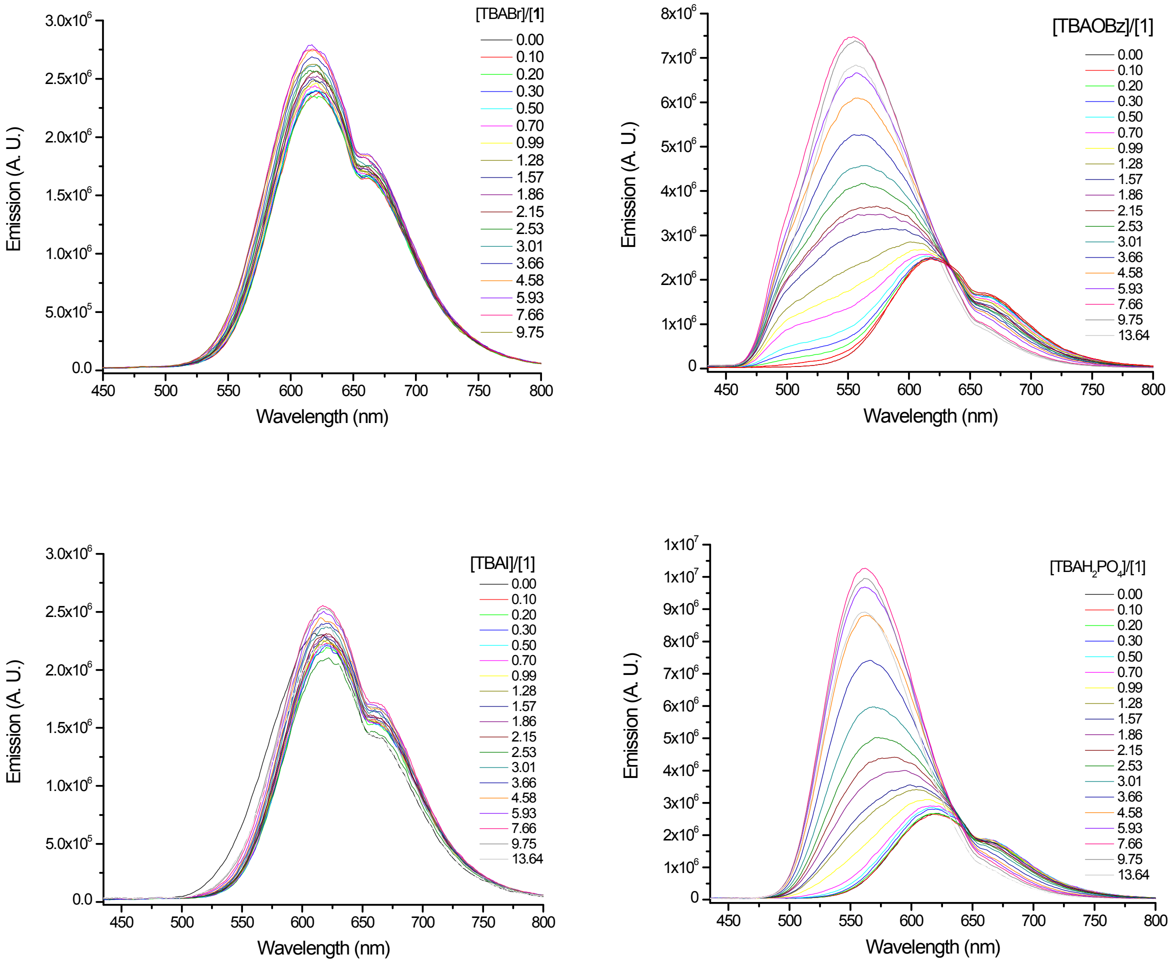


Figure SI-2. Emission spectra of **1** (10.0 μM in $CHCl_3$) upon titrating with tetrabutylammonium anion solution (1.0 mM): top left) TBA bromide; (top right) TBA benzoate; (bottom left) TBA iodide; (bottom right) TBA dihydrogen phosphate)

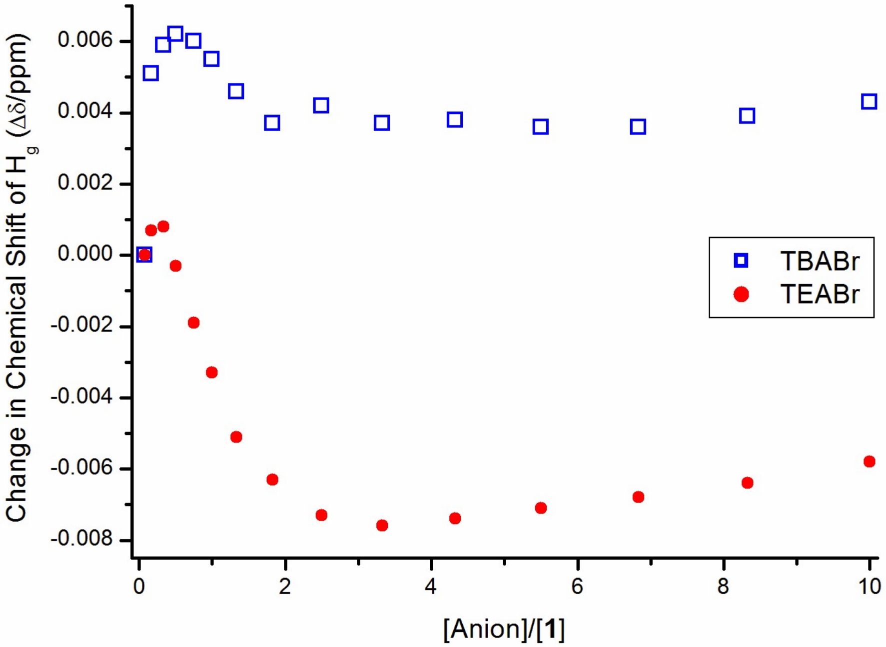


Figure SI-3. The change in the chemical shift of H_g upon titrating **1** with solutions of tetrabutylamonium bromide (TBABr) and tetraethylamonium bromide (TEABr) in $CDCl_3$. The graph shows that the signal of H_g protons on TEA cation shifts upfield to higher extent than that of TBA. The smaller size of TEA cation, as compared to TBA cation, minimizes the steric repulsion between TEA and the **A**-rings of **1**, hence allowing for closer interaction with sulfur atoms on the **B**-rings, thus supporting the proposed electrostatic interaction with these sulfur atoms.

Calculations of Binding Constants

Mathematical analysis of data and graphic presentation of results were performed using the program HypNMR2008 and HypSpec2008 from Hyperquad2008 by Protonic Software (Leeds LS15 0HD, England) handling general host−guest association equilibria. The program performs a Gauss−Newton−Marquardt least-squares fitting of the experimental data by minimizing the error square sum. The program performs simultaneous fit of multiple signals to models involving multiple equilibria. The refinement process yields best-fit values for equilibrium constants and individual absorbance on every wavelength for each chemical species. Hyperquad2008 is available at: http://www.hyperquad.co.uk/.

NMR titrations have shown that there are significant interactions of **1** with the anions only for chloride, bromide, iodide, and nitrate ions while for the acetate, benzoate, and cyanide ions, there were strong interactions of **1** with both cation (TBA) and anion. In other words, the strong 1-anion interaction (for acetate, benzoate, and cyanide ions) is crucial for significant binding to the TBA. Thus, the binding isotherms obtained from NMR titrations for chloride, bromide, iodide, and nitrate ions were fitted to the binding model: **[1 + A ⇌ 1•A]** (**A**=anion) using HypNMR2008 while absorbance spectra obtained from UV titrations for acetate, benzoate, and cyanide ions were fitted to the binding model [**1 + TA ⇌ T•1•A**] (**T**= TBA; **A**=anion) (Figure SI-4).

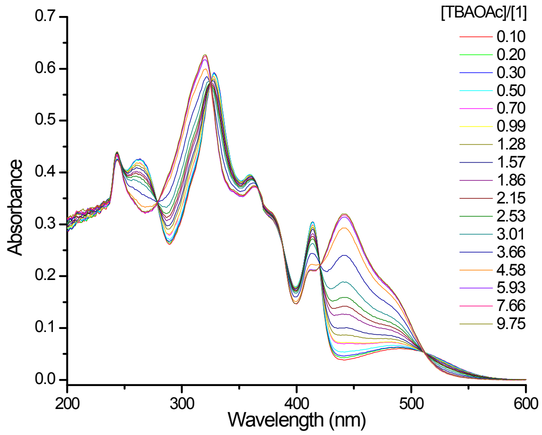
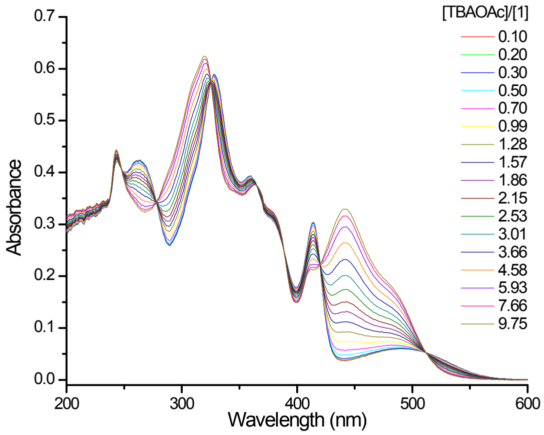
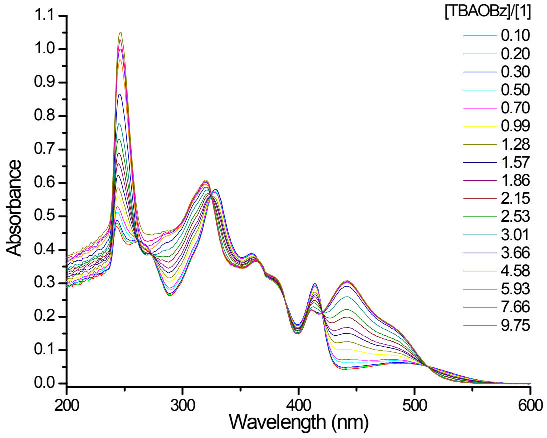
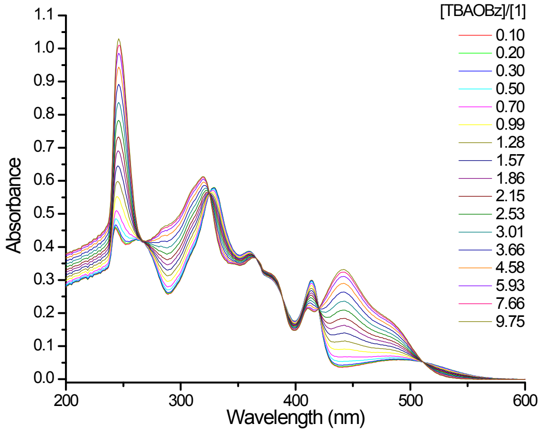
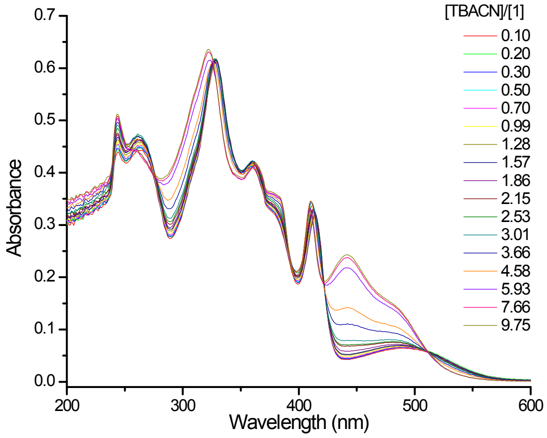
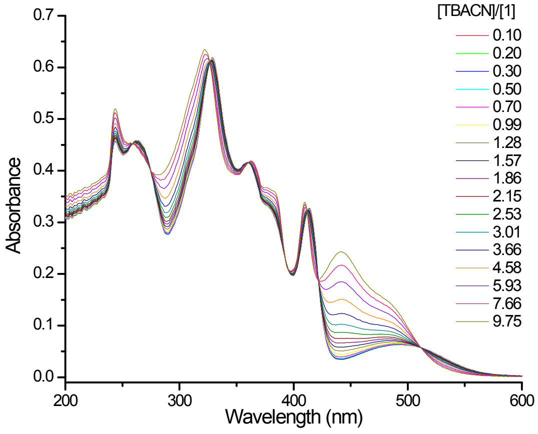
Experimental Spectra	**Calculated Spectra (from model)**
	
	
	

Figure SI-4: Experimental and calculated spectra of strong-binding anions. The calculated spectra are generated from the binding model and the calculated binding constant.

NMR Spectra of the Prepared Compounds

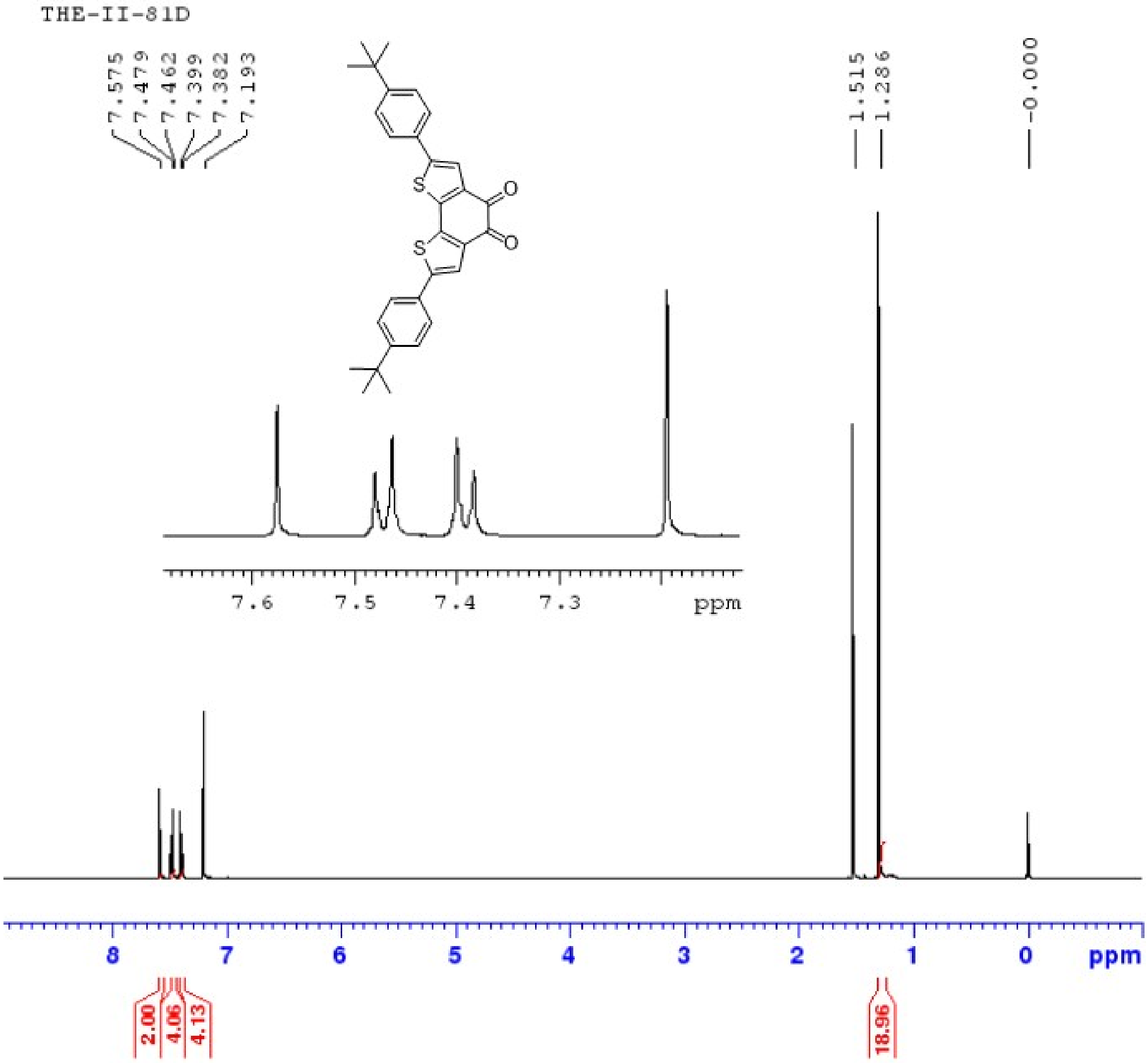


Figure SI-5. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **4**.

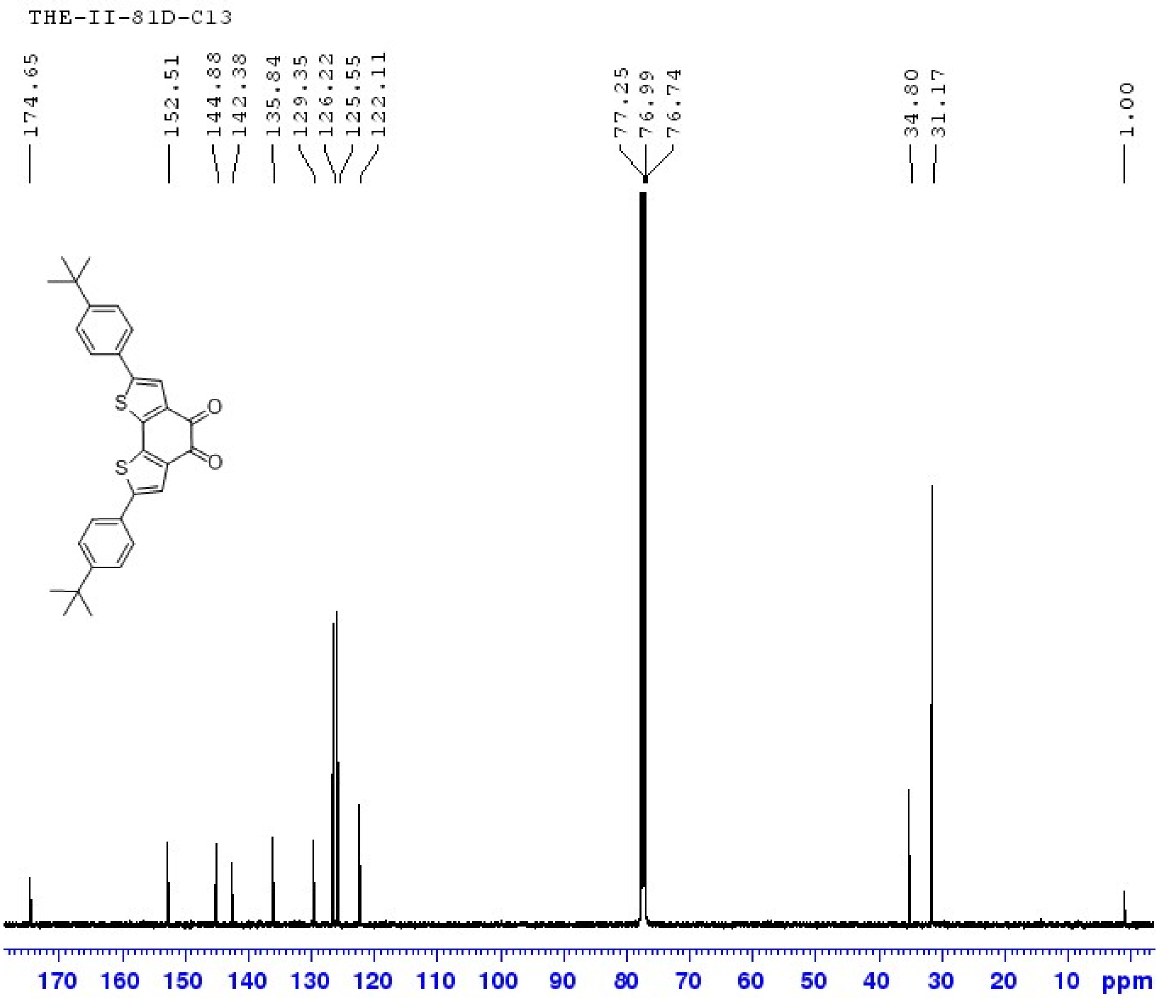


Figure SI-6. $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) spectrum of **4**.

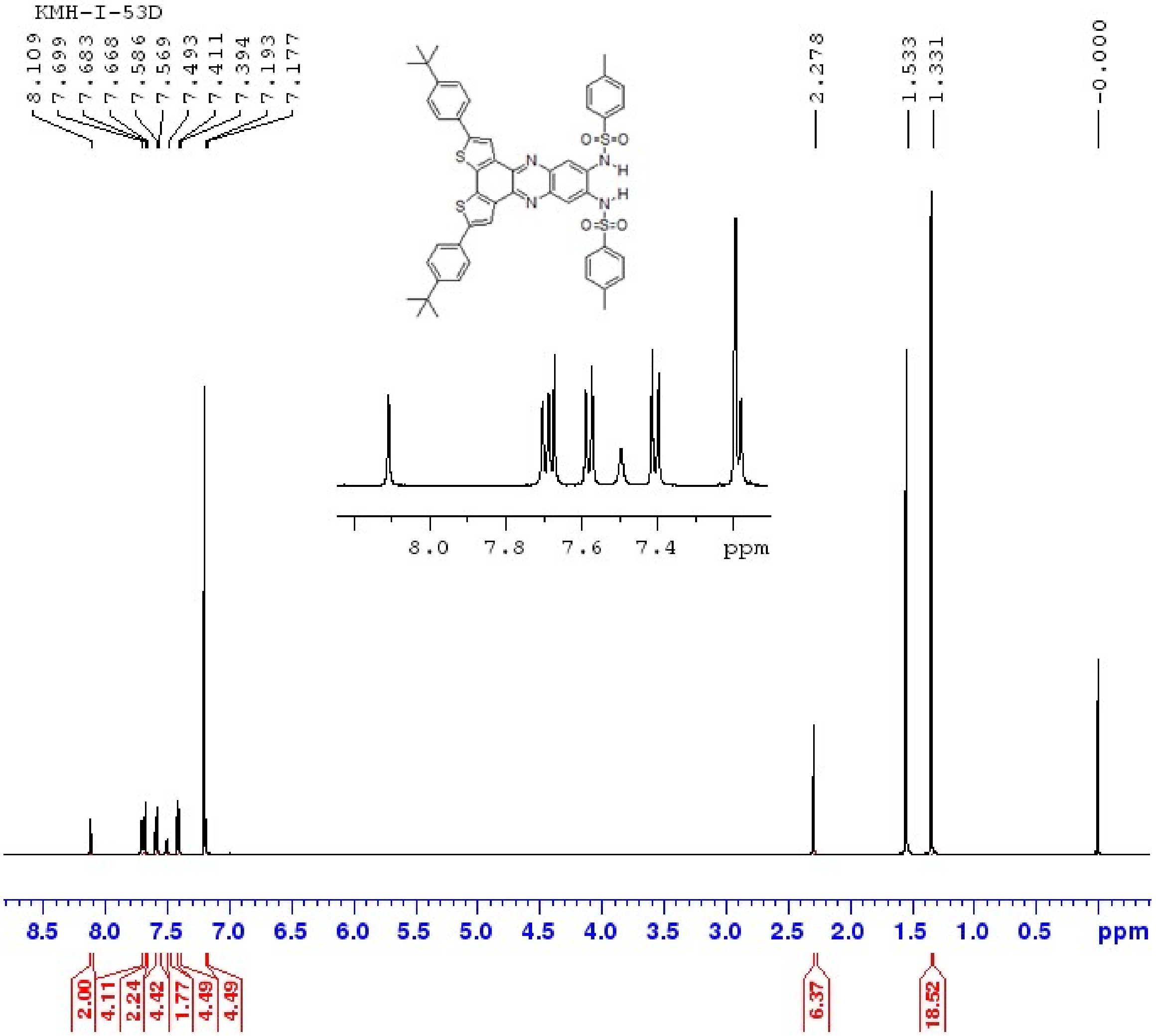


Figure SI-7. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **1**.

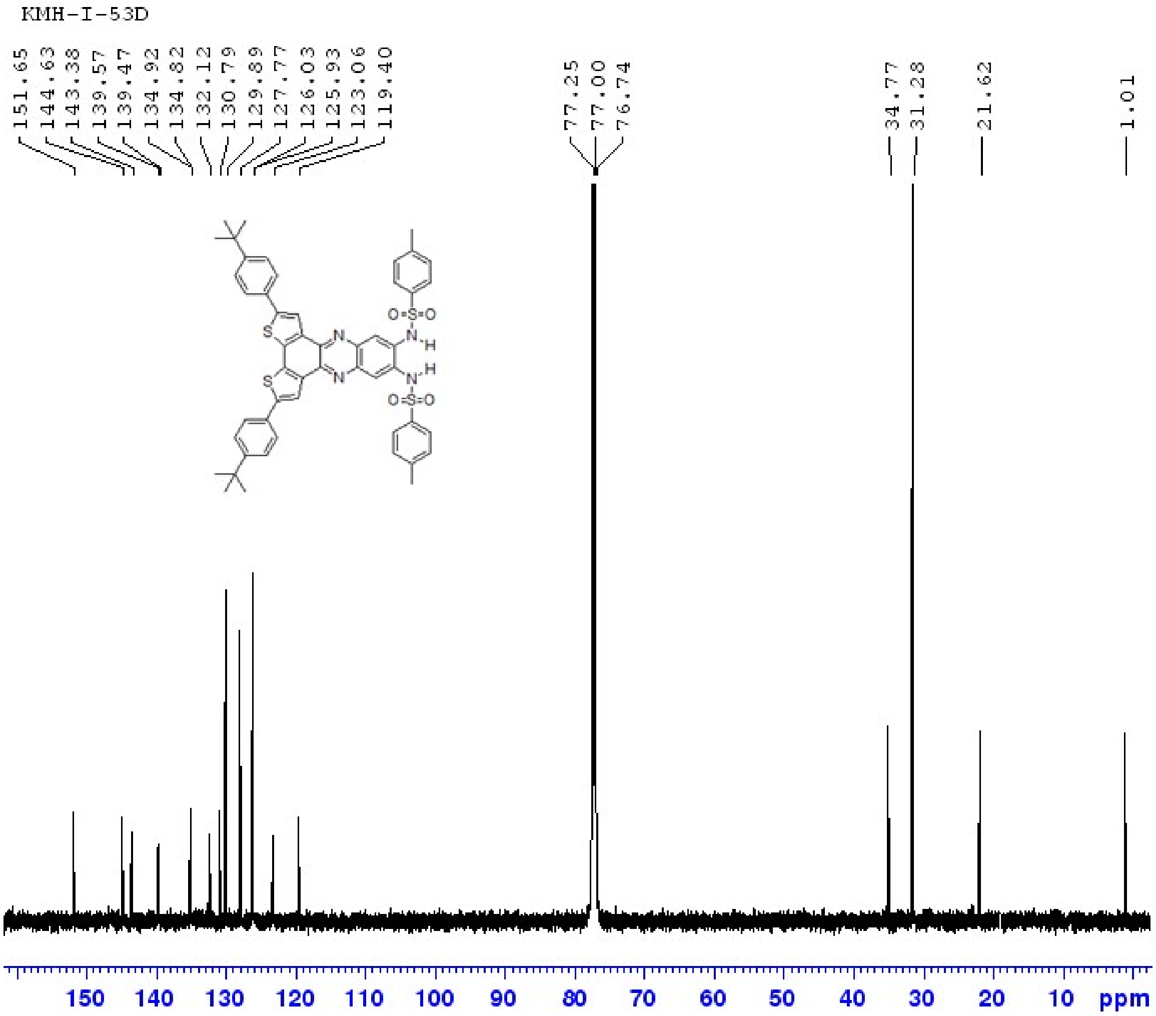


Figure SI-8. ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) spectrum of **1**.