

# Electronic Supplementary Information for **Design and synthesis of photoactive ionic amorphous molecular materials**

**Alexi K. Nedeltchev, Haesook Han and Pradip K. Bhowmik**

*Department of Chemistry, University of Nevada Las Vegas, 4505 Maryland Parkway, Las Vegas*

*NV 89154, USA*

*E-mail: pradip.bhowmik@unlv.edu*

## **Table of Contents**

**Scheme S1.** Synthetic methods of bis(pyridinium salt)s. – p.3

**Chemicals and Characterization** – p.4

**Figure S1.** (a) TGA plots of compounds **2a** and **2b** obtained at a heating rate of 10 °C/min in nitrogen. (b) A comparison plot of the thermal stabilities of the compounds **1a-1d** and **2a-2d** at 5 weight % decomposition. – p.6

**Figure S2.** Space filling models of dication (a)  $Y_1$  (18.9 Å) and (b)  $Y_2$  (31.5 Å) obtained with ChemBio 3D Ultra. – p.7

**Figure S3.** XRD plots of (a) powdered crystal and (b) glass state of compound **2a**. – p.8

**Figure S4.** Photograph of melt-drawn fibers of compounds **2a** and **2b** irradiated with white light and UV light. – p.9

**Figure S5.** Photomicrographs of melt-drawn fibers of compounds (a) **1a** (b) **1d** (c) **2c** (Magnification 400x). – p.9

**Figure S6.** SEM images of melt-drawn fibers of compounds (a) **1a** (b) **1d** (c) **2a** and (d) **2c**. – p.10

**Figure S7.** Photomicrographs of cancer cells stained with compound **2a**, examined with fluorescence microscopy studies: (a) bright field, (b) excited with UV light, (c) excited with blue light and (d) excited with green light (Magnification 100×). – p.11

**Figure S8.** Photomicrographs of cancer cells stained with compound **2a**, examined with fluorescence microscopy studies: (a) bright field and (b) excited with UV light (Magnification 400×). – p.12

**Figure S9.** (a) ethidium bromide (b) **1a**. – p.12

**Figure S10.** (a)  $^1\text{H}$  and (b)  $^{13}\text{C}$ -NMR spectra of compound **1a** in *d6*-DMSO taken at room temperature. – p.13

**Figure S11.** (a)  $^1\text{H}$  and (b)  $^{13}\text{C}$ -NMR spectra of compound **1b** in *d6*-DMSO taken at room temperature. – p.14

**Figure S12.** (a)  $^1\text{H}$  and (b)  $^{13}\text{C}$ -NMR spectra of compound **1c** in *d6*-DMSO taken at room temperature. – p.15

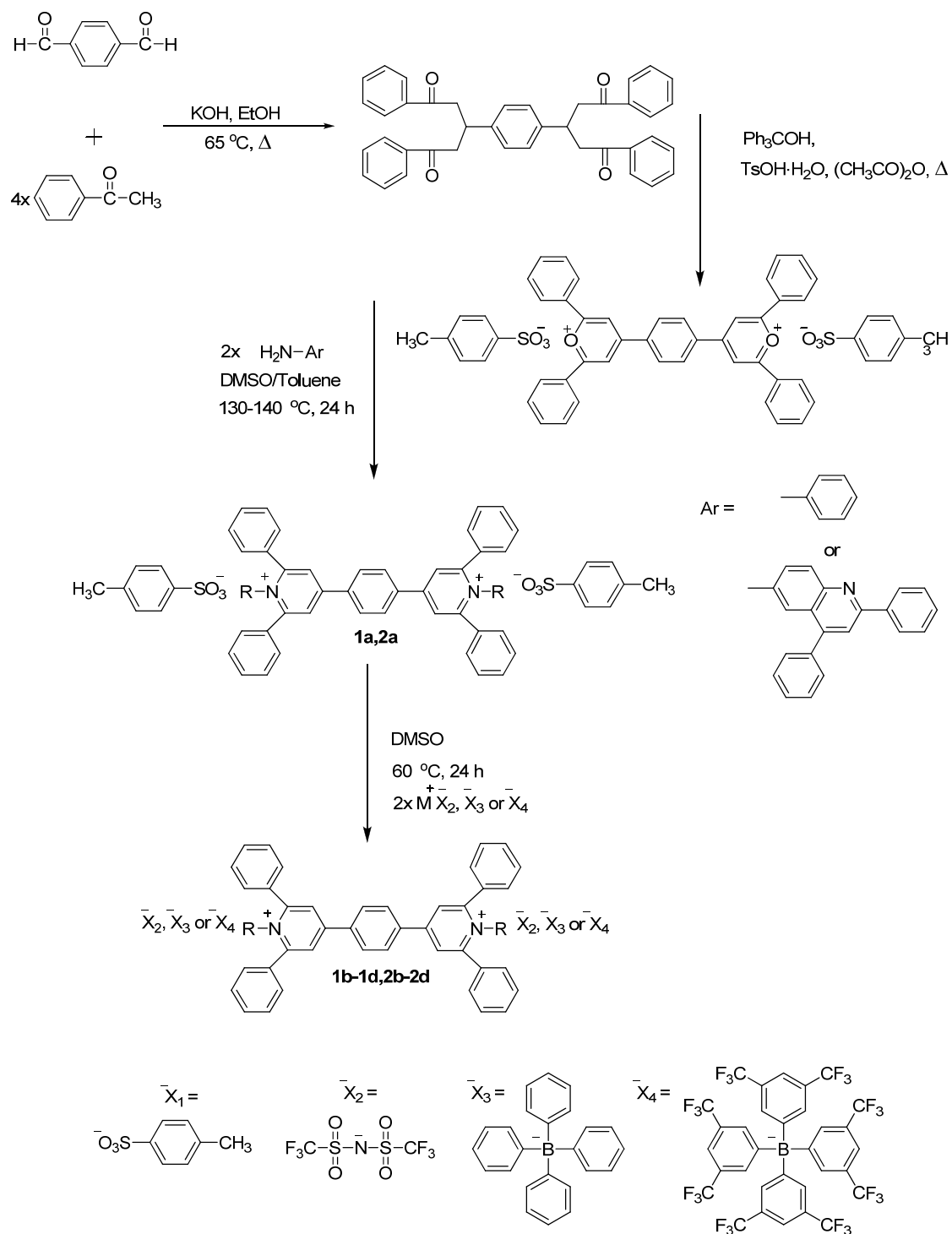
**Figure S13.** (a)  $^1\text{H}$  and (b)  $^{13}\text{C}$ -NMR spectra of compound **1d** in *d6*-DMSO taken at room temperature. – p.16

**Figure S14.** (a)  $^1\text{H}$  and (b)  $^{13}\text{C}$ -NMR spectra of compound **2a** in *d6*-DMSO taken at room temperature. – p.17

**Figure S15.** (a)  $^1\text{H}$  and (b)  $^{13}\text{C}$ -NMR spectra of compound **2b** in *d6*-DMSO taken at room temperature. – p. 18

**Figure S16.** (a)  $^1\text{H}$  and (b)  $^{13}\text{C}$ -NMR spectra of compound **2c** in *d6*-DMSO taken at 50 °C. – p.19

**Figure S17.** (a)  $^1\text{H}$  and (b)  $^{13}\text{C}$ -NMR spectra of compound **2d** in *d6*-DMSO taken at room temperature. – p.20



**Scheme S1.** Synthetic methods of bis(pyridinium salt)s.

## Chemicals and characterization

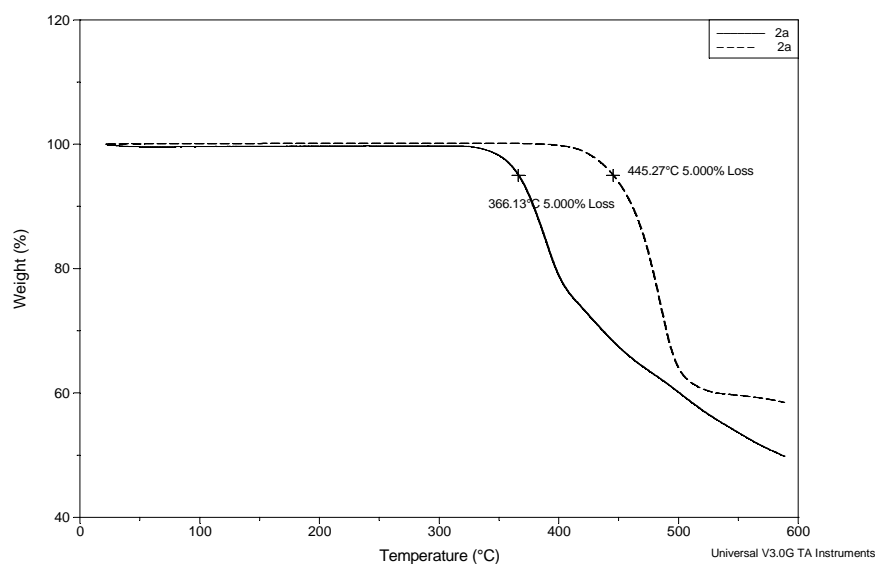
All starting materials were purchased from either Sigma-Aldrich or TCI and were used as received. The  $^1\text{H}$  and  $^{13}\text{C}$ -NMR spectra were recorded with a Varian NMR 400 spectrometer equipped with three RF channels operating at 400 MHz and 100 MHz, respectively. Each of the solutions of ionic compounds was prepared by dissolving ca. 25 mg of compound per milliliter of  $d_6$ -DMSO with TMS as an internal standard. The phase transition temperatures of ionic compounds were measured using a TA 2100 differential scanning calorimetry (DSC) under nitrogen flow at a rate of 10 °C/min. The temperature axis of the DSC thermogram was calibrated before use with reference standards of high purity indium and tin before use. An amount of 8-10 mg was used in this measurement. Thermal stability of each of the ionic compounds was analyzed through thermogravimetric analysis (TGA) using TA 2100 instrument at a rate of 10 °C/min under nitrogen using samples no less than 10 mg. The UV-Vis absorption spectra of these ionic compounds in various organic solvents were recorded using Varian Cary 50 Bio UV-Visible spectrophotometer in quartz cuvette. Their photoluminescence properties in both solution and film states were recorded and analyzed using a Perkin Elmer LS-55 luminescence spectrophotometer. Quantum yield was analyzed by adjusting the solution absorption using the UV-Vis to ca. 0.05 at 350 nm wavelength. The output was then measured using the luminescence spectrophotometer at the same wavelength and compared to known 9,10-diphenylanthracene in cyclohexane as a standard<sup>1</sup> using eq. 1:

$$\phi_{unk} = \phi_{std} \left( \frac{I_{unk}}{I_{std}} \right) \left( \frac{A_{std}}{A_{unk}} \right) \left( \frac{\eta_{unk}}{\eta_{std}} \right)^2 \quad (1)$$

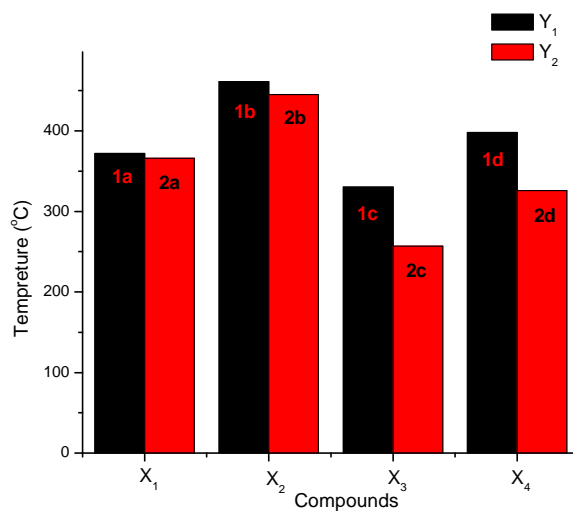
where  $\phi$  is the fluorescence quantum yield,  $I$  is the absorption of the excitation wavelength,  $A$  is the area under the emission curve and  $\eta$  is the refractive index of the solvents used. Subscript std denotes the standard while subscript unk denotes the unknown.<sup>2</sup> The X-ray diffraction studies

were performed on finely ground powdered samples with a PANalytical X'PERT Pro X-ray diffraction spectrometer. The scanning electron microscopy (SEM) images of melt-drawn fibers were taken with the JXA-8900 SuperProbe. The transmission electron microscopy (TEM) studies were performed with a 300-kV field emission TECNAI-F30-Super-twin TEM. Fluorescence microscope images were taken with a Nikon Eclipse TE2000-U. The cells for the fluorescence microscopy studies were MCF-7 breast cancer cells that were stained with 100 µg/ml solution of compound **2a** in PBS (phosphate buffer saline) for 20 min. The DNA electrophoresis gel was made using 10 µl of exACTGene low range DNA ladder (Fisher BioReagents) ran on a 2% agarose (Carolina Biological) gel in TBE (tris borate EDTA) buffer. It was run using the PowerEase 500 Power supply for 1 h (parameters: 100 V, 160 mA and 12 W). The gels were stained with solutions of ethidium bromide (1 µg/ml) and compound **1a** (50 µg/ml) for 30 min and subsequently washed with excess water. The DNA gels were visualized using a UV lightbox.

(a)

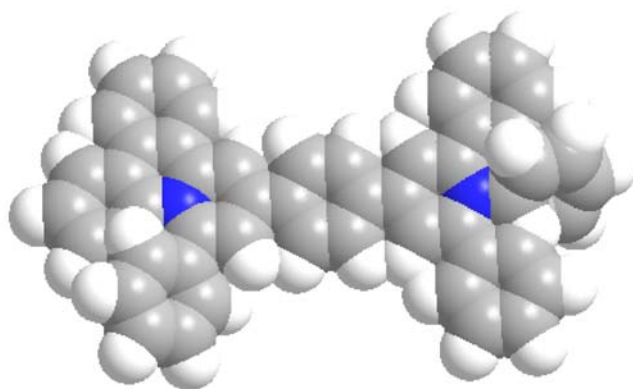


(b)

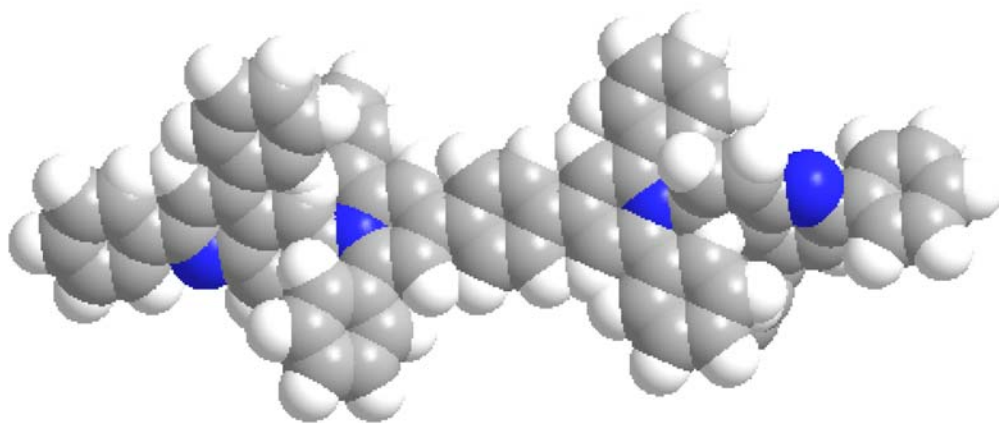


**Figure S1.** (a) TGA plots of compounds **2a** and **2b** obtained at a heating rate of 10 °C/min in nitrogen. (b) A comparison plot of the thermal stabilities of the compounds **1a-1d** and **2a-2d** at 5 weight % decomposition.

(a)

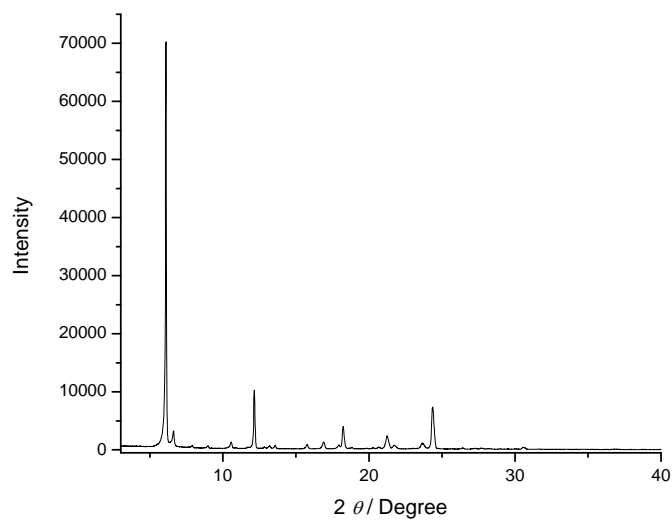


(b)

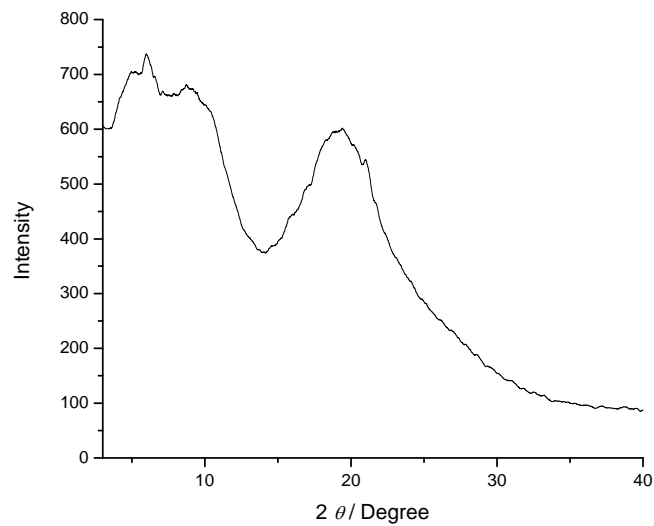


**Figure S2.** Space filling models of dication (a) Y<sub>1</sub> (18.9 Å) and (b) Y<sub>2</sub> (31.5 Å) obtained with ChemBio 3D Ultra.

(a)



(b)

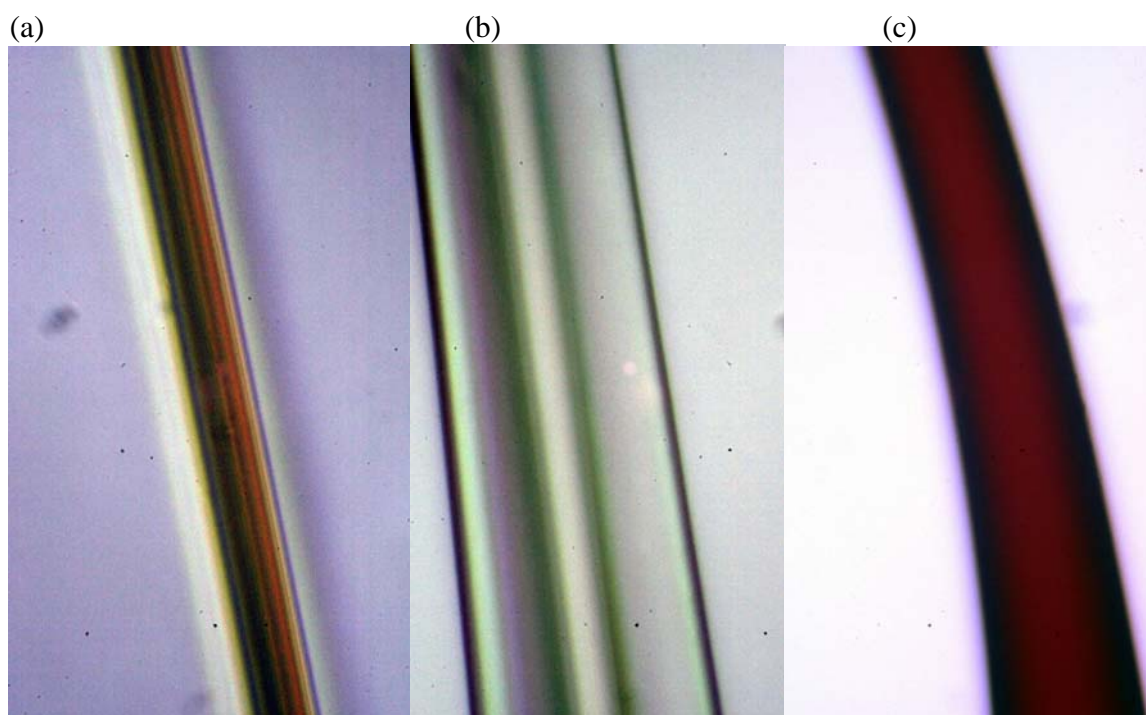


**Figure S3.** XRD plots of (a) powdered crystal and (b) glassy state of compound **2a**.

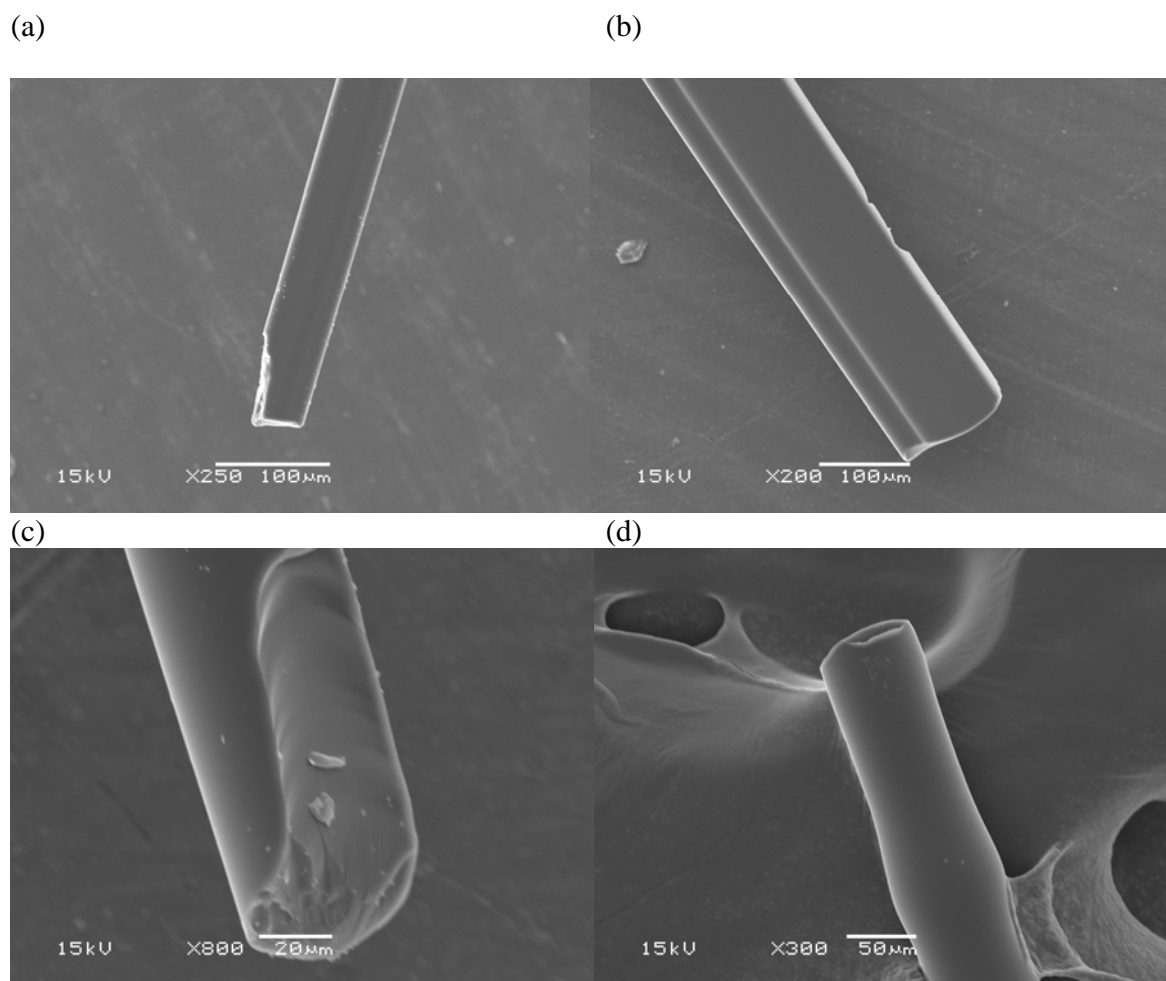




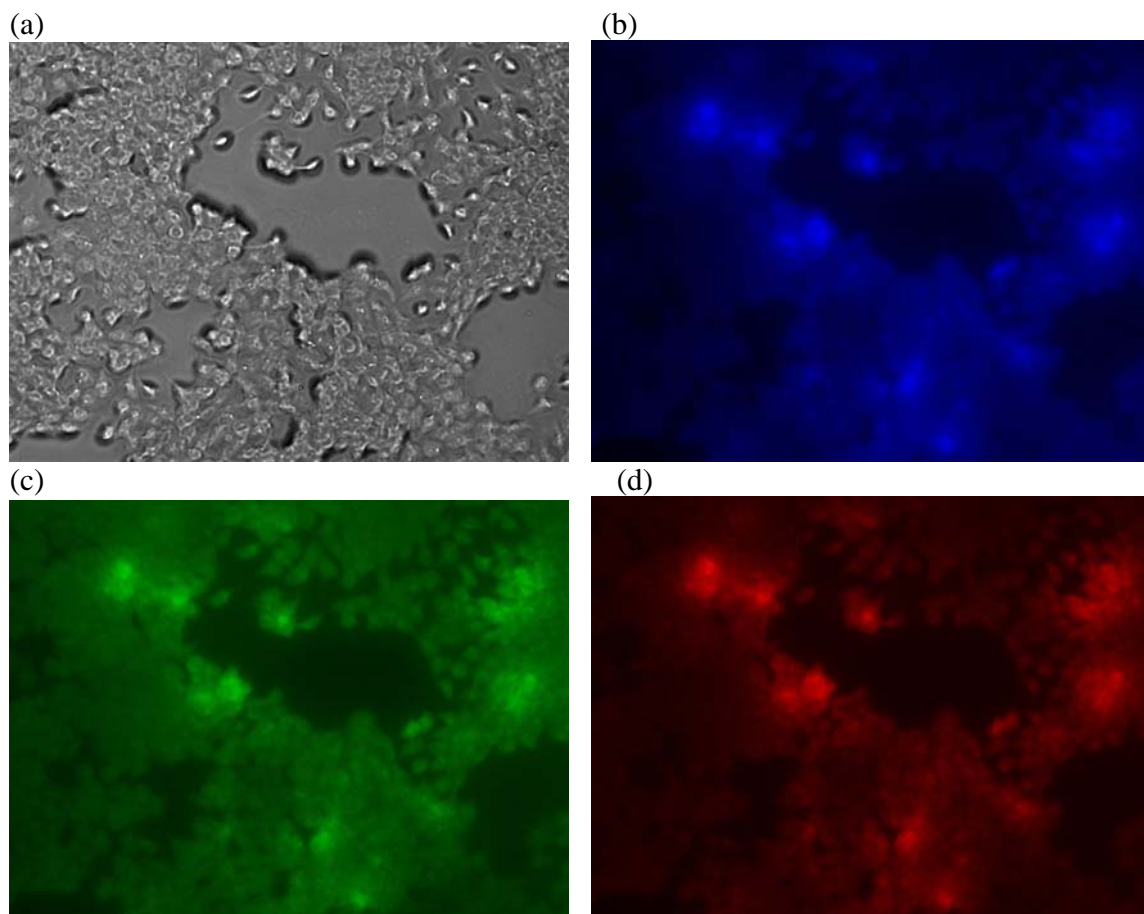
**Figure S4.** Photograph of melt-drawn fibers of compounds **2a** and **2b** irradiated with white and UV light.



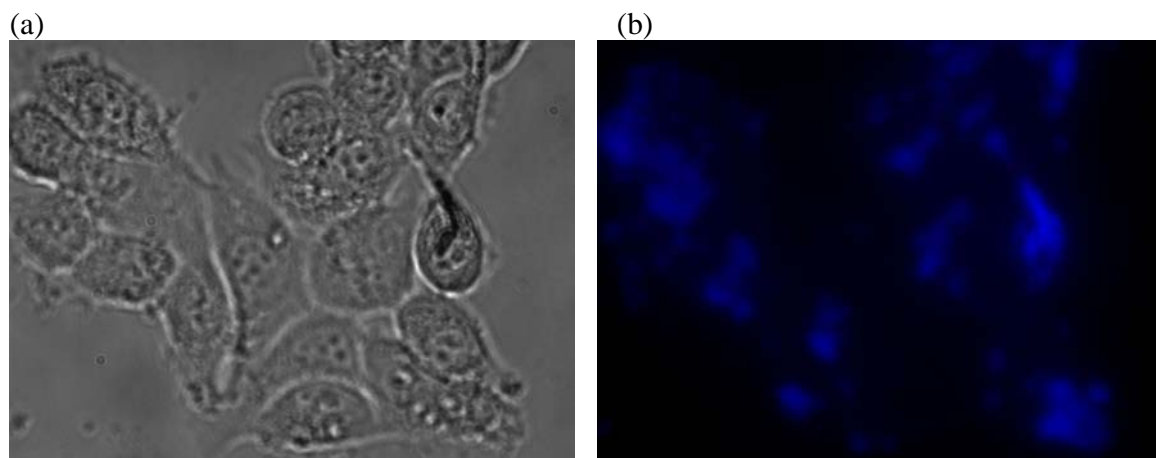
**Figure S5.** Photomicrographs of melt-drawn fibers of compounds (a) **1a** (b) **1d** (c) **2c** (Magnification 400x).



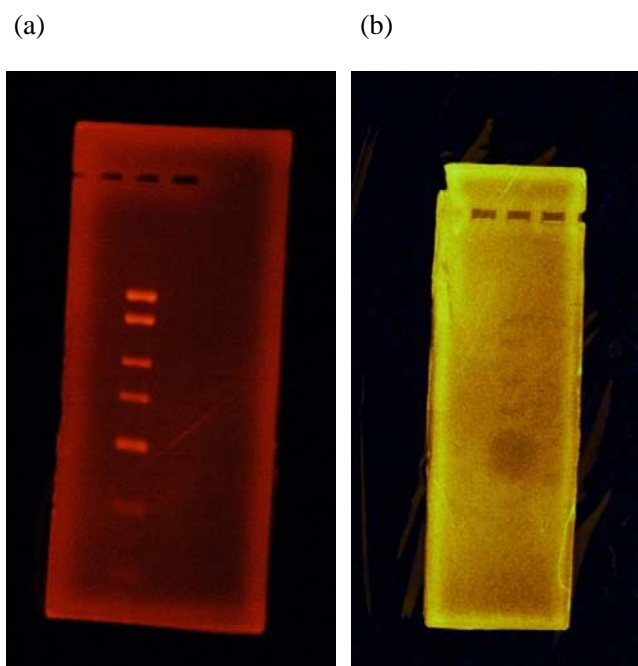
**Figure S6.** SEM images of melt-drawn fibers of compounds (a) **1a** (b) **1d** (c) **2a** and (d) **2c**.



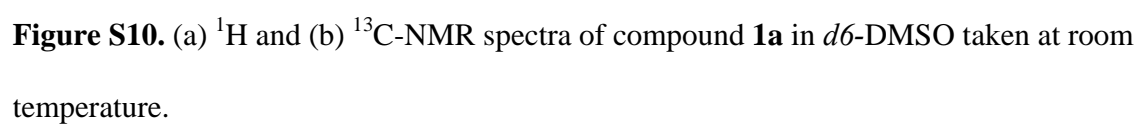
**Figure S7.** Photomicrographs of cancer cells stained with compound **2a**, examined with fluorescence microscopy studies: (a) bright field, (b) excited with UV light, (c) excited with blue light and (d) excited with green light (Magnification 100×).



**Figure S8.** Photomicrographs of cancer cells stained with compound **2a** when examined with fluorescence microscopy studies: (a) bright field and (b) excited with UV light (Magnification 400×).

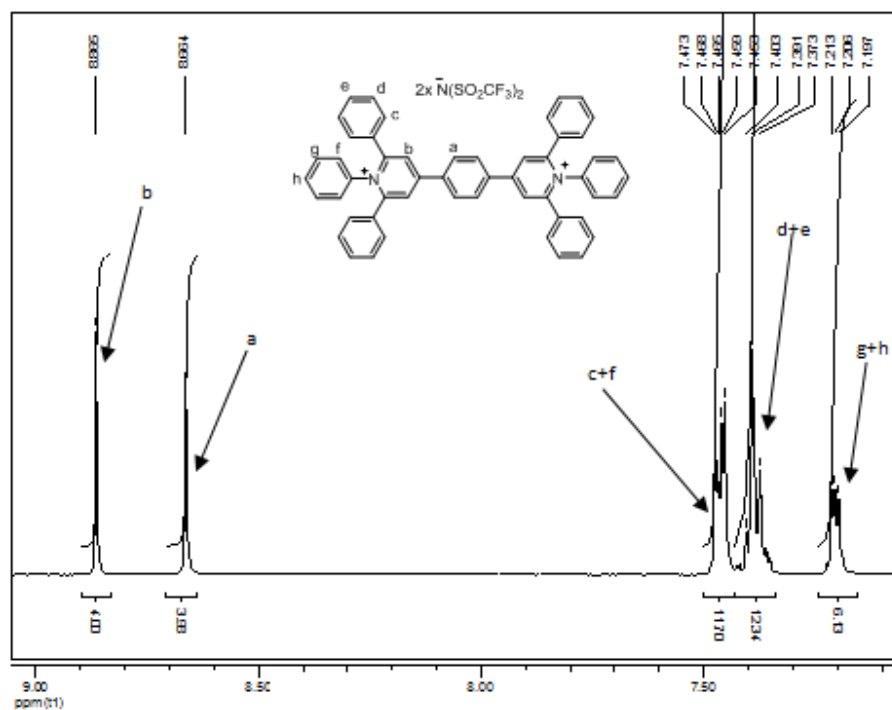


**Figure S9.** DNA gel electrophoresis stained with solutions of (a) ethidium bromide and (b) compound **1a** visualized with a UV lightbox.

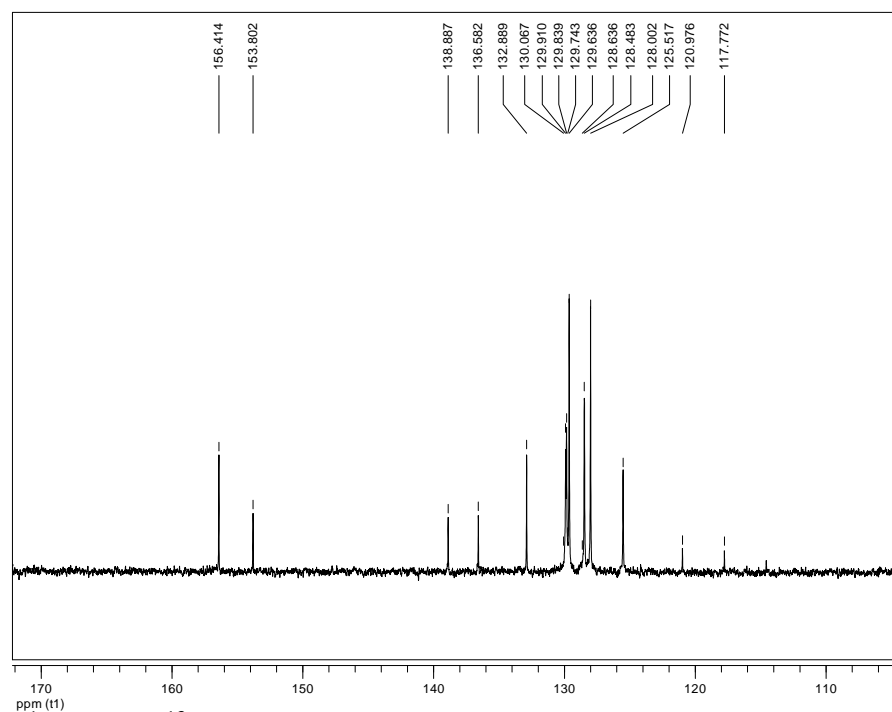


**Figure S10.** (a)  $^1\text{H}$  and (b)  $^{13}\text{C}$ -NMR spectra of compound **1a** in *d*6-DMSO taken at room temperature.

(a)

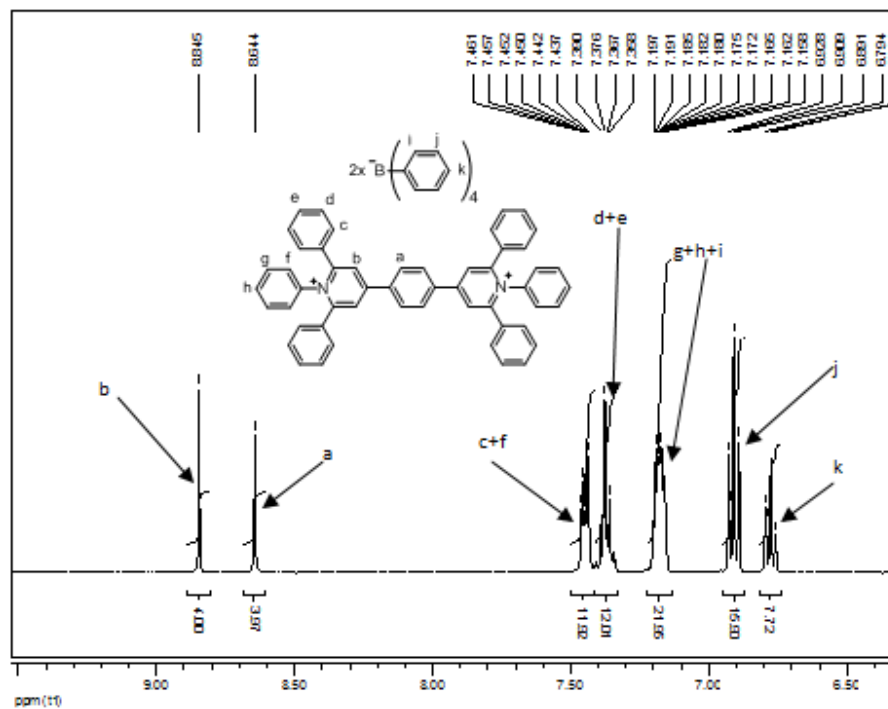


(b)

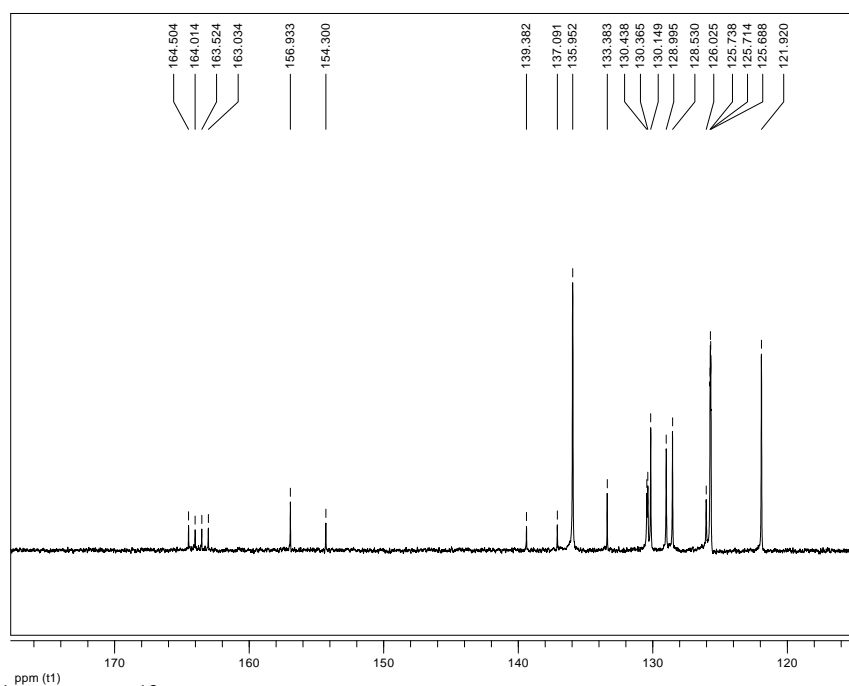


**Figure S11.** (a) <sup>1</sup>H and (b) <sup>13</sup>C-NMR spectra of compound **1b** in *d*<sub>6</sub>-DMSO taken at room temperature.

(a)



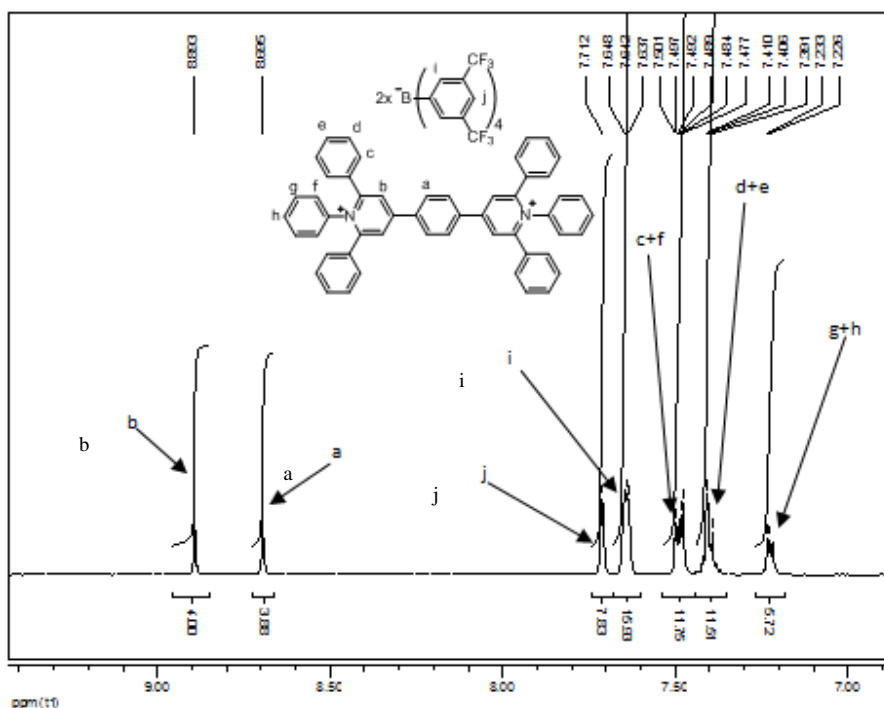
(b)



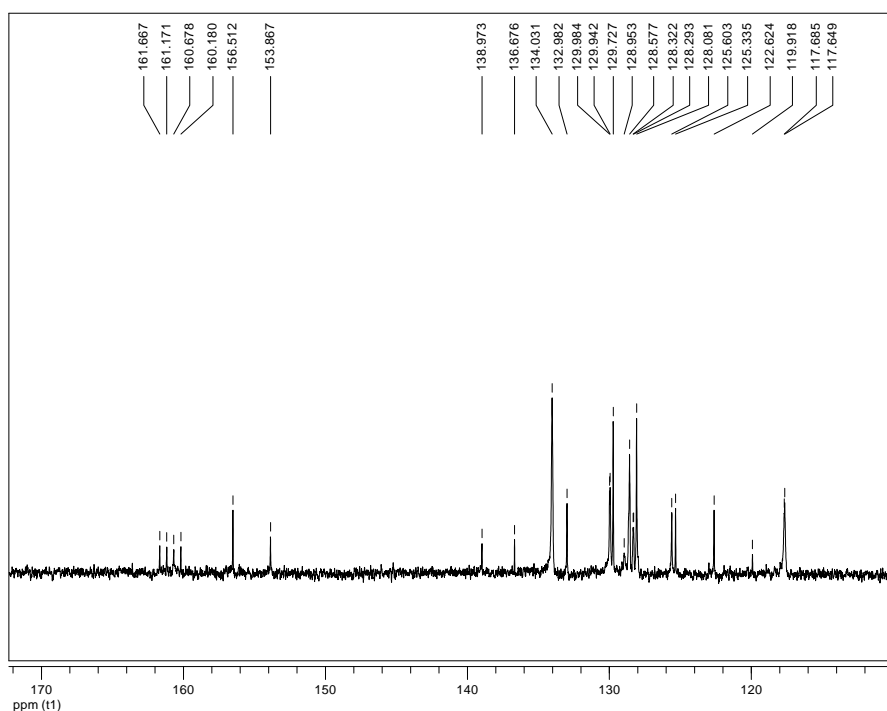
**Figure S12.** (a) <sup>1</sup>H and (b) <sup>13</sup>C-NMR spectra of compound **1c** in *d*<sub>6</sub>-DMSO taken at room temperature.



(a)



(b)

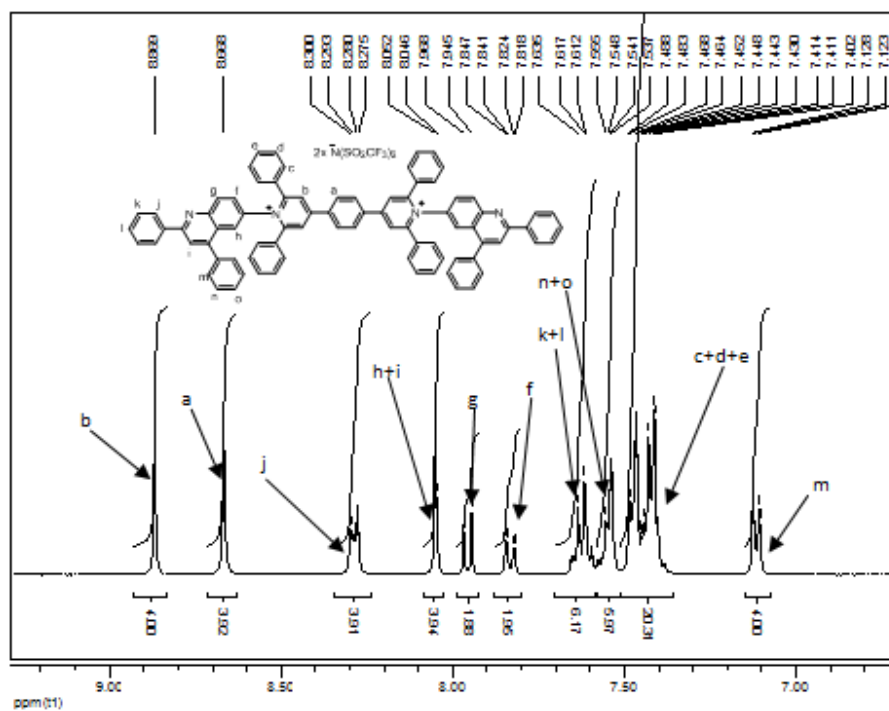


**Figure S13.** (a) <sup>1</sup>H and (b) <sup>13</sup>C-NMR spectra of compound **1d** in *d*<sub>6</sub>-DMSO taken at room temperature.

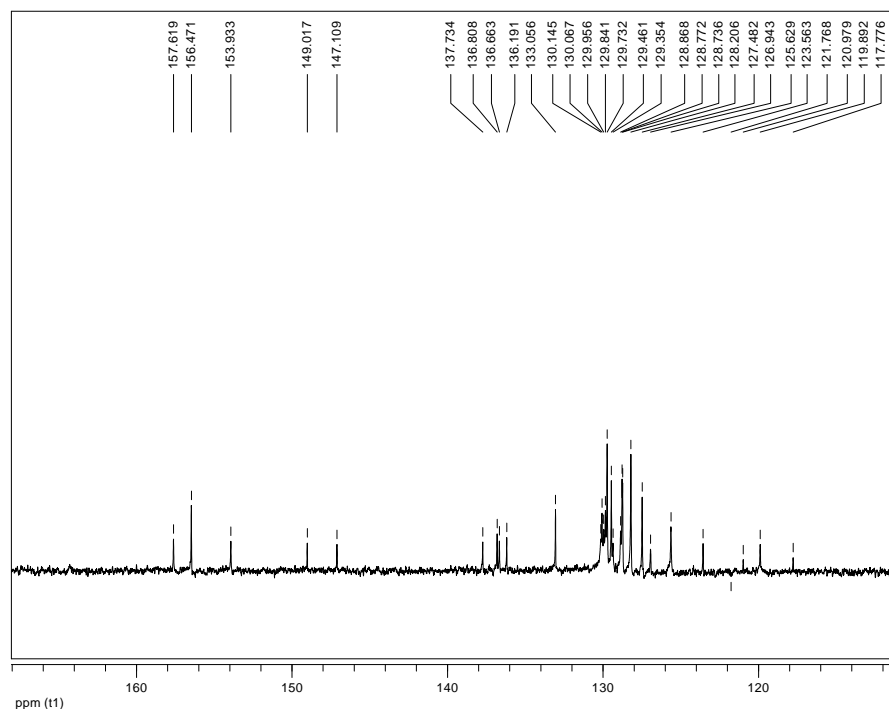


**Figure S14.** (a)  $^1\text{H}$  and (b)  $^{13}\text{C}$ -NMR spectra of compound **2a** in *d*6-DMSO taken at room temperature.

(a)

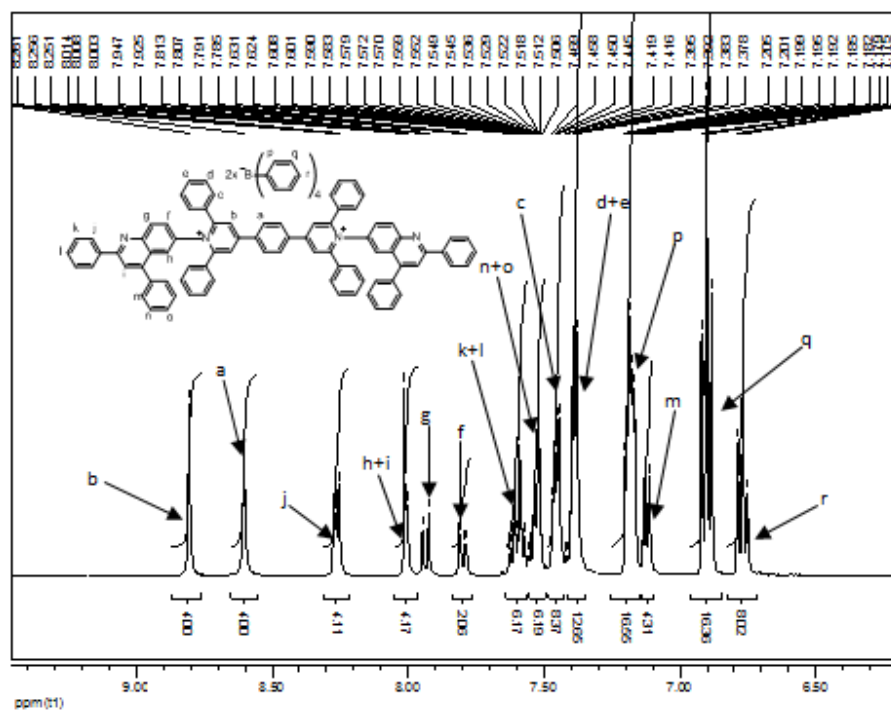


(b)

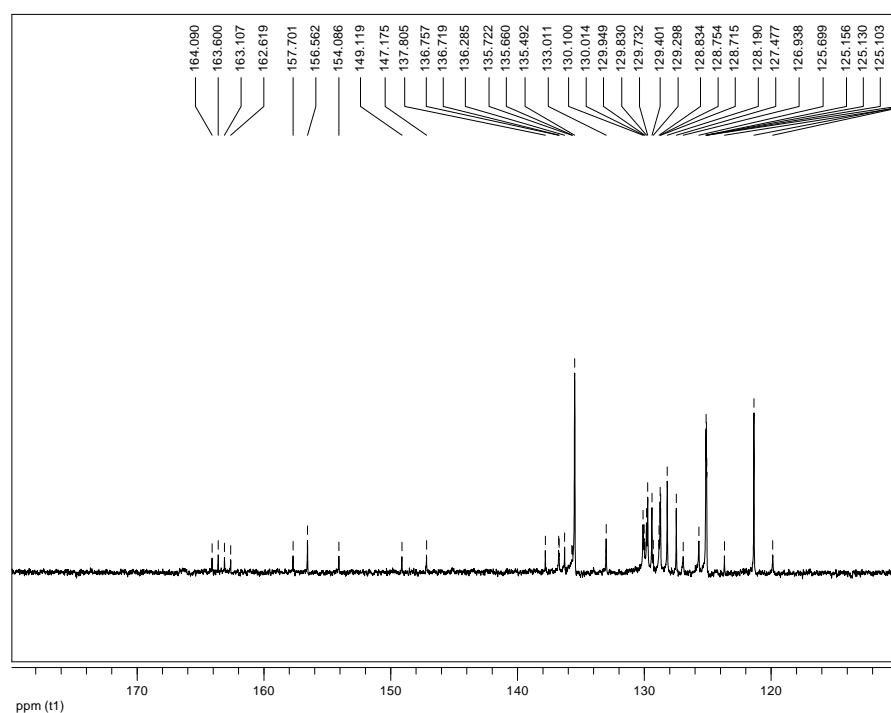


**Figure S15.** (a) <sup>1</sup>H and (b) <sup>13</sup>C-NMR spectra of compound **2b** in *d*<sub>6</sub>-DMSO taken at room temperature.

(a)

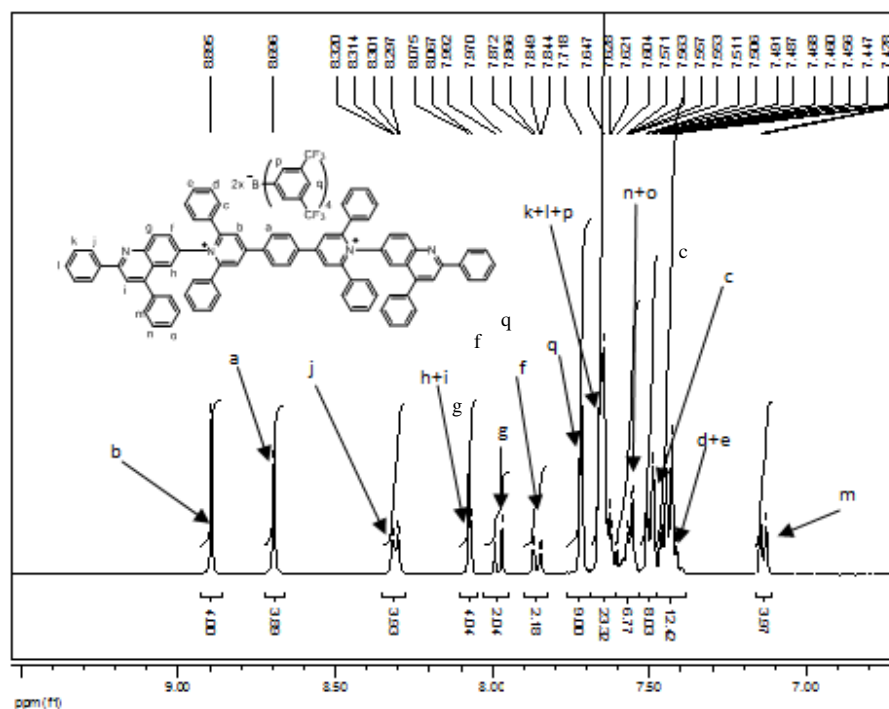


(b)

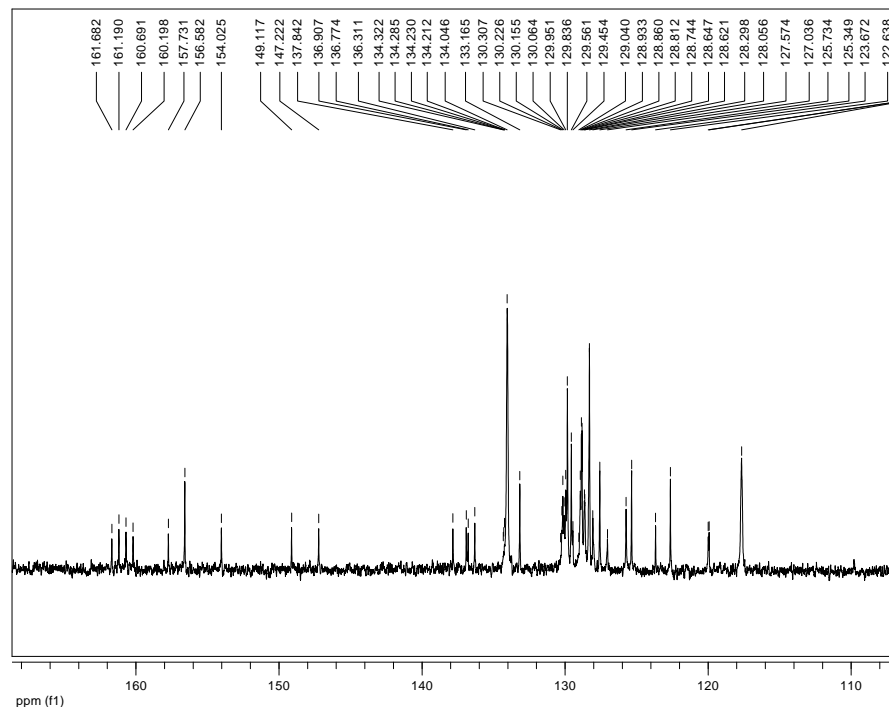


**Figure S16.** (a) <sup>1</sup>H and (b) <sup>13</sup>C-NMR spectra of compound **2c** in *d*<sub>6</sub>-DMSO taken at 50 °C.

(a)



(b)



**Figure S17.** (a) <sup>1</sup>H and (b) <sup>13</sup>C-NMR spectra of compound **2d** in *d*<sub>6</sub>-DMSO taken at room temperature.

## References

- 1 J. N. Demas, G. A. Cosby, *J. Phys. Chem.*, 1971, **75**, 991.
- 2 S. Fery-Forgues, D. Lavabre, *J. Chem. Edu.*, 1999, **76**, 1260.