

Electronic Supplementary Information

for

**Luminescent hexagonal microtubes prepared through water-induced self-assembly of a polymorphic organoboron compound: Formation mechanism and waveguide behaviour**

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## **Table of contents**

1. Material and methods	<b>S03</b>
2. Synthesis of compounds	<b>S06</b>
3. Single-crystal X-ray diffraction studies	<b>S08</b>
4. Preparation of self-assembly	<b>S12</b>
5. Powder XRD of Hexagonal microtubes (HMTs)	<b>S14</b>
6. Selected area electron diffraction pattern (SAED)	<b>S14</b>
7. TGA and DSC profile for Hexagonal microtubes (HMTs)	<b>S15</b>
8. Quantum yield measurement	<b>S15</b>
9. NMR characterization	<b>S16</b>

## 1. Materials and methods

2-Hydroxy-1-naphthaldehyde, o-phenylenediamine and phenylboronic acid were purchased from Sigma-Aldrich Chemical Company. NaHSO<sub>3</sub> and K<sub>3</sub>PO<sub>4</sub> was purchased from Spectrochem Pvt. Ltd. These chemicals were used as received. Spectroscopy-grade solvents purchased from commercial source Spectrochem Pvt. Ltd. India were used for spectroscopic analyses.

**Nuclear Magnetic Resonance (NMR):** Nuclear Magnetic Resonance (NMR) studies were performed on Bruker Ultra Shield (500 MHz) spectrometer with TMS (tetramethylsilane) as the internal standard.

**High-resolution mass spectrometry (HRMS):** The HRMS data of the compound was recorded using Bruker MicrOTOF-Q-II mass spectrophotometer in electrospray ionization (ESI) mode.

**Fourier transform infrared spectroscopy (FTIR):** Fourier transform infrared (FTIR) spectroscopy experiments were performed in the 400 cm<sup>-1</sup> to 4000 cm<sup>-1</sup> range using a Perkin-Elmer Model UATR Spectrum Two Instrument.

**Thermogravimetric analysis (TGA):** Thermo gravimetric analysis (TGA) was performed using a Perkin Elmer-TGA 4000 instrument under high-purity nitrogen.

**Differential Scanning Colorimetry (DSC):** The phase transition temperatures were measured using Perkin Elmer-DSC 6000 at heating and cooling rates of 5°C min<sup>-1</sup> under high purity nitrogen condition.

**Powder X-ray diffraction analysis (PXRD):** PANalytical Empyrean X-ray diffractometer was used in the Bragg-Brentano geometry (Cu-K<sub>α1</sub>, λ= 1.5405 Å, filter: Ni beta). The data was collected in the angular range, 2θ = 5-50°, using the Pixel3D detector. The simulated XRD pattern for both samples was produced from crystallographic data of keto-amine and enol-imine using mercury (version 4.2.0) software.

**Field emission scanning electron microscopy (FESEM):** The morphologies of the samples were observed using Carl Zeiss (Ultra plus) field emission scanning electron microscope. Samples for microscopy were prepared by drop-casting the respective sample on a freshly

cleaved mica surface. All samples were coated with a thin layer of sputtered gold before imaging. The accelerating voltage of 15 kV was used for imaging.

**High resolution transmission electron microscopy (HRTEM):** The morphology of samples was investigated using the FEI TALOS 200S instrument at a working voltage of 200 kV. Samples for TEM analysis was prepared by drop-casting samples over a carbon-coated 400 mesh Cu grid and stained with 0.3 percent phosphotungstic acid (PTA) for 20 seconds.

**Single crystal X-ray diffraction (SC-XRD):** Single Crystal X-ray Diffraction data were collected on a Bruker D8 Venture diffractometer equipped with a Photon-III detector using monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 100 K using an Oxford cryostream low-temperature device. Unit cell measurement, data integration, scaling and absorption corrections for the crystal were done with Bruker APEX II software.<sup>1</sup> Data reduction was carried out with Bruker SAINT suite.<sup>2</sup> Absorption correction was performed by the multi-scan method implemented in SADABS.<sup>3</sup> All the crystal structures were solved by direct methods using SIR 2014.<sup>4</sup> The crystal structure refinements were done in the program package OLEX2<sup>5</sup> and all non-hydrogen atoms were refined anisotropically by full-matrix least-squares calculations based on F<sup>2</sup> with SHELXL-2018/3<sup>6</sup>. Except the hydrogens of N-H and O-H all others have calculated positions as riding atoms. The PARST<sup>7</sup> and MERCURY<sup>8</sup> programs were used for structure analysis and for drawing the diagrams.

**Fluorescence spectroscopy:** Fluorescence measurements were carried out on a Jobin Yvon Horiba Model Fluorolog-3-21. Measurements were performed using a Quartz cuvette with a 10 mm path length. The absolute quantum yield of HNBI-B in different forms were calculated using BaSO<sub>4</sub>-coated integrating sphere from HORIBA Jobin Yvon attached to Fluorolog-3-21. Quantum yield in solution state were calculated using standard reference 9,10 Diphenyl anthracene (in cyclohexane, QY=1) by following equation.

$$\phi_x = \phi_s \left( \frac{Grad_x}{Grads} \right) \left( \frac{\eta_{2x}}{\eta_{2s}} \right)$$

**UV-spectroscopy:** Photophysical measurements were performed using a Quartz cuvette with a 10 mm path length. The absorbance spectra were recorded on Analytikjena specord 210 plus UV-Vis-NIR Spectrophotometer.

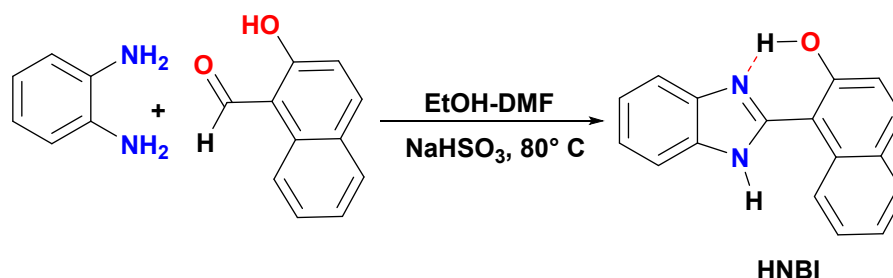
**Single crystal preparation by vapor diffusion method:** In 5 ml vial, 1mg/ml solution of HNBI-B prepared in each solvent *viz.* CHCl<sub>3</sub>, EtOAc and MeOH. These vials were kept in hexane environment at RT for one week to obtain the polymorphic crystals. Photoluminescence images were taken with inverted Olympus optical microscope.

**Time-dependent formation mechanism study by SEM/TEM:** To observe the formation mechanism by SEM/TEM, we prepare the 1 ml solution of HNBI-B in 50% H<sub>2</sub>O-MeOH with 50  $\mu$ M concentration. The prepared sample were drop-cast for SEM with different time intervals as t=0, 1, 2, 3 and 4 hrs. Results indicates the hexagonal microtubes were formed through the fusion of nano-discoids.

**Optical Waveguide study:** Waveguiding behaviour of the rod-shaped crystals and hexagonal microtubes was studied using a supercontinuum source with a spectral filter of  $\lambda = 405$  nm. Both of this (HMTs and rod-shaped crystals) were irradiated in a direction perpendicular to its long axis at different positions with a 405 nm laser from a Ti:sapphire regenerative amplifier (Astrella, Coherent) operated at 800 nm with a repetition rate of 1 kHz and pulse duration of  $\sim 35$  fs. The light was collected at the tip of the crystal that was manually aligned with a micromanipulator to the end of an optical fiber connected to a StellerNet BLUE-Wave spectrometer. Optical loss coefficients (OLCs) of HMTs and rod-shaped crystals were calculated by reported procedure.

## 2. Synthesis

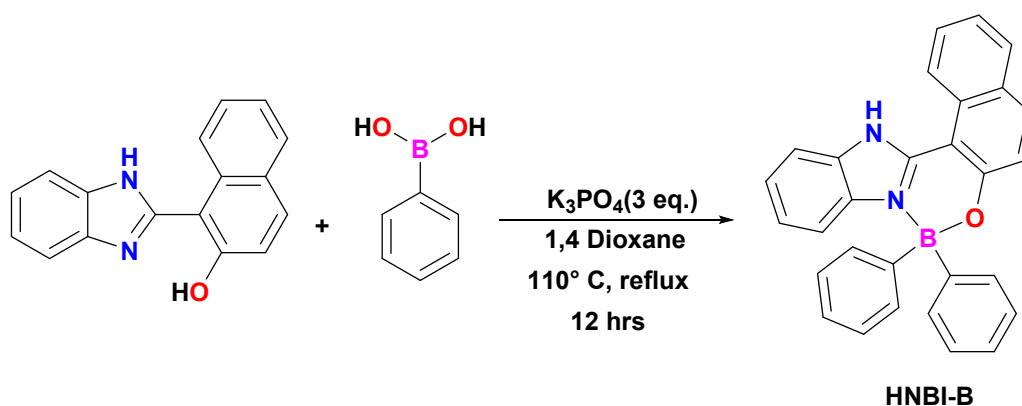
### a) Synthesis of 2-(2'-Hydroxynaphthyl) benzimidazole (HNBI)



**Scheme 1:** Synthesis of HNBI by condensation of diamine and aldehyde

**HNBI** was synthesized by the reported process.<sup>1,2</sup> In 25 ml of ethanol, 2-hydroxy-1-naphthaldehyde (0.86 g, 5 mmol) and NaHSO<sub>3</sub> (0.624 g, 6 mmol) were added as a catalyst and stirred for 4 hours at room temperature. After 4 hours, the white precipitate was observed. The reaction mixture was then heated with *o*-Phenylenediamine (0.54 g, 5 mmol, in 15 ml DMF) at 80° C for 2 h. The progress of the reaction was monitored by the TLC. After the reaction was completed, the reaction mixture was allowed to cool to room temperature. Then the reaction mixture was added dropwise in 450 ml of distilled water, resulting in a large number of yellow precipitations, then left undisturbed, filtered, and washed three times with distilled water. The product HNBI was recrystallized with absolute ethanol to obtain yellow crystals in 90% yield. <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>): δ 12.27 (s, 2H), 8.24 (d, *J* = 8.6 Hz, 1H), 7.97 (d, *J* = 8.9 Hz, 1H), 7.92 (d, *J* = 8.1 Hz, 1H), 7.72 – 7.65 (m, 2H), 7.56 – 7.51 (m, 1H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.34 (d, *J* = 8.9 Hz, 1H), 7.28 (dd, *J* = 5.9, 3.1 Hz, 2H). ESI-HRMS calculated for C<sub>17</sub>H<sub>12</sub>N<sub>2</sub>O **260.10**, found **261.10** [M+H]<sup>+</sup>

**b) Synthesis of HNBI-B complex:**



**Scheme 2:** Synthesis of HNBI-B from condensation of phenyl boronic acid and HNBI.

0.2 g (0.77 mmol) **HNBI** and 0.8 g (6.92 mmol) Ph-B(OH)<sub>2</sub> was dissolved in 15 ml of 1, 4 dioxane. Then 0.5 g (2.3 mmol) K<sub>3</sub>PO<sub>4</sub> was added to it. The mixture was refluxed at 110 °C for 12 hrs. Progress of the reaction monitored by thin layer chromatography. After completion of the reaction, concentrated under reduced pressure. To this 10 ml water was added and compound was extracted with DCM (3× 40 ml). Finally, obtained solid was washed with distilled water 3 times and purified by flash column chromatography. **HNBI-B** was obtained in 85% of yield after purification.

<sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>): δ 13.90 (s, 1H), 8.38 – 8.30 (m, 1H), 8.05 (d, *J* = 9.0 Hz, 1H), 7.94 (d, *J* = 7.7 Hz, 1H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.68 (t, *J* = 7.1 Hz, 1H), 7.45 (t, *J* = 7.3 Hz, 1H), 7.37 (dd, *J* = 12.0, 6.4 Hz, 2H), 7.24 (dd, *J* = 7.6, 1.7 Hz, 4H), 7.18 – 7.07 (m, 7H), 6.63 (d, *J* = 8.3 Hz, 1H).

<sup>13</sup>C NMR (125 MHz, DMSO-d<sub>6</sub>): δ 165.41, 157.17, 140.38, 135.57, 134.36, 132.90, 129.34, 127.99, 127.69, 123.62, 120.52, 119.30, 119.13, 118.84, 116.07, 109.69. HRMS-ESI: *m/z* For C<sub>29</sub>H<sub>21</sub>BN<sub>2</sub>O calculated- 424.18, found 425.18 [M+H]<sup>+</sup>.

### 3. Single-crystal X-ray diffraction studies

Identification code	HNBI-B in CHCl <sub>3</sub>
<b>CCDC</b>	<a href="#">2150129</a>
Empirical formula	C <sub>29</sub> H <sub>21</sub> BN <sub>2</sub> O
Formula weight	424.29
Temperature/K	296 (2)
Crystal system	triclinic
Space group	<i>P</i> -1
<i>a</i> /Å	11.7055(2)
<i>b</i> /Å	11.9927(2)
<i>c</i> /Å	16.2739(3)
$\alpha$ /°	73.063(1)
$\beta$ /°	74.387(1)
$\gamma$ /°	88.940(1)
Volume/Å <sup>3</sup>	2100.36(7)
<i>Z</i>	4
$\rho_{\text{calc}}$ /cm <sup>3</sup>	1.342
$\mu$ /mm <sup>-1</sup>	0.081
<i>F</i> (000)	888.0
Crystal size/mm <sup>3</sup>	0.55 × 0.42 × 0.35
Radiation	Mo K $\alpha$ ( $\lambda$ = 0.71073)
2 $\Theta$ range for data collection/°	2.72 to 59.14
<b>Treatment of Hydrogen</b>	mixed
Index ranges	-16 ≤ <i>h</i> ≤ 16, -16 ≤ <i>k</i> ≤ 16, -22 ≤ <i>l</i> ≤ 22
Reflections collected	42650
No. of unique Ref/obs. Ref.	11699/8328
Data/restraints/parameters	11699/0/595
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.073
Final <i>R</i> indexes [ <i>I</i> ≥ 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0551, <i>wR</i> <sub>2</sub> = 0.1278
Final <i>R</i> indexes [all data]	<i>R</i> <sub>1</sub> = 0.0823, <i>wR</i> <sub>2</sub> = 0.1404
Largest diff. peak/hole / e Å <sup>-3</sup>	0.34/-0.28



Identification code	HNBI-B in Ethyl acetate
CCDC	<a href="#">2207239</a>
Empirical formula	C <sub>33</sub> H <sub>29</sub> BN <sub>2</sub> O <sub>3</sub>
Formula weight	512.42
Temperature/K	296(2)
Crystal system	triclinic
Space group	<i>P</i> -1
<i>a</i> /Å	10.8845(7)
<i>b</i> /Å	11.1645(7)
<i>c</i> /Å	12.9737(8)
$\alpha$ /°	98.148(4)
$\beta$ /°	105.243(4)
$\gamma$ /°	112.124(4)
Volume/Å <sup>3</sup>	1357.02(15)
Z	2
$\rho_{\text{calc}}$ /cm <sup>3</sup>	1.254
$\mu$ /mm <sup>-1</sup>	0.080
F(000)	540.3
Crystal size/mm <sup>3</sup>	0.59 × 0.47 × 0.33
Radiation	Mo K $\alpha$ ( $\lambda$ = 0.71073)
2 $\Theta$ range for data collection/°	3.378 to 50.7
Treatment of Hydrogen	Mixed
Index ranges	-12 ≤ <i>h</i> ≤ 13, -13 ≤ <i>k</i> ≤ 13, -14 ≤ <i>l</i> ≤ 15
Reflections collected	18827
No. of unique Ref/obs. Ref.	4957/3601
Data/restraints/parameters	4957/0/354
Goodness-of-fit on F <sup>2</sup>	1.037
Final R indexes [ <i>I</i> ≥ 2 $\sigma$ ( <i>I</i> )]	R <sub>1</sub> = 0.0539, wR <sub>2</sub> = 0.1363
Final R indexes [all data]	R <sub>1</sub> = 0.0758, wR <sub>2</sub> = 0.1489
Largest diff. peak/hole / e Å <sup>-3</sup>	0.23/-0.25

<b>Table S3: Crystal data and structure refinement for HNBI-B in methanol</b>	
Identification code	HNBI-B in MeOH
CCDC	<a href="#">2143299</a>
Empirical formula	C <sub>88</sub> H <sub>67</sub> B <sub>3</sub> N <sub>6</sub> O <sub>4</sub>
Formula weight	1304.90
Temperature/K	100.00
Crystal system	orthorhombic
Space group	<i>Pbca</i>
<i>a</i> /Å	18.0502(19)
<i>b</i> /Å	15.0301(15)
<i>c</i> /Å	47.798(5)
$\alpha$ /°	90
$\beta$ /°	90
$\gamma$ /°	90
Volume/Å <sup>3</sup>	12967(2)
Z	8
$\rho_{\text{calc}}$ /cm <sup>3</sup>	1.337
$\mu$ /mm <sup>-1</sup>	0.082
F(000)	5472.0
Crystal size/mm <sup>3</sup>	0.37 × 0.077 × 0.061
Radiation	MoK $\alpha$ ( $\lambda$ = 0.71073)
2 $\Theta$ range for data collection/°	3.916 to 60.348
Treatment of Hydrogen	Mixed
Index ranges	-25 ≤ <i>h</i> ≤ 25, -21 ≤ <i>k</i> ≤ 17, -67 ≤ <i>l</i> ≤ 67
Reflections collected	262021
No. of unique Ref/obs. Ref.	19197/9591
Data/restraints/parameters	19197/0/930
Goodness-of-fit on F <sup>2</sup>	1.021
Final R indexes [ <i>I</i> ≥ 2 $\sigma$ ( <i>I</i> )]	R <sub>1</sub> = 0.0904, wR <sub>2</sub> = 0.1696
Final R indexes [all data]	R <sub>1</sub> = 0.1871, wR <sub>2</sub> = 0.1999
Largest diff. peak/hole / e Å <sup>-3</sup>	0.46/-0.35

**Table S4: List of important intermolecular interactions in HNBI-B<sub>2</sub>CHCl<sub>3</sub>**

Interactions	D...H(Å)	D...A (Å)	H...A (Å)	D-H...A(°)	Symmetry code
C10A-H10A...O1	0.93	3.407(2)	2.50	166	x, y, z
C10-H10...O2	0.93	3.518(2)	2.68	150	x, y, z
C15-H15...N2	0.93	3.017(2)	2.39	124	x, y, z
C15A-H15A...N4	0.93	3.069(2)	2.47	122	x, y, z
N2-H2...C11( $\pi$ )	0.93(2)	3.269(2)	2.82	111(2)	-x+1, -y+1, -z
N4-H4...C23( $\pi$ )	0.92(2)	3.223(2)	2.35	157(2)	x, +y-1, +z
C14( $\pi$ )...C3A( $\pi$ )		3.375(2)			x, +y+1, +z
C12( $\pi$ )...C6( $\pi$ )		3.310(2)			-x+1, -y+1, -z
C15A( $\pi$ )...C15A( $\pi$ )		3.324(2)			-x+1, -y+2, -z+1
C5-H5...C27A( $\pi$ )	0.93	3.576(3)	2.87	134	-x+1, -y+1, -z
C12-H12...C28( $\pi$ )	0.93	3.577(2)	2.85	136	x+1, +y, +z
C29-H29...C14( $\pi$ )	0.93	3.671(3)	2.84	150	-x+1, -y+1, -z

**Table S5: List of important intermolecular interactions in HNBI-B<sub>2</sub>EA**

Interactions	D...H(Å)	D...A(Å)	H...A (Å)	D-H...A(°)	Symmetry code
C10-H10...O1	0.93	3.410(2)	2.49	173	-x, -y+1, -z
N2-H2...O2	0.91(2)	2.770(3)	1.91(2)	158(2)	-x, -y+1, -z+1
C15-H15...O2	0.93	3.342(2)	2.70	127	-x, -y+1, -z+1
C22-H22...O3	0.93	3.384(3)	2.69	132	-x-1, -y+1, -z
C6( $\pi$ )...C4( $\pi$ )		3.329(3)			-x+1, -y+2, -z+1
C33-H33...C17( $\pi$ )	0.93	3.760(4)	2.87	155	x-1, +y, +z
C14-H14...C19( $\pi$ )	0.93	3.615(3)	2.87	138	-x, -y+1, -z+1
C20-H20...C4( $\pi$ )	0.93	3.612(4)	2.79	148	-x, -y+2, -z+1

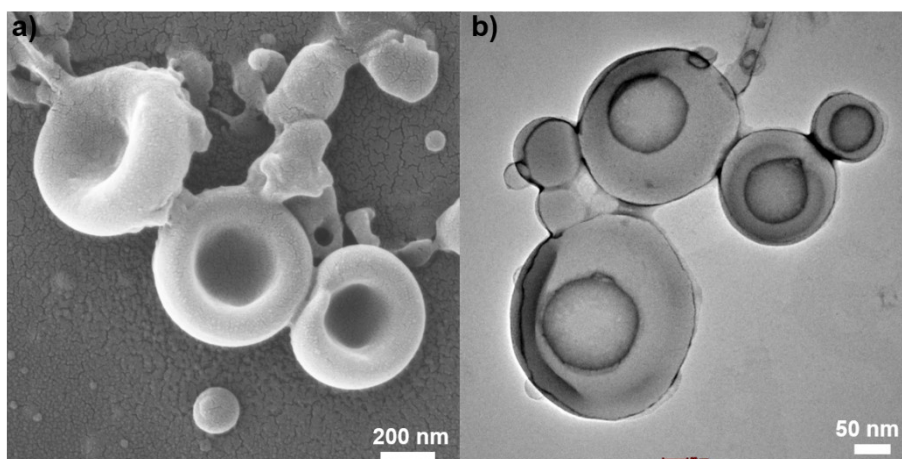
**Table S6: List of important intermolecular interactions in HNBI-B<sub>2</sub>MeOH**

Interactions	D...H(Å)	D...A (Å)	H...A (Å)	D-H...A(°)	Symmetry code
N4-H4...O1	0.91(3)	2.930(3)	2.13(3)	147(3)	x, y, z
C55-H55...N4	0.95	3.046(4)	2.44	122	x, y, z
C86-H86...O4	0.95	3.660(4)	2.93	134	x, y, z
N6-H6...O4	0.92(3)	2.752(3)	1.87(3)	160(3)	-x+3/2, +y+1/2, +z
O4-H4B...O3	0.88(4)	2.854(3)	2.07(4)	147(4)	x-1/2, -y+3/2, -z+1
C15( $\pi$ )...C5( $\pi$ )		3.395(4)			-x+3/2, +y+1/2, +z
C18( $\pi$ )...C45( $\pi$ )		3.342(4)			-x+3/2, +y+1/2, +z
C47( $\pi$ )...C52( $\pi$ )		3.340(4)			-x+3/2, +y+1/2, +z
C75( $\pi$ )...C81( $\pi$ )		3.390(4)			-x+2, -y+2, -z+1
C58( $\pi$ )...C84( $\pi$ )		3.364(5)			-x+3/2, +y-1/2, +z
C57-H57...C60( $\pi$ )	0.95	3.620(4)	2.69	166	-x+3/2, +y-1/2, +z
C57-H57...C61( $\pi$ )	0.95	3.758(4)	2.89	154	-x+3/2, +y-1/2, +z
C39-H39...C68( $\pi$ )	0.95	3.494(4)	2.90	122	x-1/2, -y+3/2, -z+1
C40-H40...C69( $\pi$ )	0.95	3.454(4)	2.82	125	x-1/2, -y+3/2, -z+1
C40-H40...C68( $\pi$ )	0.95	3.475(4)	2.51	125	x-1/2, -y+3/2, -z+1

## 4. Preparation of self-assembly

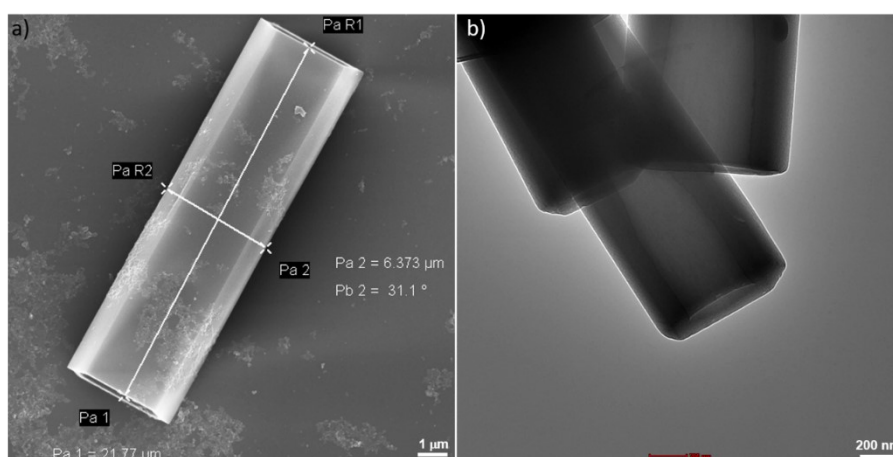
**Synthesis of Nano-discoids and Hexagonal Microtubes:** Initial concentration of **HNBI-B** used for the preparation of both nano-corpules and hexagonal microtubes is always kept constant i.e., 50  $\mu\text{M}$  in MeOH.

**Nano-discoids (NDs):** Preparation of nano-corpules are obtained at 20%  $\text{H}_2\text{O}$ -MeOH system where 200 $\mu\text{l}$  of Milli-Q water was added rapidly to 800 $\mu\text{L}$  HNBI-B solution in MeOH at RT. Kept undisturbed for 4 hrs at RT. After 4 hrs nano-discoids settled down by centrifugation and washed twice with Milli-Q water. Finally, re-suspended in water to dropcast for SEM, TEM and fluorescence microscopic characterization. After three days of ageing these nano-corpules converts to microtubes. The largest nanodiscoid observed with a diameter of 1  $\mu\text{m}$ .



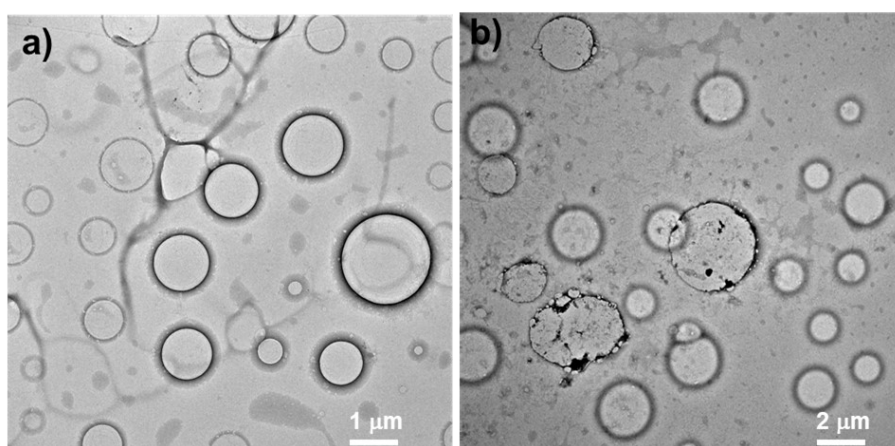
**Figure S1:** a) SEM and b) TEM images of the nano-discoids. The samples were prepared after 4 hrs of ageing.

**Hexagonal Microtubes (HMTs):** HMTs were prepared in 50% H<sub>2</sub>O-MeOH system. Milli-Q water (1 ml) was added quickly to a solution of HNBI-B in MeOH (1 ml). After the addition of H<sub>2</sub>O, solution was kept undisturbed for 4 hrs at RT. Floating HMTs were observed on the surface of the solution, which shows strong blue fluorescence. After the centrifuge, the precipitate was washed with Milli-Q water repeatedly to get pure hexagonal microtubes only. Finally, re-suspended in water to dropcast for SEM, TEM and optical microscopic characterization. The samples after dropcast dried in a desiccator for 12 hrs.



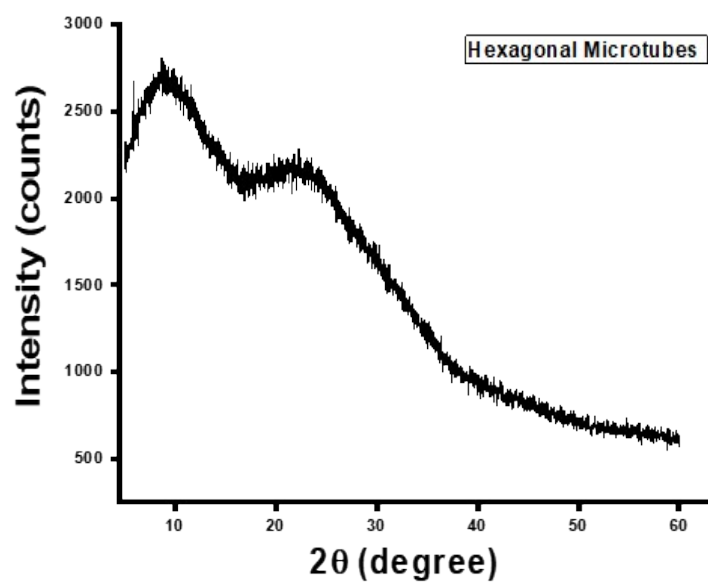
**Figure S2:** a) SEM and b) TEM images of hexagonal microtubes (HMTs).

**Spherical morphology in pure solvents:** Spherical self-assemblies of HNBI-B obtained from pure solvents like CHCl<sub>3</sub> and EtOAc at 50 μM concentrations. The TEM imaging was done after 12 hrs of sample preparation.

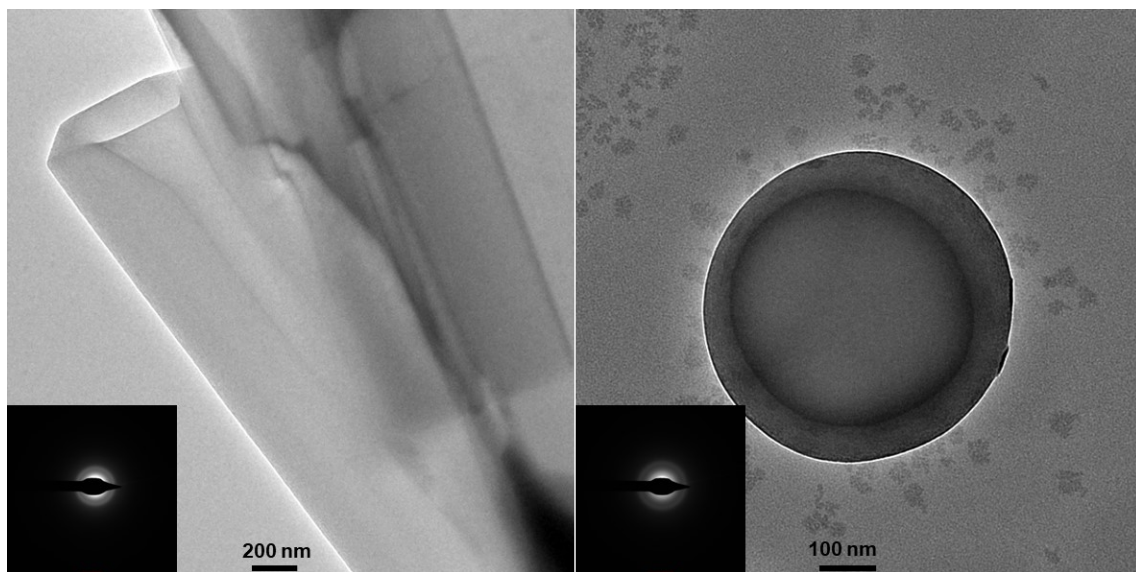


**Figure S3:** TEM images of Spherical particles. a) CHCl<sub>3</sub> b) EtOAc solvent (50 μM).

## 5. Powder XRD of Hexagonal microtubes (HMTs)



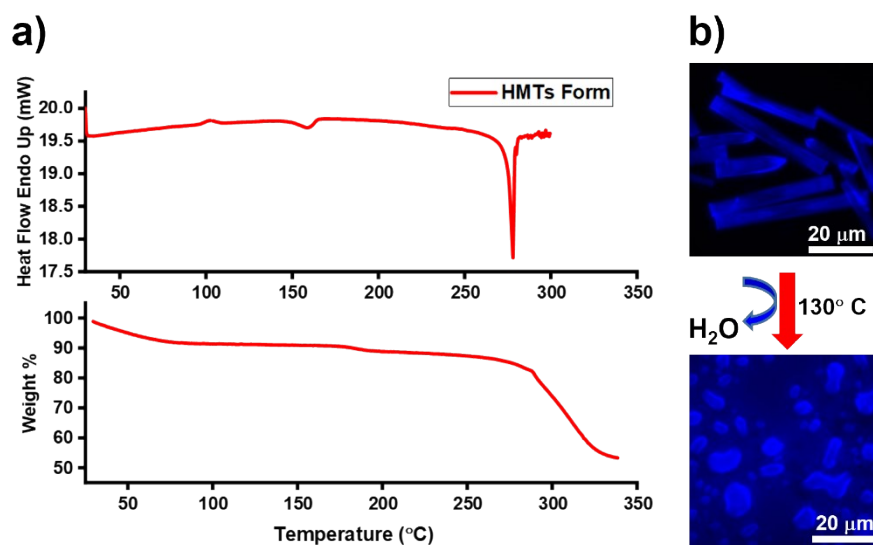
**Figure S4:** PXRD of hexagonal microtubes (HMTs) indicating their amorphous nature.



**Figure S5:** Selected area electron diffraction (SAED) pattern for HMTs and NDs.

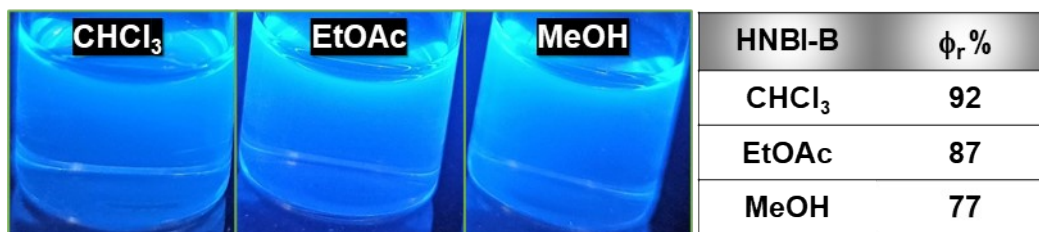
## 6. Selected area electron diffraction pattern (SAED)

## 7. TGA and DSC profile for Hexagonal microtubes (HMTs)



**Figure S6:** a) DSC and TGA of hexagonal microtubes and b) Optical microscopy images before and after dismantling at 130 °C.

## 8. Quantum Yield measurement



**Figure S7.** Photograph of HNBI-B in CHCl<sub>3</sub>, EtOAc and MeOH under UV illumination. The relative quantum yields ( $\phi_r$ ) in each solvent w.r.t the 9,10-diphenylanthracene standard dye are also tabulated alongside.

## 9. NMR and Mass characterization

### Mass spectra: ESI-HRMS

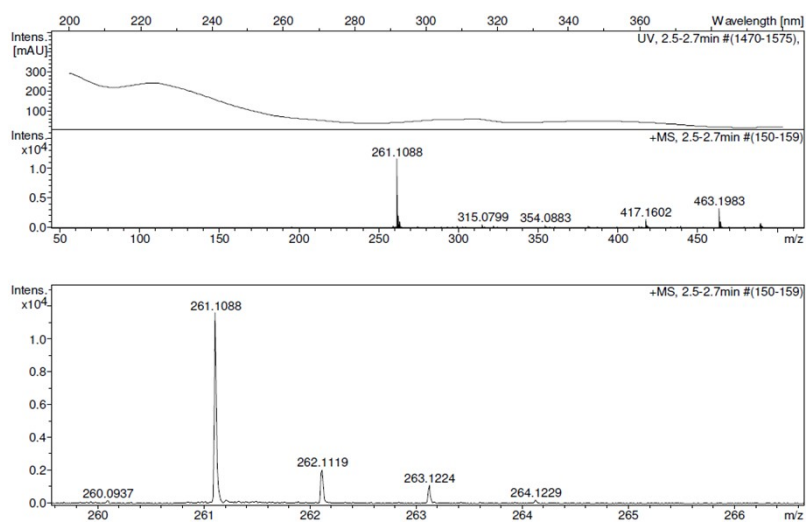


Figure S8: ESI-HRMS spectrum of HNBI

### <sup>1</sup>H-NMR

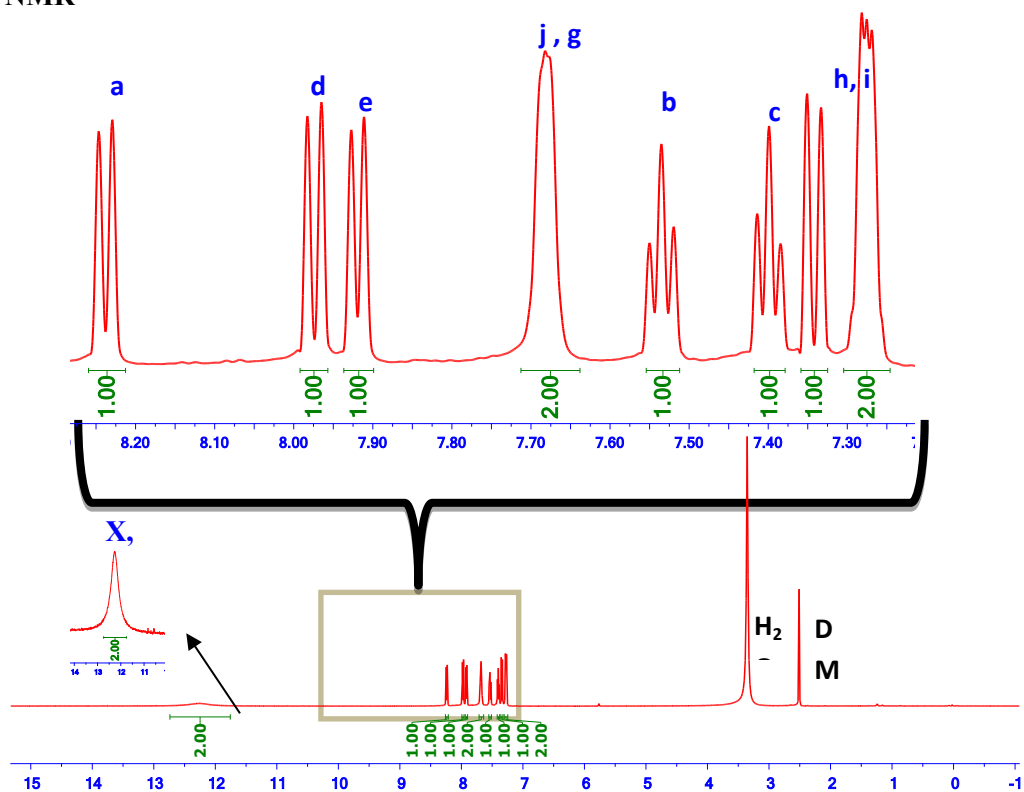


Figure S9: <sup>1</sup>H NMR of HNBI molecule in DMSO-d<sub>6</sub> (500 MHz) at 298 K.



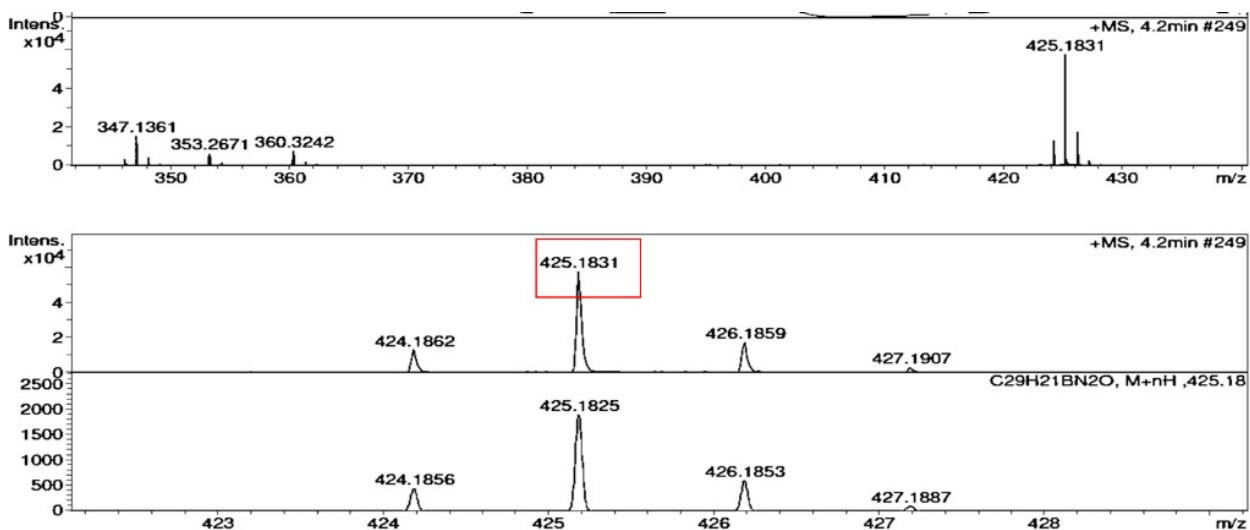


Figure S10: ESI-HRMS of HNBI-B complex

### Mass spectrum: ESI-HRMS

### $^1\text{H-NMR}$ of HNBI-B complex

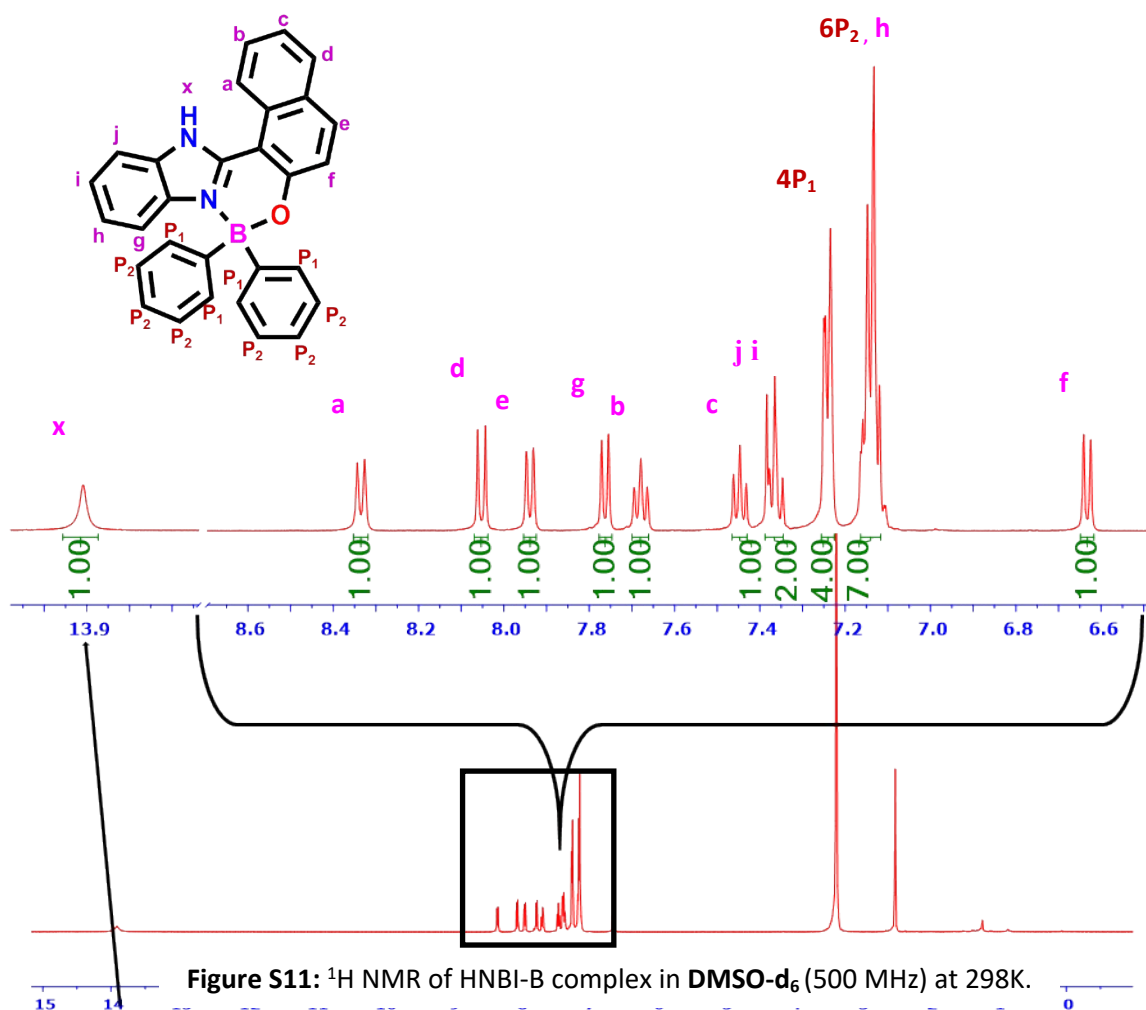


Figure S11:  $^1\text{H NMR}$  of HNBI-B complex in  $\text{DMSO-d}_6$  (500 MHz) at 298K.

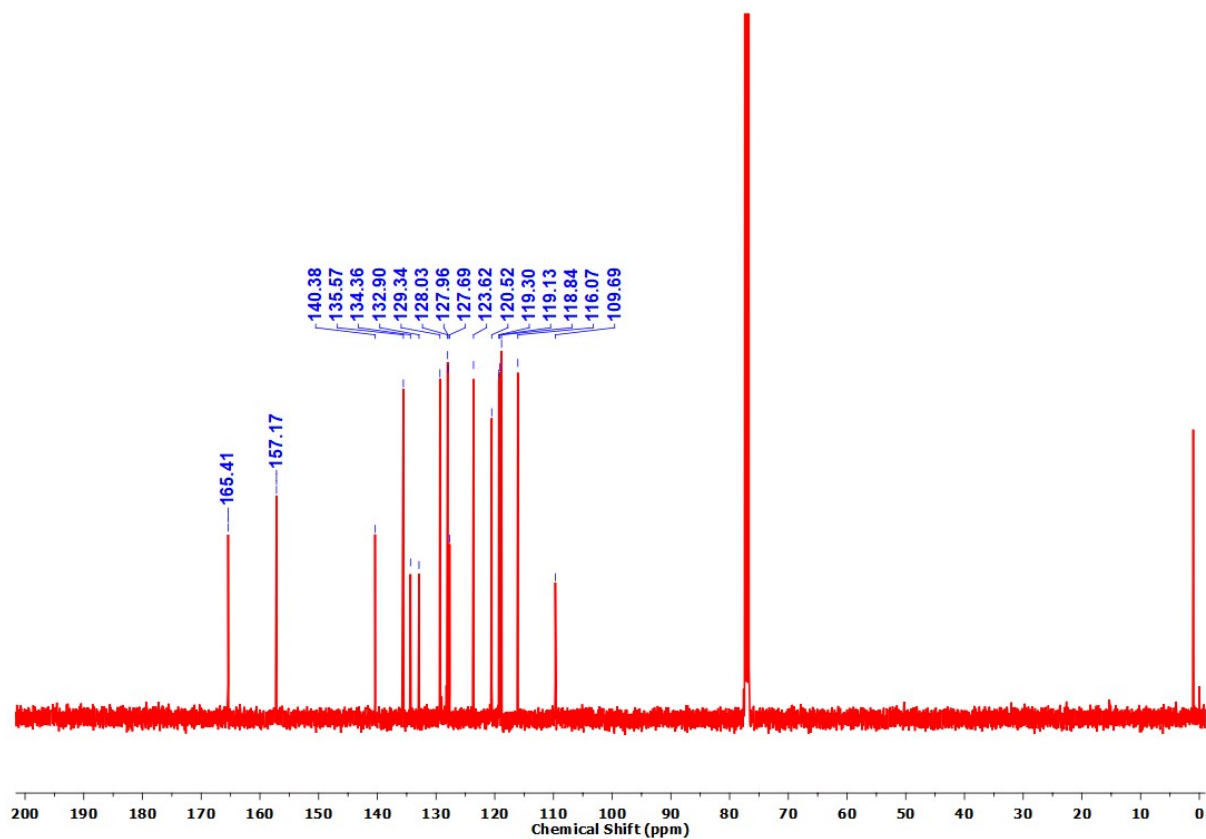


Figure S12:  $^{13}\text{C}$  NMR of HNBI molecule in  $\text{DMSO-d}_6$  (125 MHz) at 298 K.

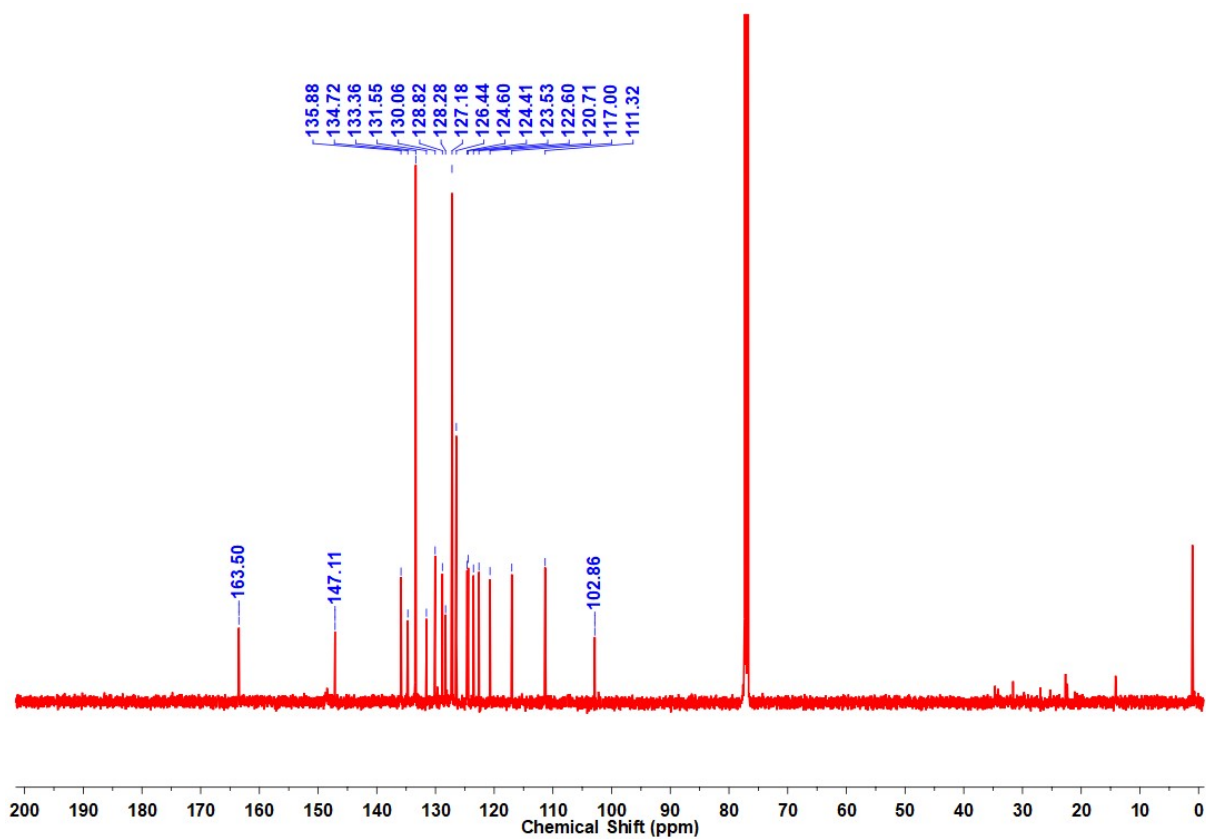


Figure S13:  $^{13}\text{C}$  NMR of HNBI-B complex in  $\text{DMSO-d}_6$  (125 MHz) at 298 K.