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Hierarchical self-assembly of naphthalene bisimides to fluorescent microspheres and fluoride sensing

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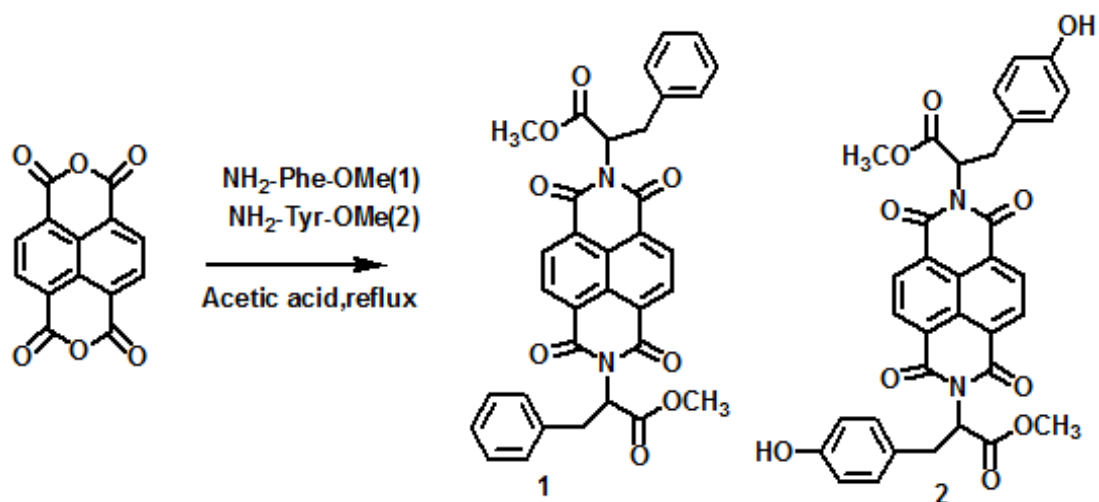
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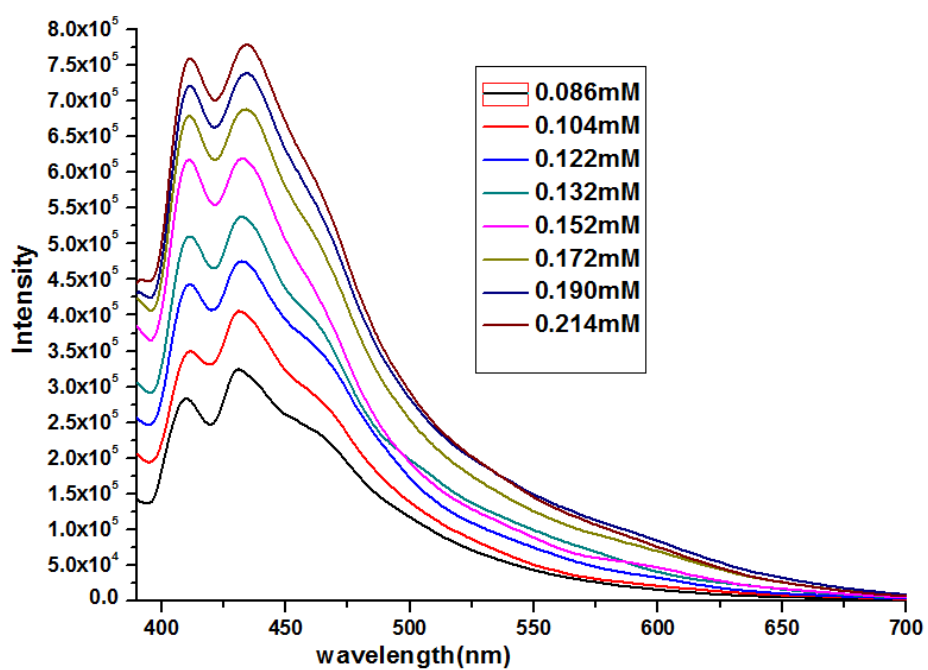
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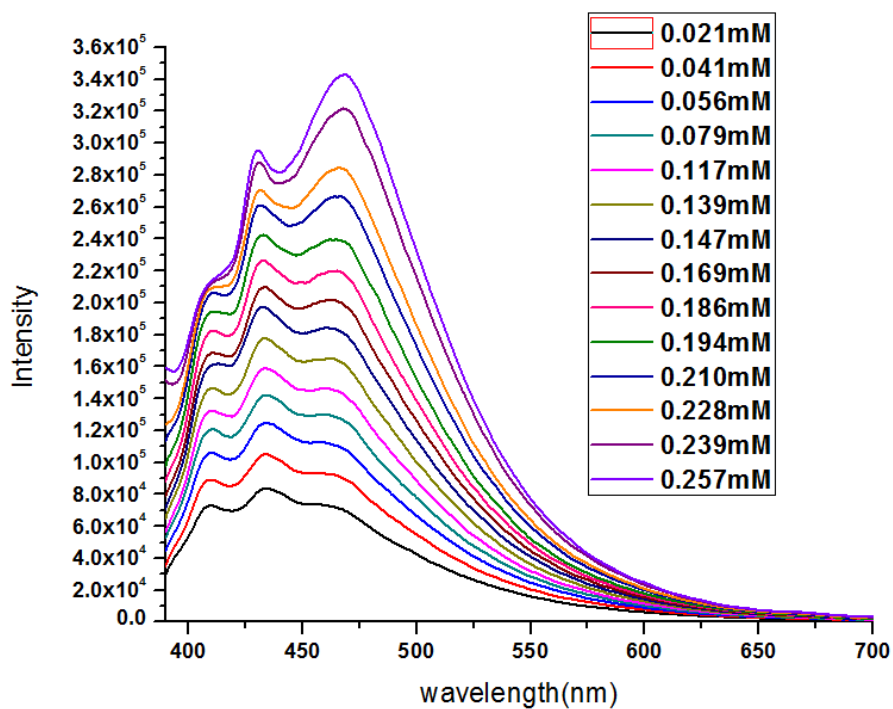
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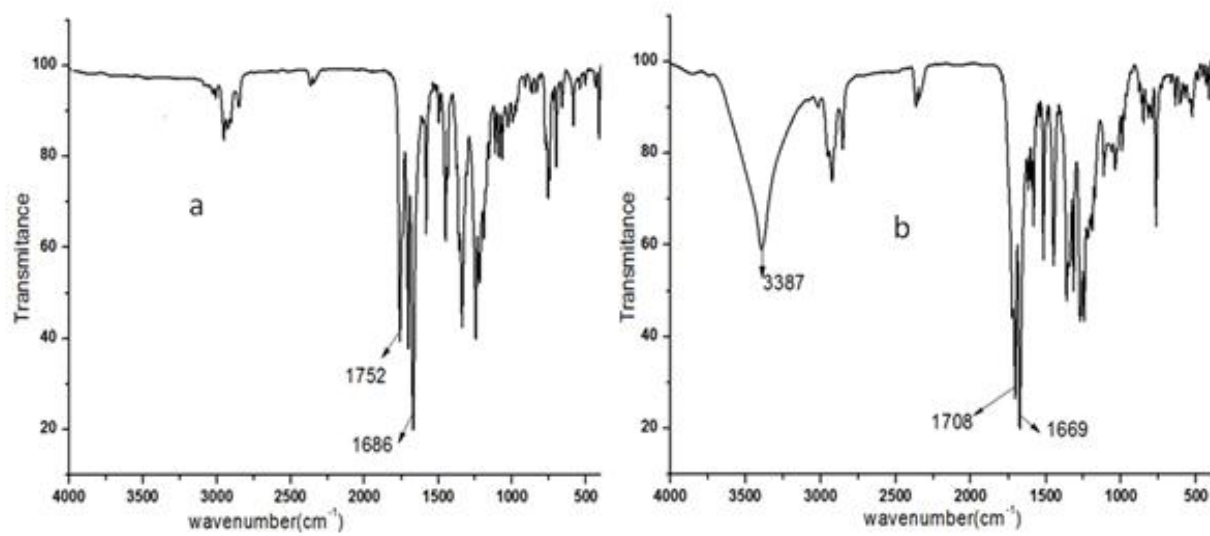
ESI Figure S1: Schematic presentation of naphthalene bisimide synthesis.



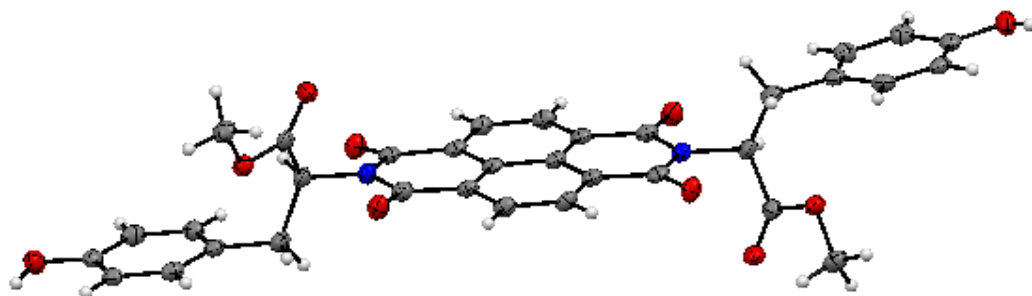
ESI Figure S2 : Emission spectra of bisimide **1** in DCM/Methanol solution.



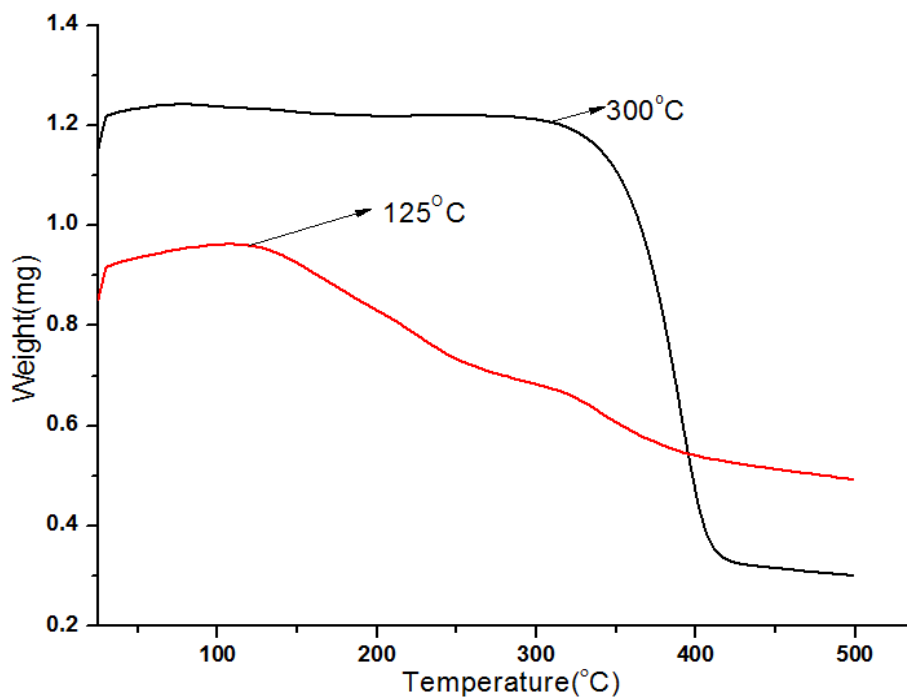
ESI Figure S3 : Emission spectra of bisimide 2 in DCM/Methanol solution.



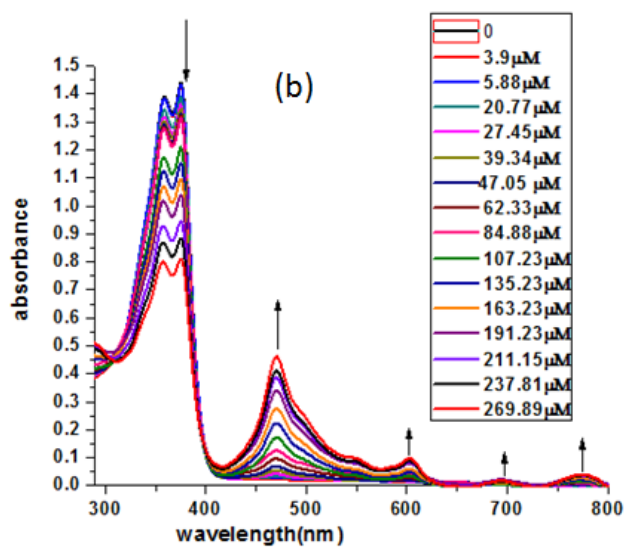
ESI Figure S4: (a) FT-IR spectra of bisimide 1 and (b) bisimide 2.



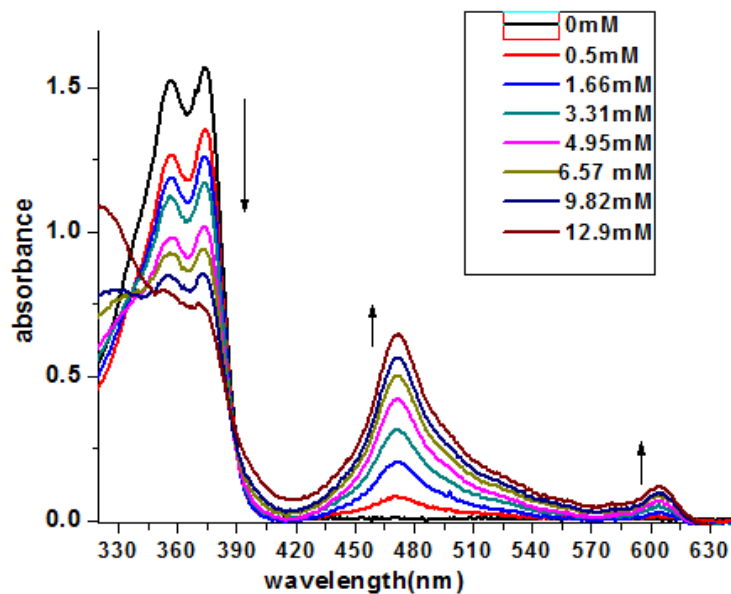
ESI Figure S5: The ORTEP diagram of bisimide **2** showing the atomic numbering scheme. Ellipsoids are drawn at the 50% probability level.



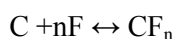
ESI Figure S6: TGA of bisimide **1**(black line) and bisimide **2**(red line).



ESI Figure S7: UV-VIS of NBI **1** (0.13 mM) in DMF/H₂O (95:5) with different fluoride ion concentration, clear isobastic point at 394 nm.



ESI Figure S8: UV-Visible of NBI 2 (0.18 mM) with different concentration of fluoride ion in THF solvent, isobastic point at 387 nm.



$$K = \frac{[CF_n]}{[C][F]^n}$$

From this we get the below equation

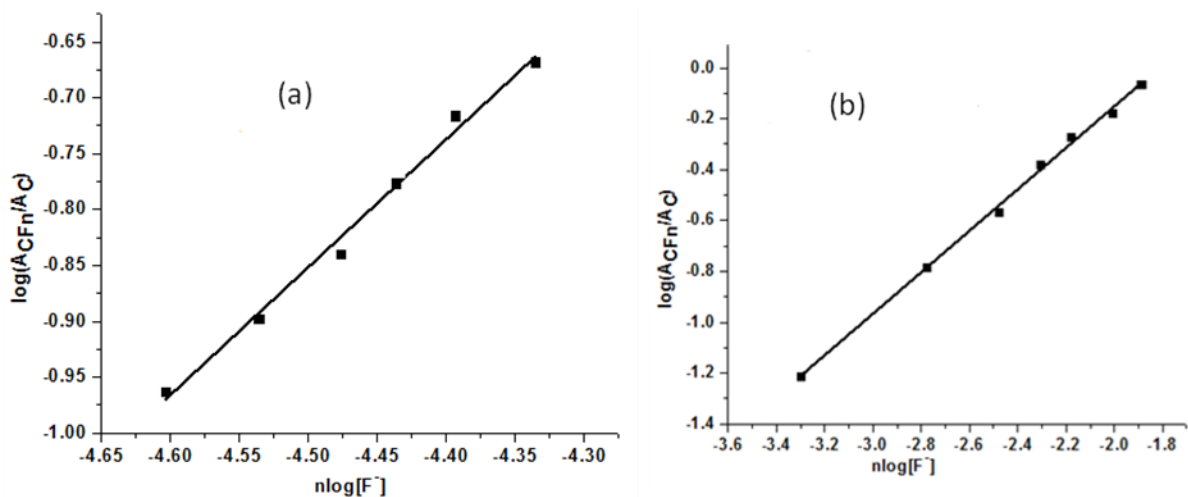
$$\log (A_{CF_n}/A_c) + \log (\epsilon_c/\epsilon_{CF_n}) = n \log [F] + \log K \dots \dots \dots \text{Equation 1}^1$$

Here, C = naphthalene diimide (NDI), F = fluoride ion, n = no. of F ion

K = binding constant, A_{CF} = absorbance of complex, A_c = absorbance of NDI,

ϵ_c = molar absorptivity coefficient of NDI, ϵ_{CF_n} = molar absorptivity coefficient of Complex.

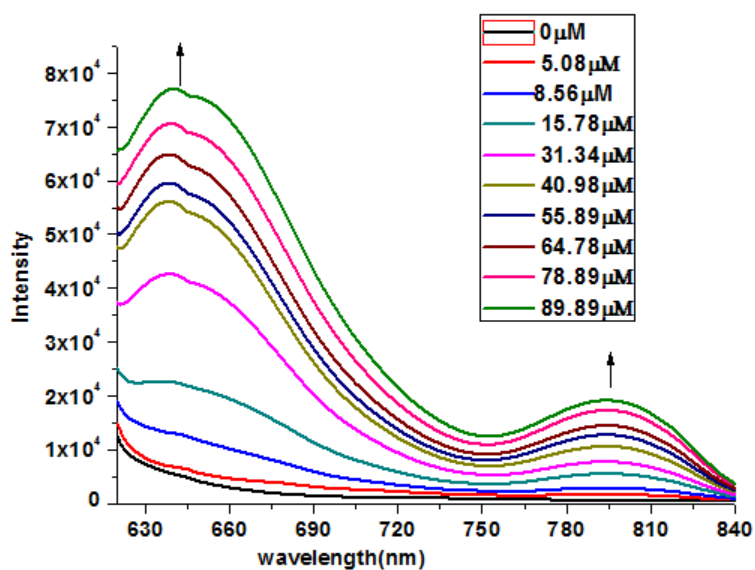
1. J. K. Basu, M. Shannigrahi and S. Bagchi, *J. Phys. Chem. A*, 2006, **110**, 9051-9056 .



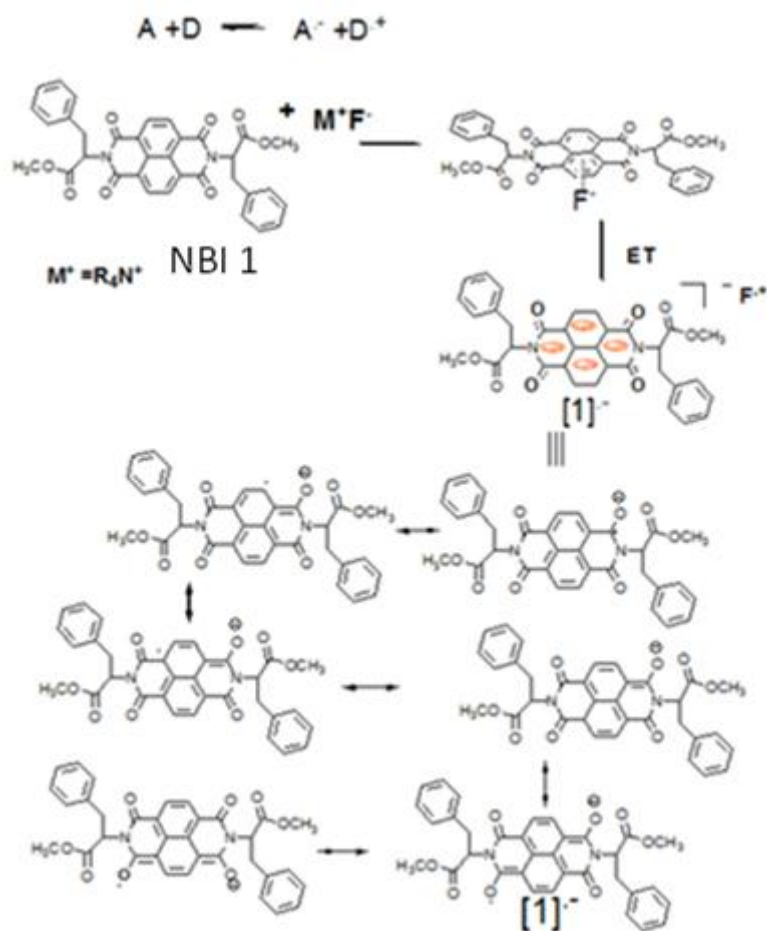
ESI Figure S9: (a) Plot of $\log(A_{CFn}/A_C)$ vs $n\log[F^-]$ for NBI 1-F complex. (b) Plot of $\log(A_{CFn}/A_C)$ vs $n\log[F^-]$ for NBI 2-F complex.

ESI Table-1 Binding constant of complex and stoichiometric ratio

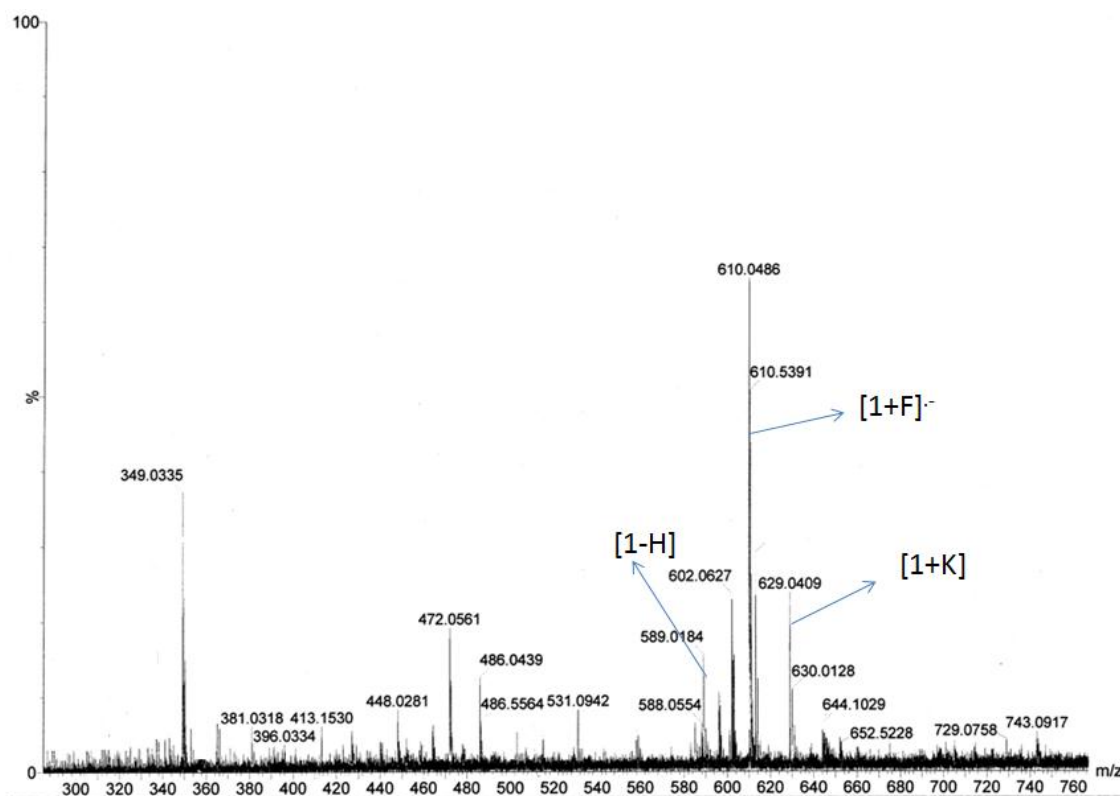
NBI1-F Complex	$10^{5.02} M^{-1}$	1:1.14 \approx 1:1
NBI2-F Complex	$10^{1.86} M^{-1}$	1:0.815 \approx 1:1



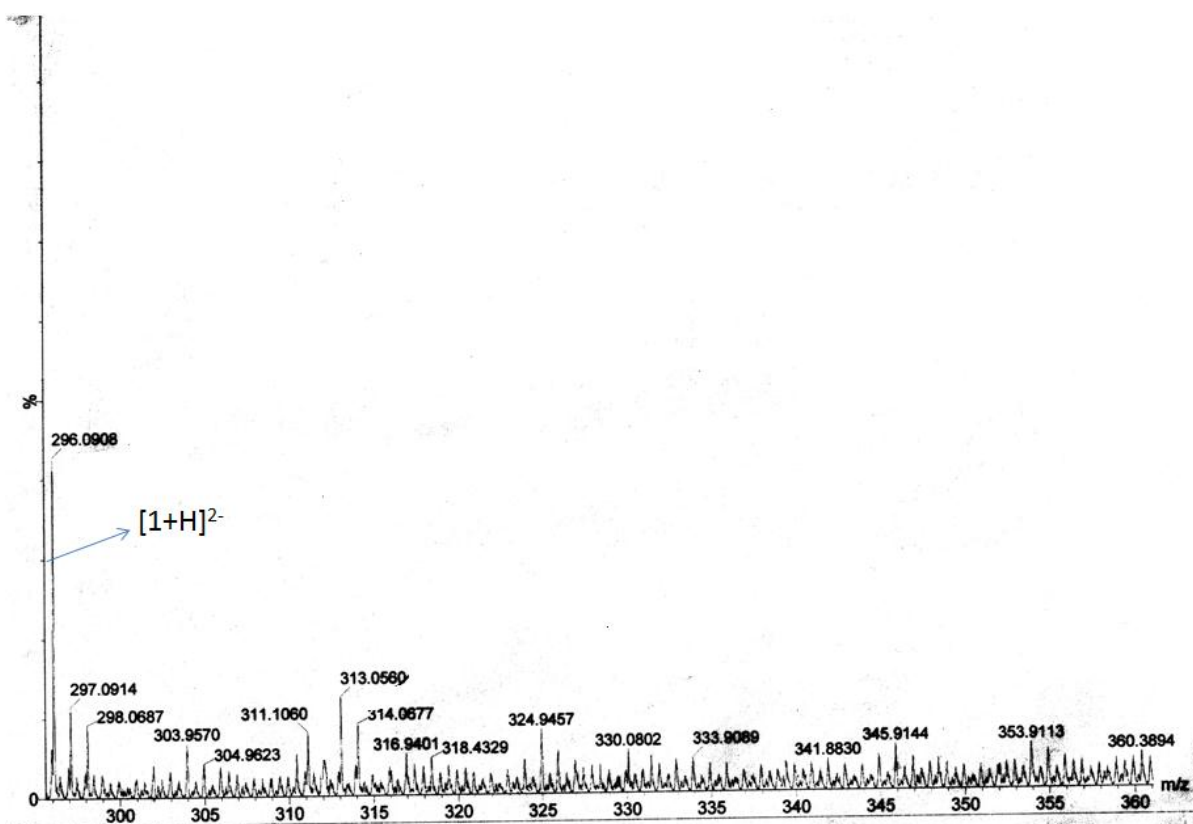
ESI Figure S10: Emission spectra of NBI 1(0.06mM) with different fluoride ion concentration. Exciting at 600nm.



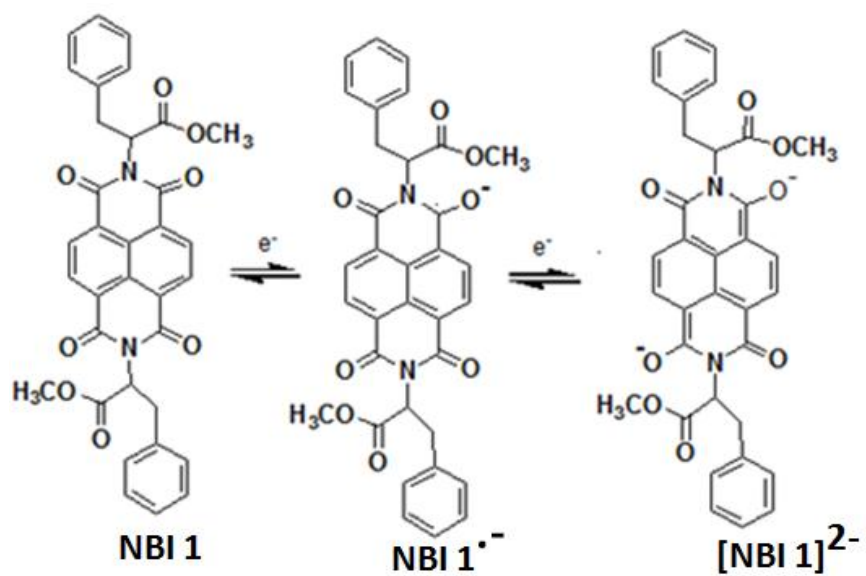
ESI Figure S11: Single electron transfer (SET) driven sensing of fluoride anion by the sensor NBI 1 and the resonating structures of the radical anion sensor [1]^{•-}. **A= acceptor, D= donor.**



ESI Figure S12: Mass spectra of NBI 1-F⁻ (0.2 equiv. F⁻) complex.



ESI Figure S13: Mass spectra of NBI 1 with F⁻ (10 equiv.) complex.



ESI Figure S14: Reversible reduction processes for NBI 1.

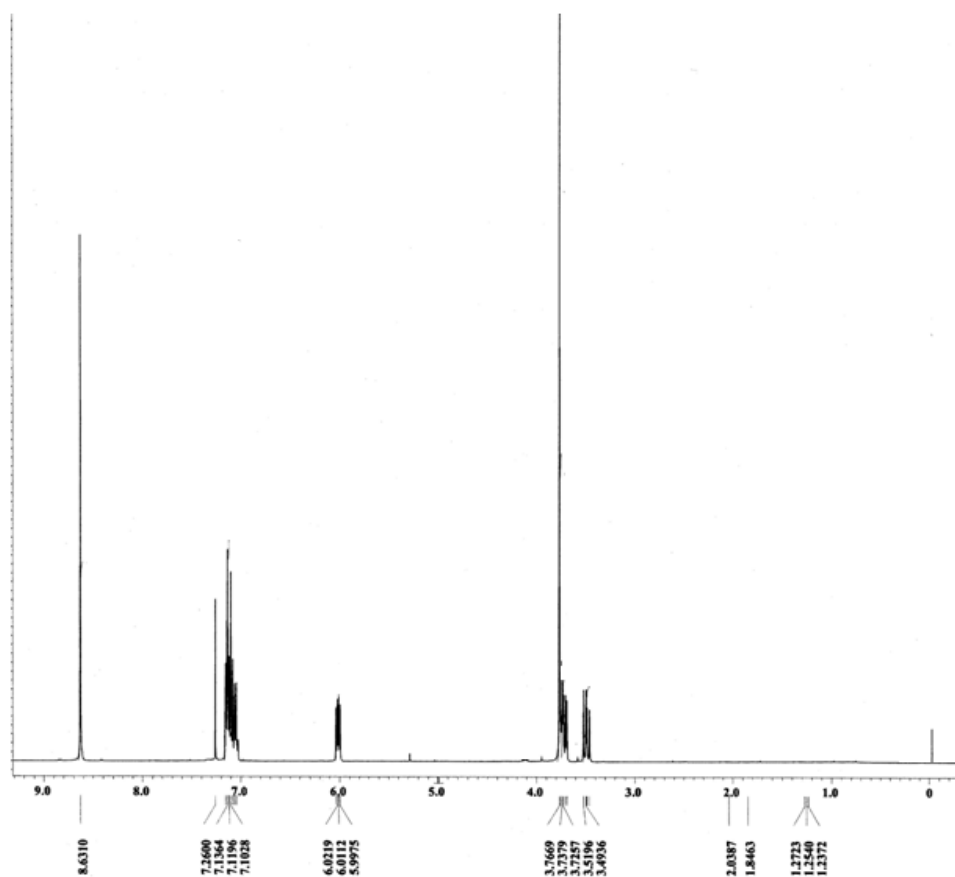


Figure S15: ^1H NMR spectra of NBI **1** in CDCl_3 .

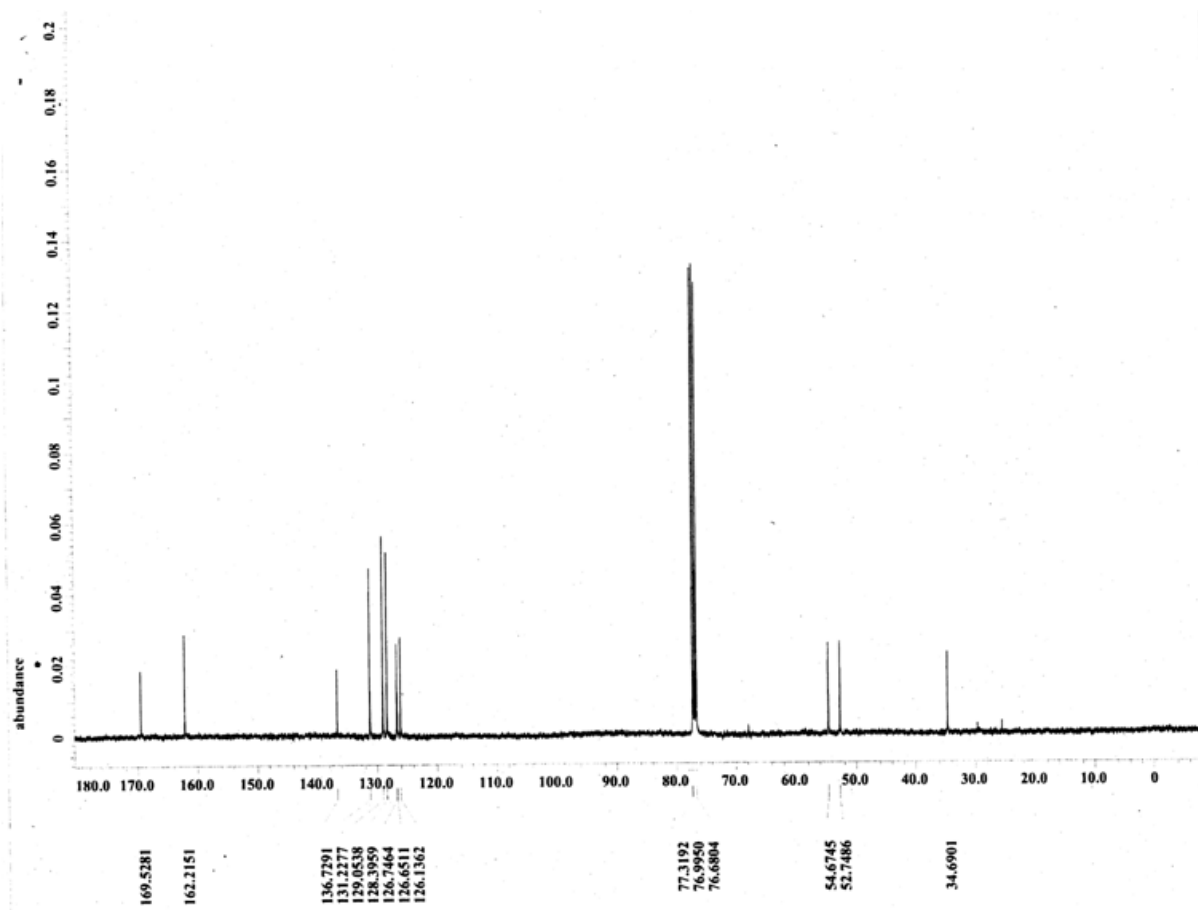


Figure S16: ^{13}C NMR spectra of NBI **1** in CDCl_3 .

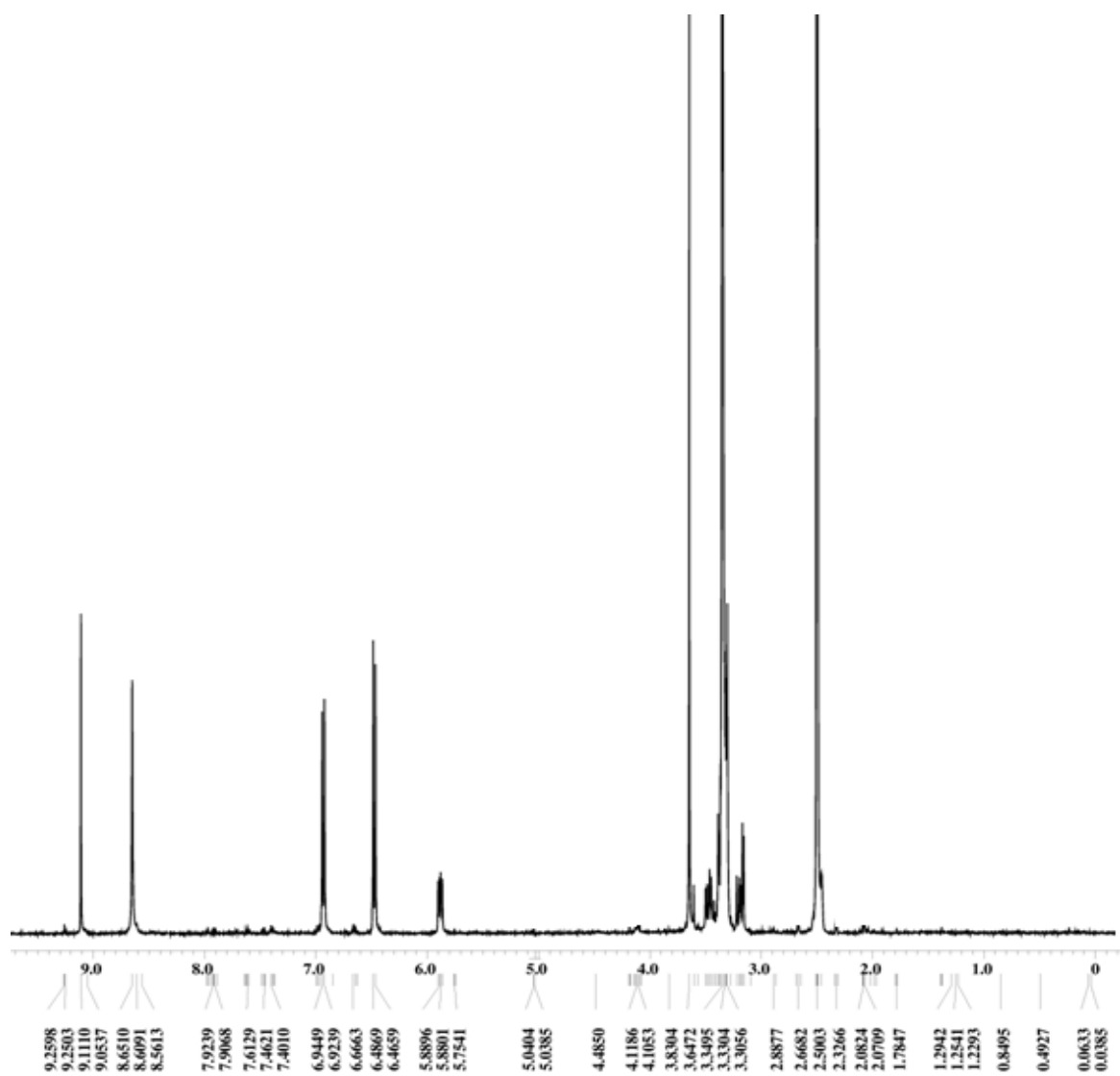


Figure S17: ^1H NMR spectra of NBI 2 in $\text{DMSO-}d_6$.

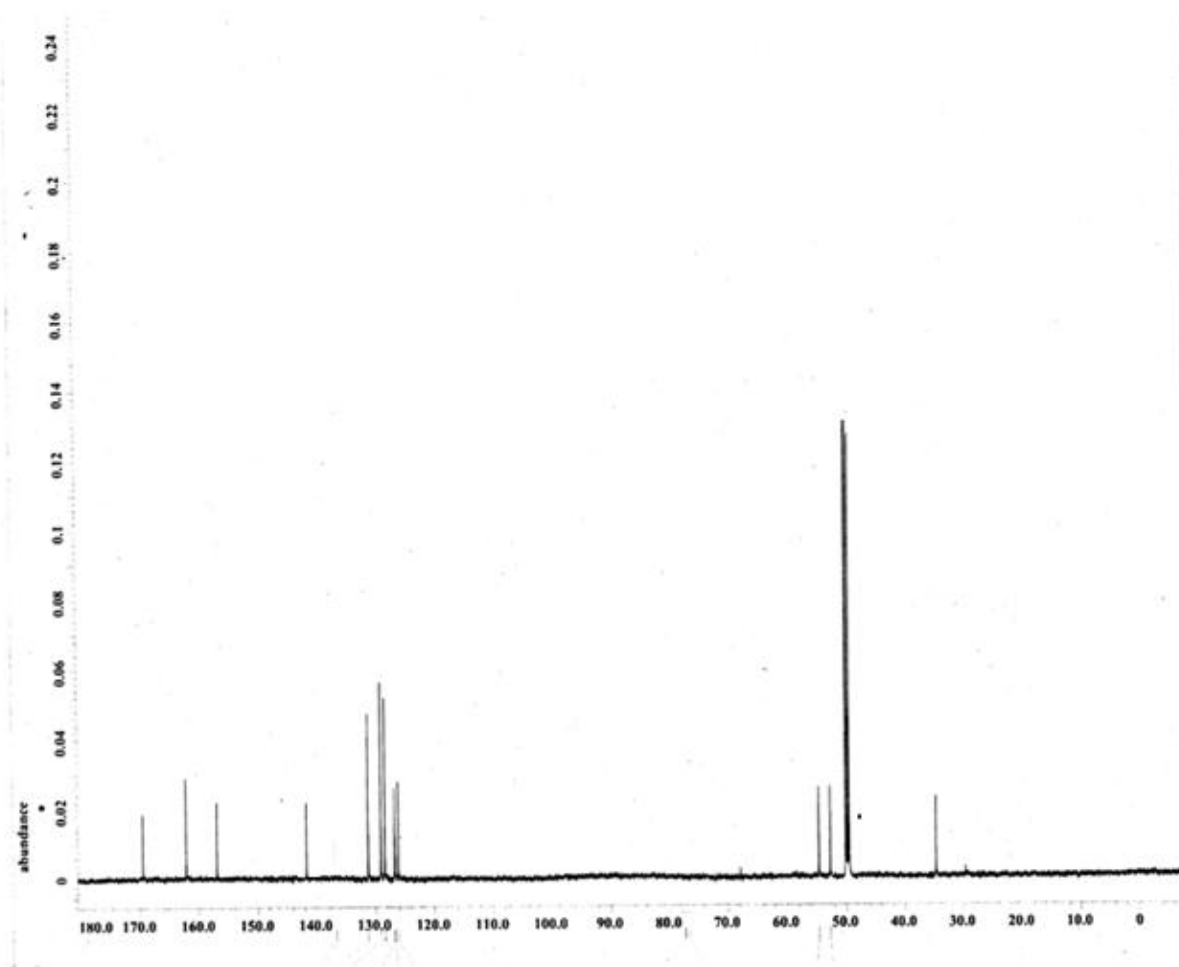


Figure S18: ^{13}C NMR spectra of NBI 2 in CD_3OD .

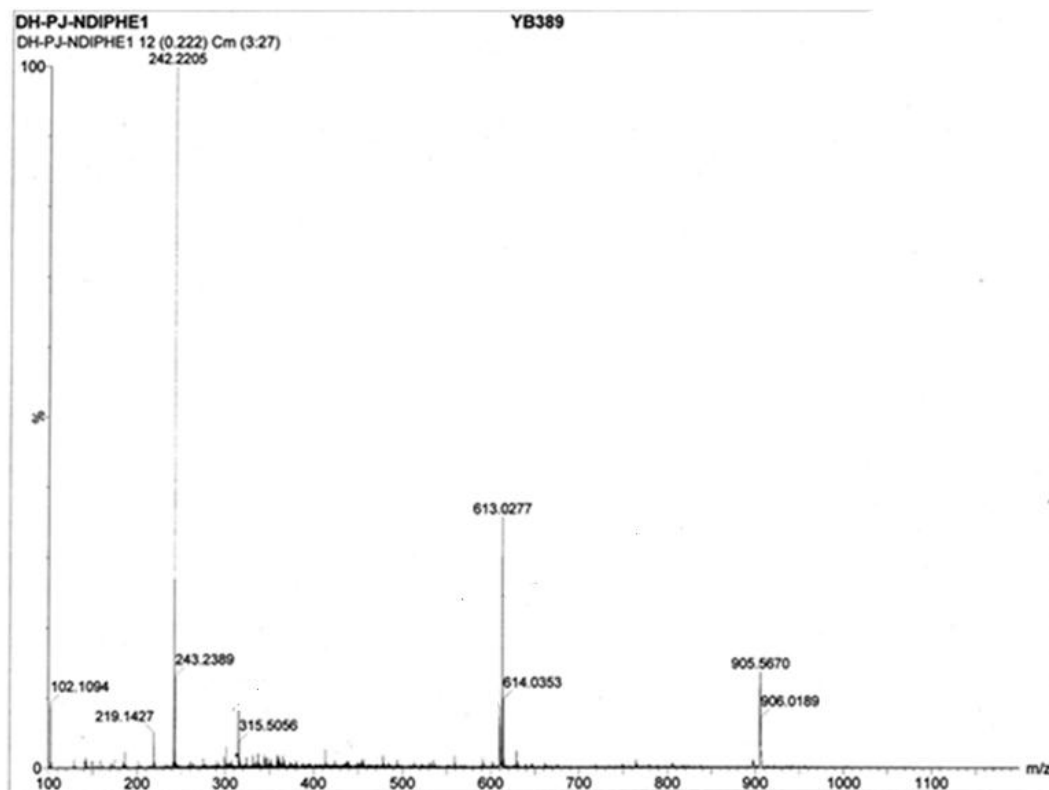


Figure S19: Mass spectra of NBI 1.

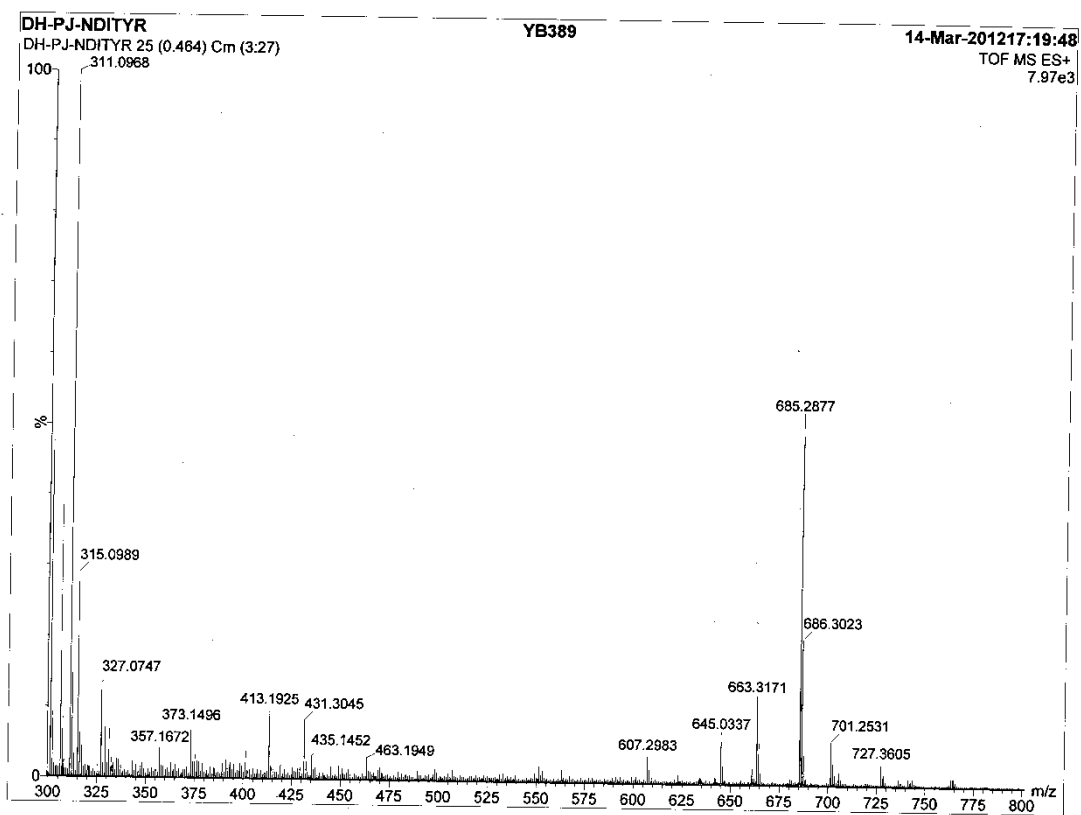


Figure S20: Mass spectra of NBI 2.

NMR Spectroscopy. All NMR studies were carried out on a Bruker AVANCE 500 MHz and JEOL 400 MHz spectrometer at 298 K. Compound concentrations were in the range 1–10 mmol in CDCl₃, CD₃OD and DMSO.

FT-IR Spectroscopy. All reported solid-state FT-IR spectra were obtained with a Perkin Elmer Spectrum RX1 spectrophotometer with the KBr disk technique.

Mass Spectrometry. Mass spectra were recorded on a Q-ToF Micro YA263 high-resolution (Waters Corporation) mass spectrometer by positive-mode electrospray ionization.

UV/vis Spectroscopy. UV/vis absorption spectra of the reported compounds were recorded on a Perkin Elmer UV/vis spectrophotometer.

Fluorescence Spectroscopy. Fluorescent spectrum of the reported bisimides were recorded on a fluorescent spectrometer (Perkin Elmer).

Thermo gravimetric analysis. To accrue the information about thermal stability of bisimides thermo gravimetric analysis were carried out on METTLER TGA instrument. The samples 2-5 mg was placed in aluminum standard 40μL vessels without pin. The samples were then heated under nitrogen atmosphere from 30°-500°C at the heating rate 10°C/min.

Computational Studies. Geometry optimizations and vibrational frequency analyses were carried out without any symmetry constraints at the level of density functional theory (DFT) based methods using the electronic structure program Gaussian 03. The Beck's three parameters hybrid exchange functional combined with the Lee-Yang-Parr non-local correlation function abbreviated as B3LYP has used for calculation. The split-valence bases set with diffuse functions, namely 6-311++G (d, p), have been employed for all atoms. Vibrational frequencies were calculated for optimized molecular structures to verify that no negative frequencies were present for minimum energy structures.

Cyclic Voltametric Study. The cyclic voltametric experiment was carried out by using Princeton Applied Research Potentiostat/ Galvanostat Model/236A. All experiments were

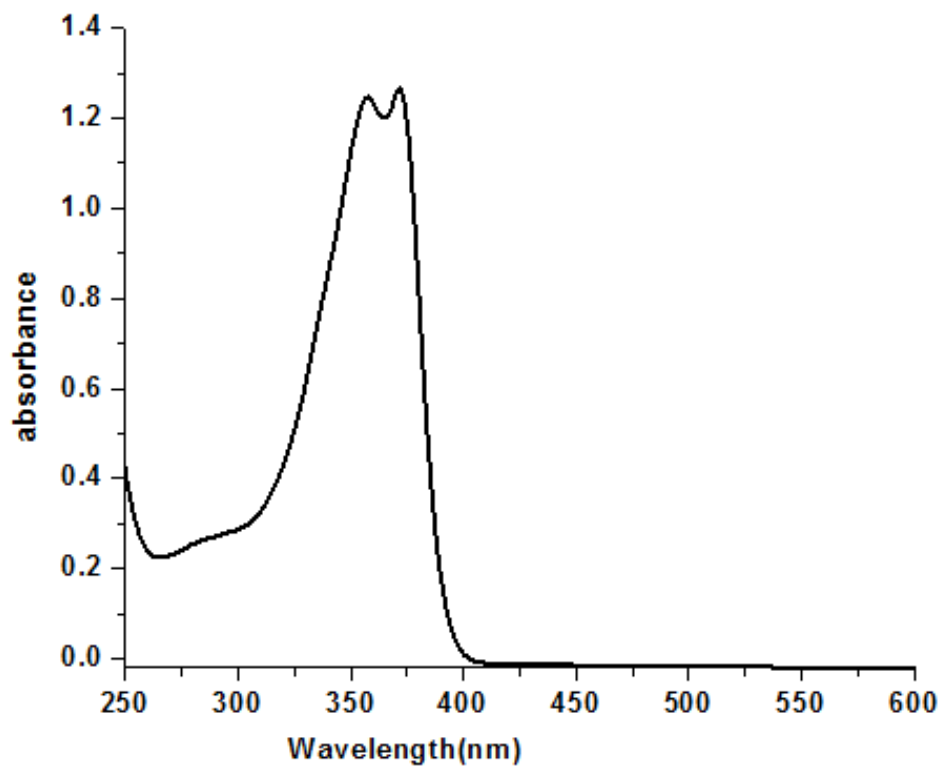
performed in the three-electrode mode using an Ag/AgCl as a reference electrode and a platinum wire as counter electrode. The CV experiments were recorded by scanning the potential from 0 to -2.0 V (vs Ag/AgCl), employing a scan rate of 50 mV/s under N₂ atmosphere. Measurements were recorded in 5 mL of DMF, with 0.1 M (Bu₄N)ClO₄ (TBAPC) as the supporting electrolyte.

Fluorescent Microscopy. The sphere formed by the reported compounds were first drop-casted on a glass slide from methanol/DCM solution, the slides were dried under vacuum, and images were taken.

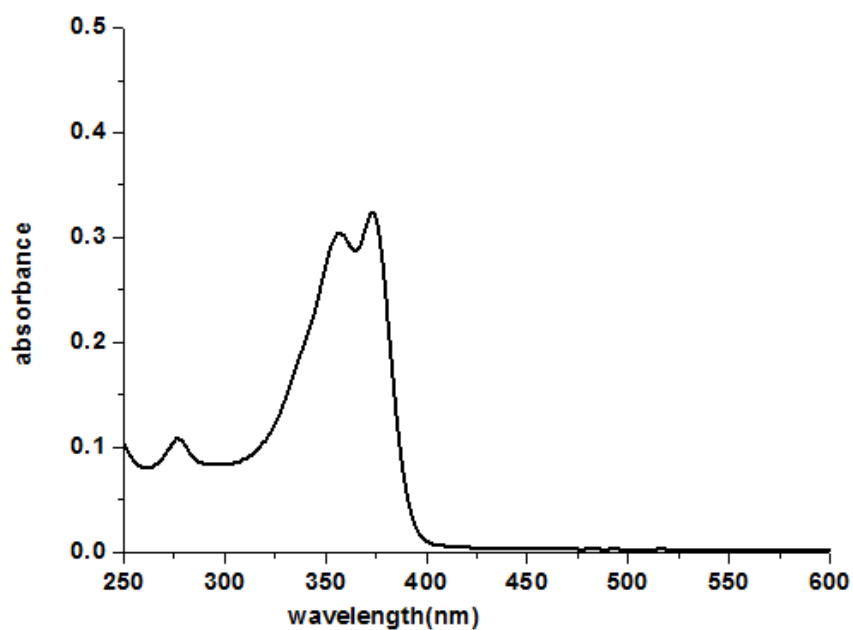
Atomic force microscopy. The morphology of the reported compound was investigated by atomic force microscopy (AFM). A drop of the bisimides **1** or **2** solution in methanol/DCM were placed on a clean microscope cover glass and then dried by slow evaporation. The material was then allowed to dry under vacuum at 30 °C for two days. Images were taken with an NTMDT instrument, model no. AP-0100 in semi contact-mode.

X-ray Crystallography. Single crystal X-ray analysis of bisimide **2** was recorded on a Bruker high resolution X-ray diffractometer instruments with CuK α radiation. Data were processed using the Bruker SAINT Package and the structure solution and refinement procedures were performed using SHELX97.¹ All non-hydrogen atoms were refined with anisotropic thermal parameters.

1. G. M. Sheldrick, SHELX 97. University of Gottingen, Germany, 1997.



ESI Figure S21. Absorption of compound 1 in methanol [0.122 mM] without fluoride anion..



ESI Figure S22. Absorption of compound 2 in methanol [0.049 mM] without fluoride anion..