

## Supporting Information

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## Experimental section:

### Materials:

4'-chloro-2,2':6'',2''-terpyridine chloride, 3-aminopropanol, potassium hydroxide, glycine, *cis*-5-norbornene-*endo*-2,3-dicarboxylic anhydride, diethylchlorophosphate (SAS-Cl), pinacoly methyl phosphonic acid (SOS), tributylphosphate (TBP), diphenylphosphate (DPP), triphenyl phosphate (TPP), triethylamine (TEA), triethylphosphate (TEP) and phosphoric acid (PA), europium(III) chloride, dicyclohexyl carbodiimide (DCC), triethylamine, dimethylsulfoxide (DMSO), dichloromethane (DCM), methanol, toluene, CDCl<sub>3</sub> were purchased as reagent grade from Aldrich, Acros, Merck and used as received. Dichloromethane (DCM) was distilled over calcium hydride and used for reactions.

### Methods:

**Procedures for Lanthanide Metal Incorporation:** All solutions were prepared so that the molar ratio of terpy units to metal ion was known. In a typical experiment, independent solutions of Europium (III) chloride, (typically 0.012 mM), and molecule **1** (0.15 mM) were first prepared in a MeOH-CHCl<sub>3</sub> (1:1) mixture. Then aliquots of each solution were mixed to the appropriate molar ratios.

**NMR Characterization:** NMR spectroscopy was carried out on a Geol 400 MHz spectrometer using CDCl<sub>3</sub> as a solvent. NMR spectra of solutions in CDCl<sub>3</sub> were calibrated to tetramethylsilane as internal standard ( $\delta_{\text{H}}$  0.00).

**Fluorescence Measurements:** Fluorescence emission spectra were recorded on a Fluorescence spectrometer (Horiba Jobin Yvon, Fluoromax-3, Xe-150 W, 250-900 nm). Emission spectra for all solutions were measured with an excitation wavelength of 350 nm. The solutions were diluted to an OD between 0.05-0.02 at 350 nm. Typically the slit widths were 2.5 mm and the scan rate was 200 nm/min. Slit widths and scan rates were adjusted to allow adequate intensity, if needed.

**Mass Analysis:** HRMS analyses were performed with Q-TOF YA263 high resolution (Waters Corporation) instruments by +ve mode electrospray ionization.

**IR Spectroscopy:** IR spectra were obtained on FT-IR Perkin-Elmer spectrometer at a nominal resolution of  $2\text{ cm}^{-1}$ . UV-visible absorption measurements were carried out on U-4100 spectrophotometer HITACHI UV-vis spectrometer, with a scan rate of 500 nm/min.

**UV-Vis experiments:** UV-visible absorption measurements were carried out on U-4100 spectrophotometer HITACHI UV-vis spectrometer, with a scan rate of 500 nm/min. The absorption spectra for all solutions were measured in a quartz cell at concentrations so that the total absorbance was less than 1 abs. units.

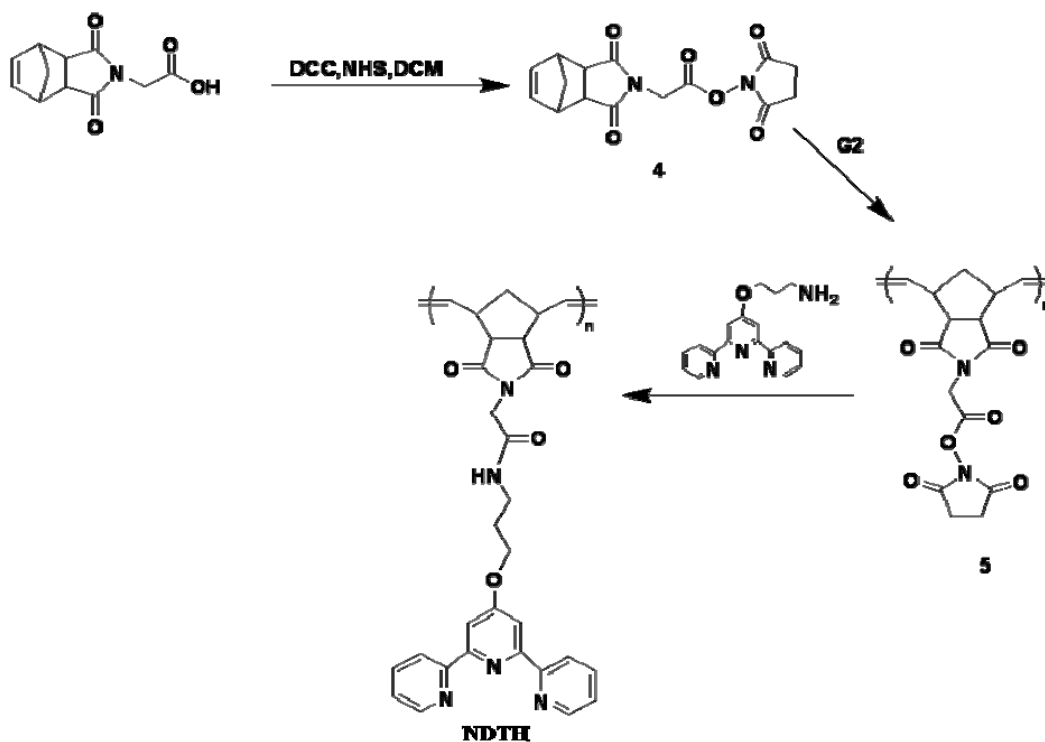
### Synthetic Procedure:

**Synthesis of 1:** 3-aminopropanol (175 mg, 2.24 mmol) was added slowly to a suspension of potassium hydroxide (KOH) (115 mg, 2 mmol) in 10 ml dry dimethylsulfoxide (DMSO). The solution was stirred at  $60\text{ }^{\circ}\text{C}$  for 30 min in an oil bath, followed by addition of 4'-chloro-2,2':6'',2''-terpyridine (300 mg, 1.12 mmol) and continued stirring at  $60\text{ }^{\circ}\text{C}$  for 37 h.<sup>27</sup> The reaction mixture was removed from oil bath and allowed to cool to room temperature. It was poured into 20 mL of deionized water (DI) and stirred for an hour and allowed to stand to form the precipitate. The solid was filtered and dried under vacuum to give 271 mg of compound **1** with 79 % yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.69 (d, 2H), 8.62 (d, 2H), 8.00 (s, 2H), 7.83 (t, 2H), 7.33 (dd, 2H), 4.22 (t, 2H), 2.28 (t, 2H), 1.84 (m, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  167.0, 157.0, 156.0, 148.9, 136.7, 123.7, 121.2, 107.3, 66.0, 38.9, 32.3. IR (KBr,  $\text{cm}^{-1}$ ): 3426, 2354, 2134, 1645, 1412, 1353, 1204, 1020, 948, 793. MS (ESI) calculated: 306.36; found: 306.15.

**Synthesis of 2:** Compound **2** was synthesized following a reported procedure.<sup>28</sup> A round bottom flask was charged with *cis*-5-norbornene-*endo*-2, 3-dicarboxylic anhydride (5.00 g, 30.5 mmol) and glycine (2.38 g, 31.7 mmol, 1.04 equiv). To the solid mixture 30 ml of  $\text{PhCH}_3$  and  $\text{Et}_3\text{N}$  (0.51 ml, 3.7 mmol, 0.12 equiv) were then added. The flask was fitted with a Dean-Stark trap and heated to reflux for 12 h, and then the mixture was allowed to cool to room temperature. The volatiles were removed under reduced pressure and the remaining residue transferred to a separating funnel with 60 ml of EtOAc and extracted with  $2 \times 20$  ml of 0.2 N aqueous HCl. The organic layer was collected and concentrated under reduced pressure. The white solid was dissolved in DCM and washed with brine. Organics layer was separated, dried over sodium sulfate and evaporated in vacuum to get white solid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  9.98 (s, 1H), 6.1 (t, 2H), 4.27 (s, 2H), 3.31 (t, 2H), 3.2 (d, 2H), 1.61 (d, 1H), 1.50 (dt, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 400

MHz) :  $\delta$  177.54, 172.28, 138.32, 48.37, 45.75, 43.18, 39.45. IR (KBr,  $\text{cm}^{-1}$ ): 2991, 1746, 1419, 1329, 1186, 888, 722, 615. MS (ESI) calculated: 222.0766; found: 222.0769.

**Synthesis of NDT:** To a clean, dry round bottomed flask, norbornene (endo) functionalized acid (130 mg, 0.587 mmol) was taken and dissolved in 5 ml of dry DCM and stirred for 10 mins to dissolve. DCC (121 mg, 0.587 mmol) was added to it and stirred for 15 min to form white ppt. Compound **1** was added to it and stirred for overnight. The white precipitate of dicyclohexylurea (DCU) was removed by filtration and the filtrate was washed with brine. Organic layer was separated and dried over sodium sulphate. DCM was evaporated to get white solid. Crude product was purified through alumina with DCM-MeOH. Product came as white fluffy solid yielding 69%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.69 (d, 2H), 8.62 (d, 2H), 8.00 (s, 2H), 7.83 (t, 2H), 7.33 (dd, 2H), 6.1 (s, 2H), 4.3 (t, 2H), 4.2 (s, 2H), 3.4 (d, 2H), 3.3 (d, 2H), 2.28 (t, 2H), 1.84 (m, 2H), 1.75 (dd, 1H), 1.5 (s, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  175.5, 165.2, 164.3, 155.4, 154.2, 147.3, 135.2, 133.0, 122.2, 119.7, 105.6, 64.3, 50.6, 44.4, 43.2, 37.8, 28.0. IR (KBr,  $\text{cm}^{-1}$ ): 3324, 2925, 1711, 1603, 1389, 1228, 996, 805, 745. MS (ESI) calculated: 509.56; found: 509.21.



Scheme: Synthesis of terpy-norbornene polymer by post-polymerization method.

#### Synthesis of **4**:

Norbornene functionalized acid (300 mg, 1.35 mmol) was taken in two neck round bottom flask with a magnetic bar and 8 ml of dry DCM was added to it to dissolve. DCC (364 mg, 1.76 mmol) was added to it and stirred for 15 min to form white ppt. N-hydroxysuccinimide (297 mg, 2.7 mmol) was added to it and stirred for overnight at room temperature. DCU was removed by filtration and filtrate was washed with saturated sodium bicarbonate solution followed by brine solution. Organic layer was separated and dried over Na<sub>2</sub>SO<sub>4</sub>. DCM evaporated to get white solid as product as 92% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 6.1 (t, 2H), 4.27 (s, 2H), 3.31 (t, 2H), 2.8 (s, 4H), 3.2 (d, 2H), 1.61 (d, 1H), 1.50 (dt, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 400 MHz): δ 177.5, 176.2, 157.9, 134.3, 52.0, 45.9, 44.9, 39.0, 25.2. MS (ESI) calculated: 318.28; found: 318.09.

#### Synthesis of **5**:

Compound **1** (200 mg, 0.628 mmol) was taken in a round bottom flask and purged with nitrogen. Dry DCM (5 ml) was added to it under inert atmosphere and stirred to dissolve. **G2** (2 mg, 0.002 mmol) was taken in a separate vial under nitrogen and dissolved in dry DCM. Catalyst dissolved in DCM was added to the stirred solution of the monomer under inert atmosphere and continued stirring at room temperature for 24 h. Polymer formed as precipitate in DCM. Unreacted monomer was washed with DCM and polymer was collected by scratching from the round bottom flask. From the GPC measurement the observed molecular weight, Mn was 45,000 with PDI=1.3. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 5.5 (br, 2H), 5.39 (br, 1H), 4.58 (br, 2H), 3.5-3.3 (br, 4H), 2.8 (s, 8H), 1.61 (br, 1H), 1.50 (br, 1H).

#### Synthesis of **NDTH**:

Compound **5** (30 mg) was taken in a dry round bottom flask and dissolved in 5 ml of dry DMF. Compound **1** (30 mg) was added to it and stirred for 24 h at room temperature. Acetone was poured into the reaction mixture to form a colloidal precipitate. 60 ml of hexane was taken in a beaker and the colloidal solution was added to it and stirred with glass rod. White precipitate appeared and the beaker was kept undisturbed for half an hour to settle the precipitate. The clear solution was decanted and the precipitate was collected and dried under vacuum. From the GPC measurement the observed molecular weight, Mn was 46,000 with PDI=1.4. <sup>1</sup>H NMR analysis suggested that the NHS was replaced by amino

functionalized terpyridine.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  : 8.69-8.62 (br, 2H), 8.00 (br, 2H), 7.4 (br, 1H), 5.39 (br, 2H), 4.7 (br, 1H), 4.1 (br, 2H), 3.5-3.3 (br, 4H), 2.3 (br, 2H), 1.84 (br, 2H) 1.61 (br, 1H), 1.50 (br, 1H).

### Characterization:

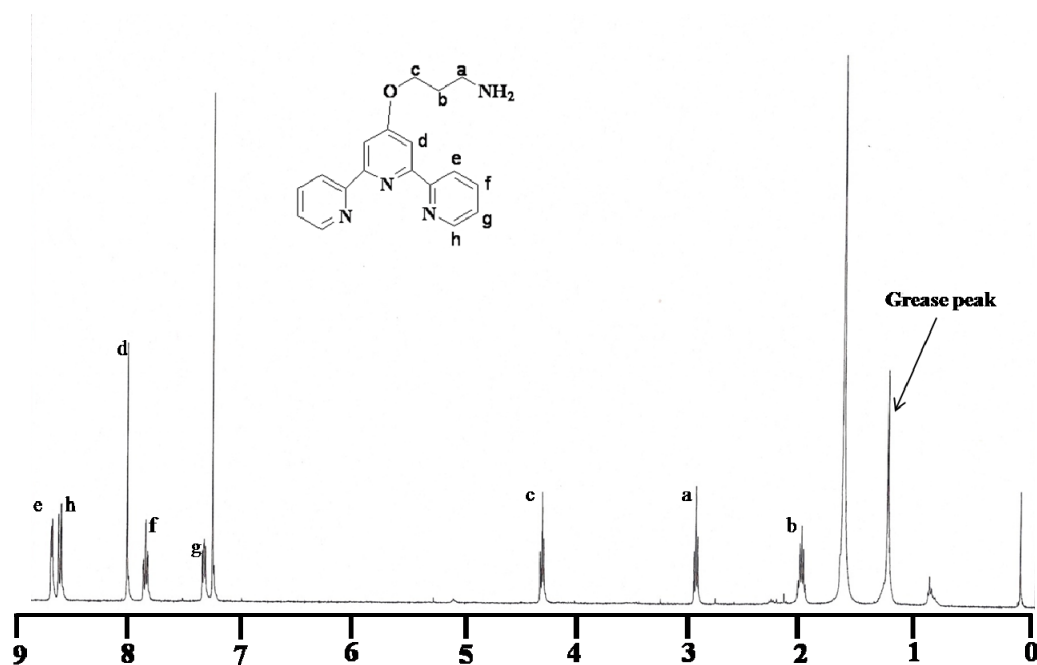


Fig. S1  $^1\text{H}$  NMR spectrum of amino functionalized terpy 1 in  $\text{CDCl}_3$

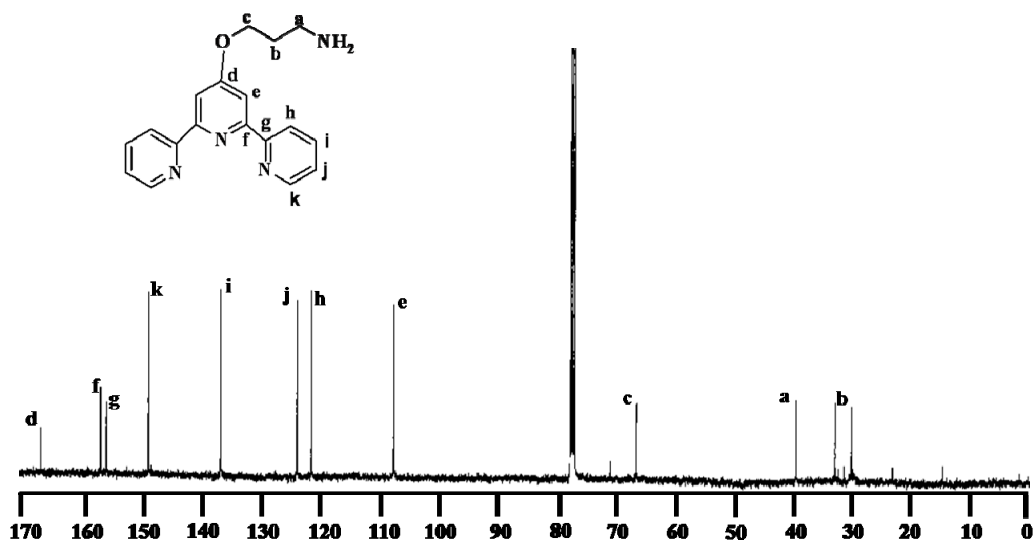


Fig. S2  $^{13}\text{C}$  NMR spectrum of amino functionalized terpy 1 in  $\text{CDCl}_3$

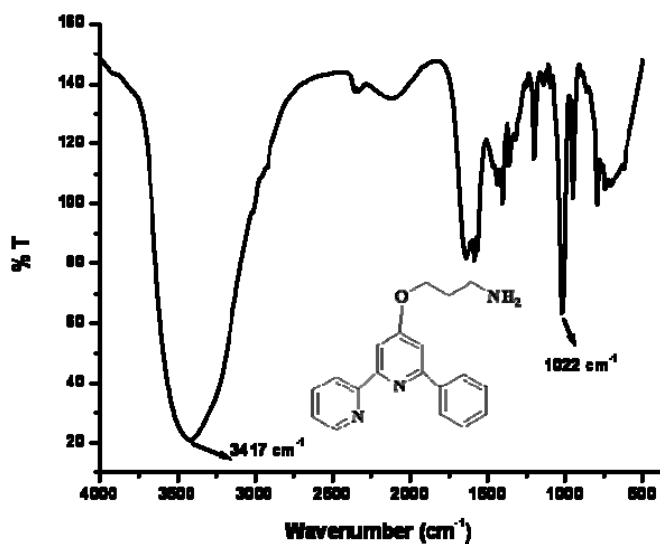


Fig. S3 FT-IR spectrum of amino functionalized terpy 1

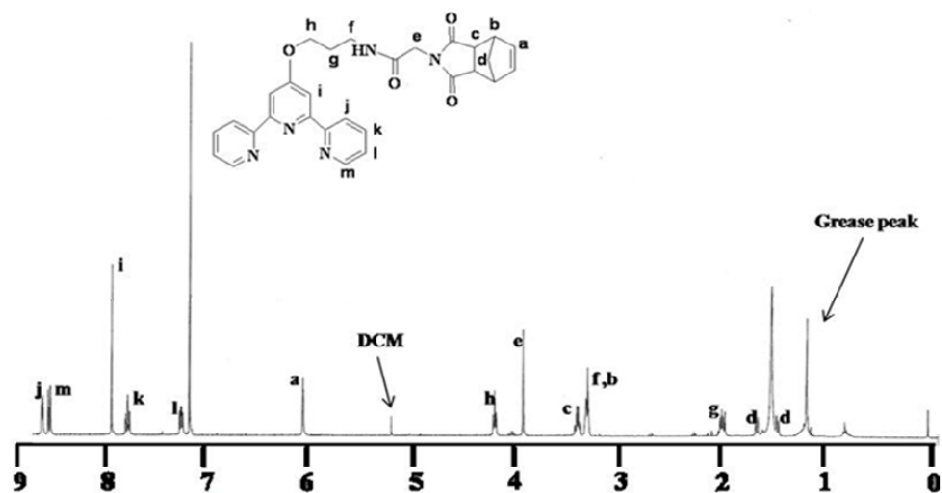


Fig. S4 <sup>1</sup>H NMR spectrum of NDT in CDCl<sub>3</sub>

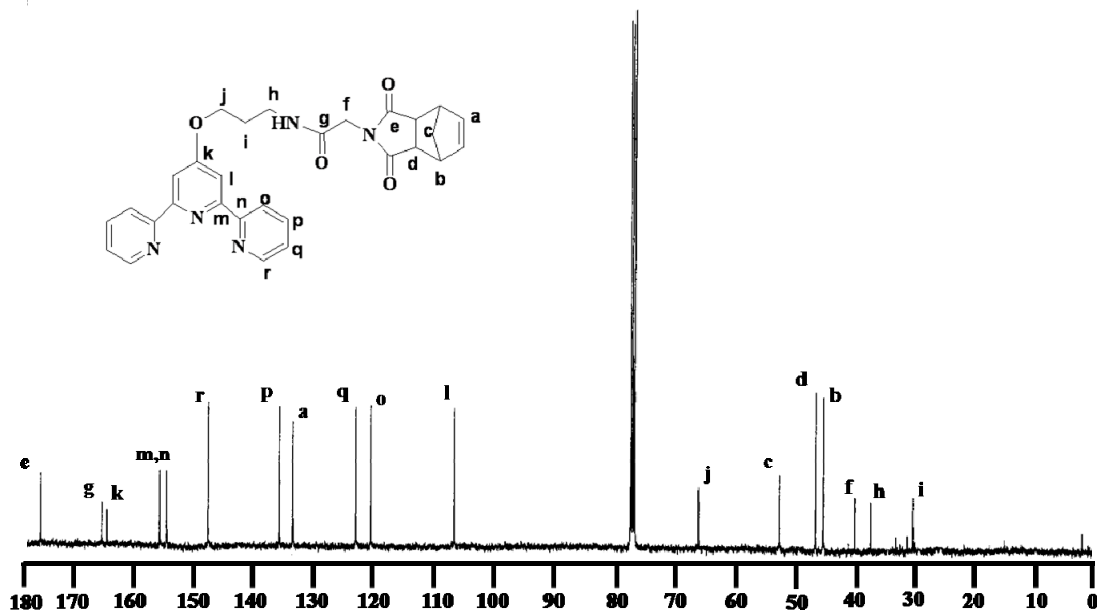


Fig. S5 <sup>13</sup>C NMR spectrum of NDT in CDCl<sub>3</sub>



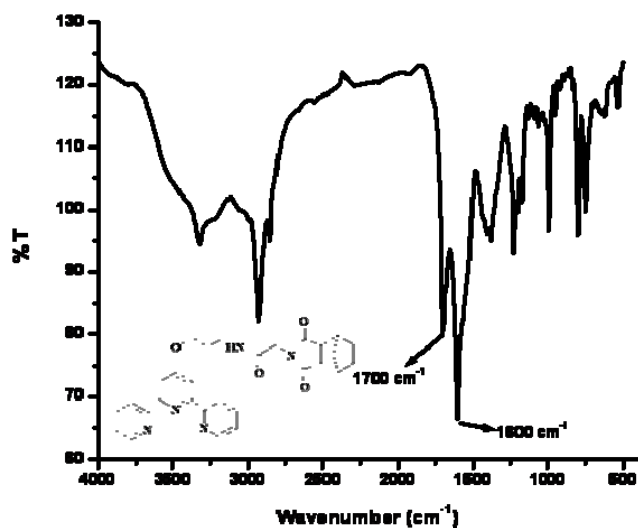


Fig. S6 FT-IR spectrum of NDT

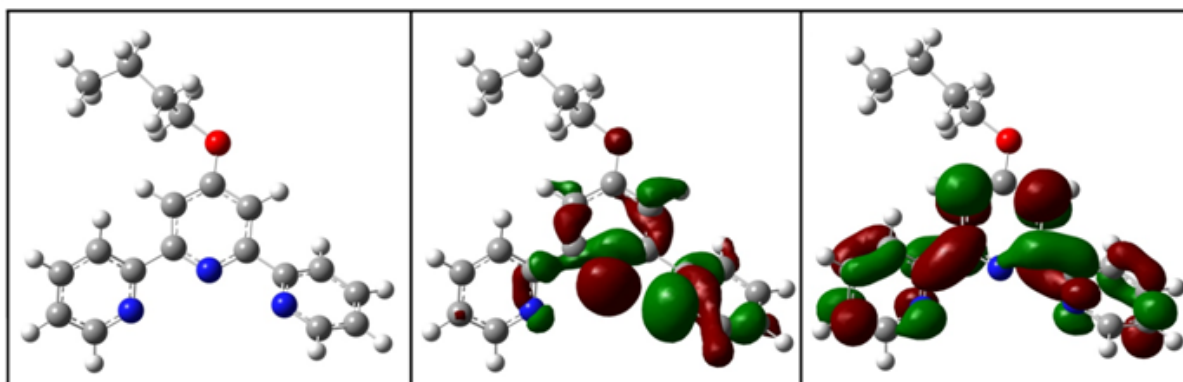


Fig. S7 Optimized structure and Molecular orbital amplitude plots of HOMO and LUMO energy levels of **3c** calculated with the use of B3LYP/6-31G basis set is shown.

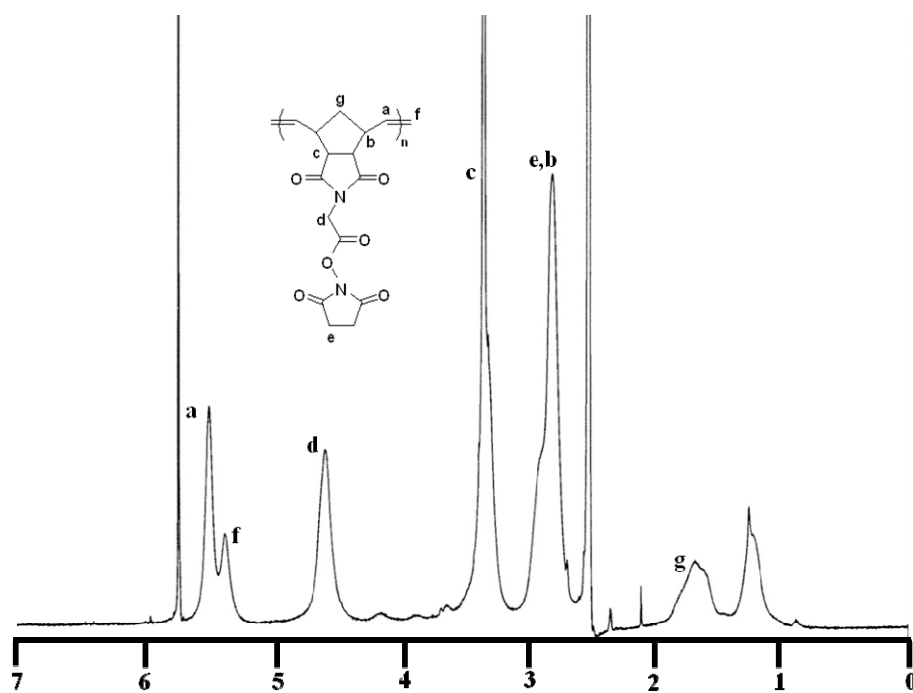


Fig. S8 <sup>1</sup>H NMR spectrum of 5 in DMSO-d<sub>6</sub>

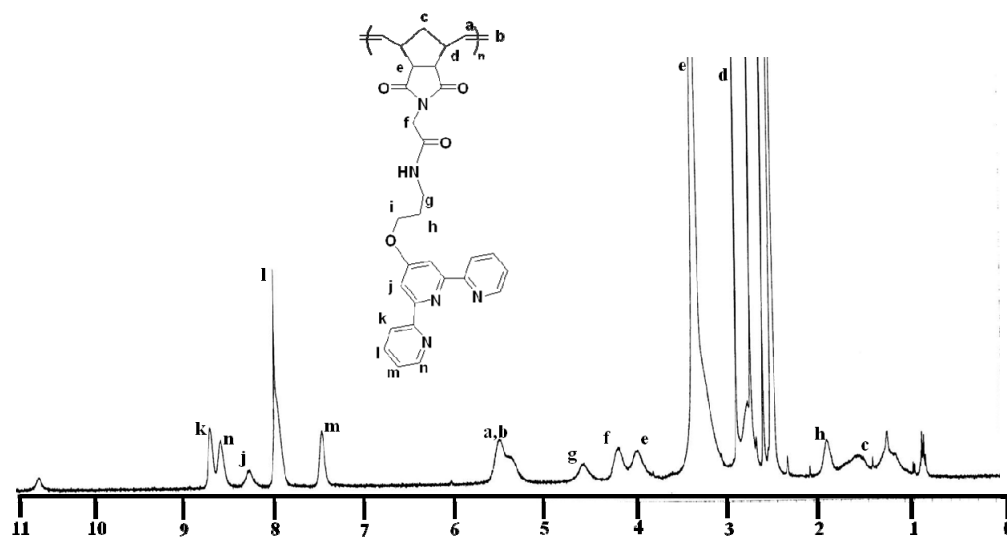


Fig. S9 <sup>1</sup>H NMR spectrum of NDTH in DMSO-d<sub>6</sub>

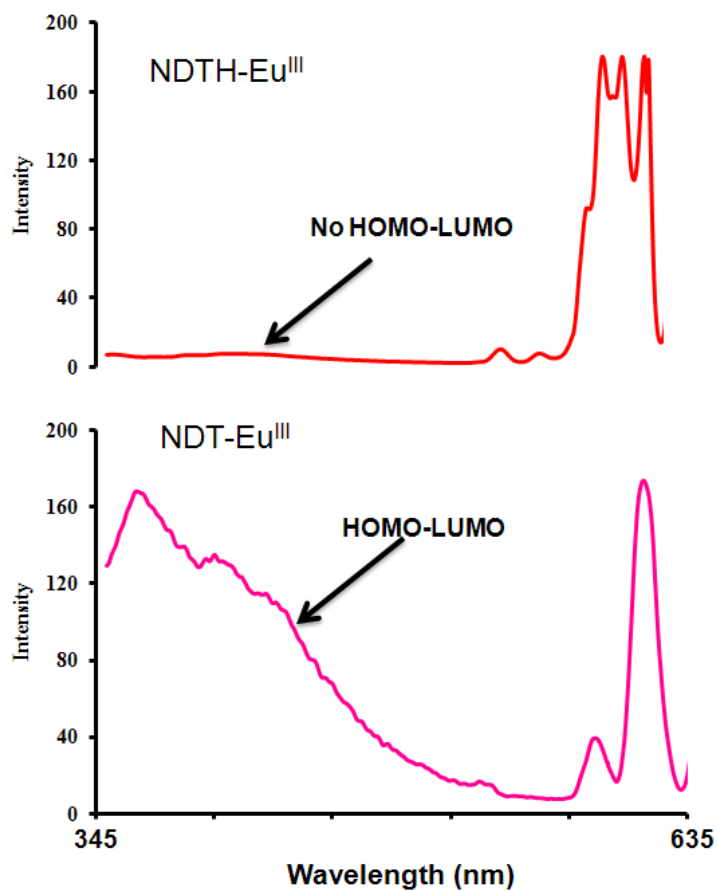


Fig. S10 Fluorescence spectra of NDTH-Eu<sup>III</sup> in DMF and NDT-Eu<sup>III</sup> in methanol.

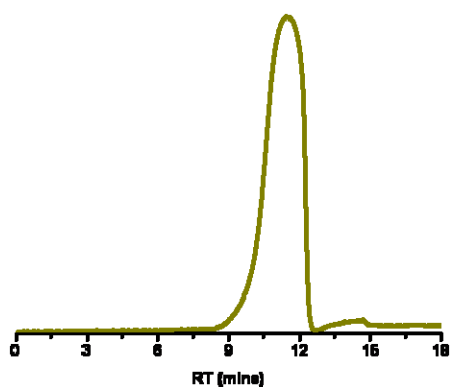


Fig. S11 GPC analysis of NDTH ( $M_n = 46,000$  &  $PDI = 1.4$ )

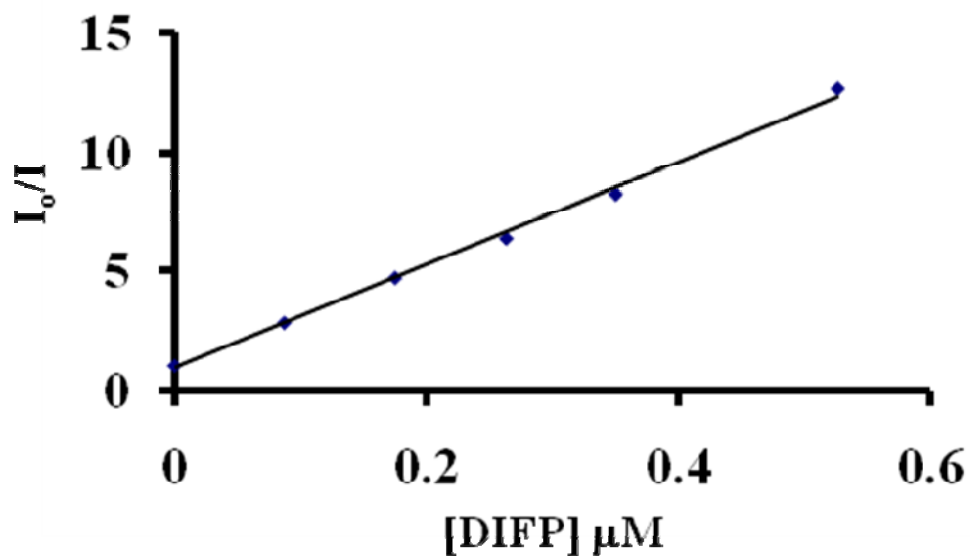


Fig. S12. A plot of  $I_0/I$  values against [DIFP].

Note: Different stock solutions of diethyl chlorophosphate of 10ppb, 20ppb, 30ppb, 40ppb, 50ppb were prepared in methanol. NDT-Eu(III) complex solution (1:1 molar ratio) in methanol was taken in five different vials and different conc of SAS-Cl (of same volume) was added to observe change in fluorescence spectrum. Upto 30ppb there was no change in fluorescence but after addition of 40ppb stock solution of SAS-Cl change in fluorescence was observed.

10 ppb=8.4μL of diethyl chlorophosphate in 1lit.

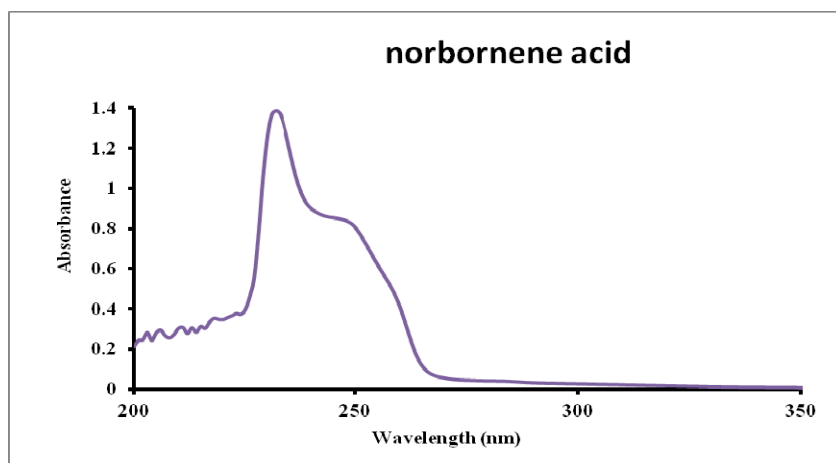


Fig. S13. UV-Vis absorption spectrum of norbornene functionalized acid (2) in dichloromethane.

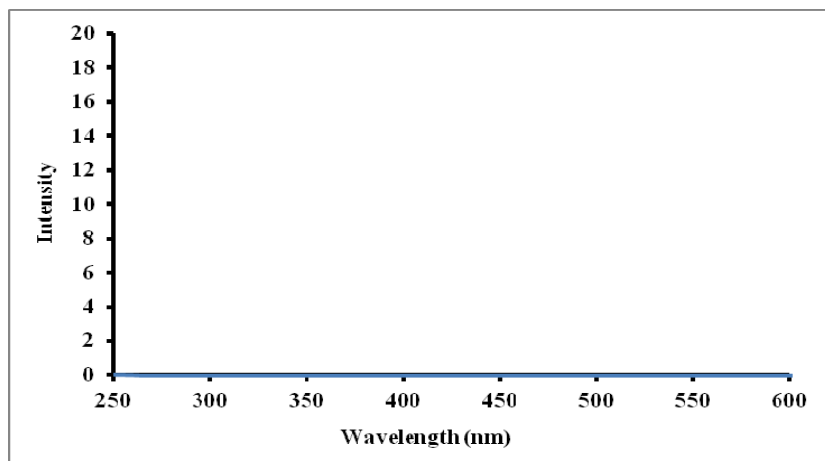


Fig. S14. Fluorescence spectrum of norbornene functionalized acid (**2**) in dichloromethane which showed no emission.