Supporting Information

Synthesis and 2D self-assembly at the liquid-solid interface of end-substituted star-shaped oligophenylenes.

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Mass Spectra

Thermal Data

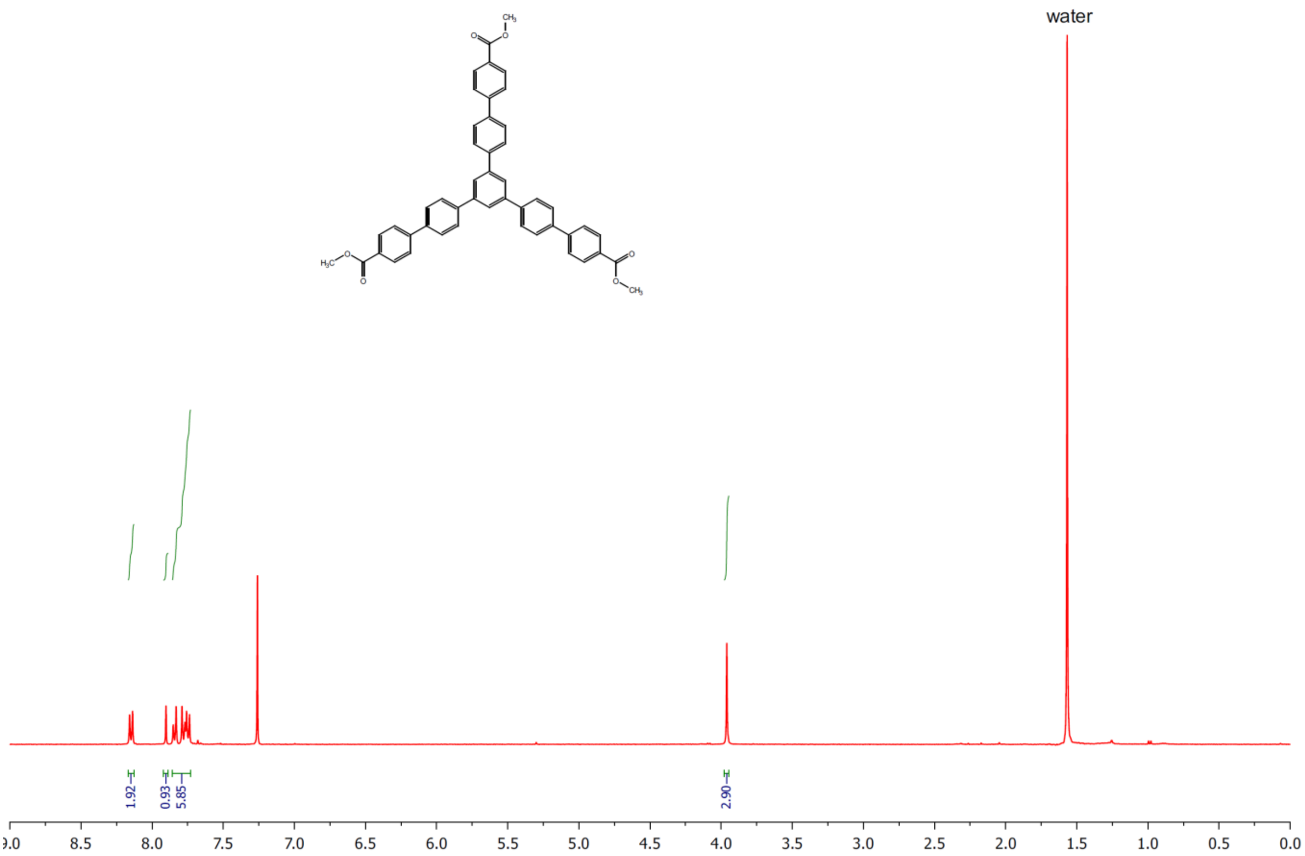


Fig S1. ^{1}H NMR spectrum of TBB **1** (400 MHz, $CDCl_3$).

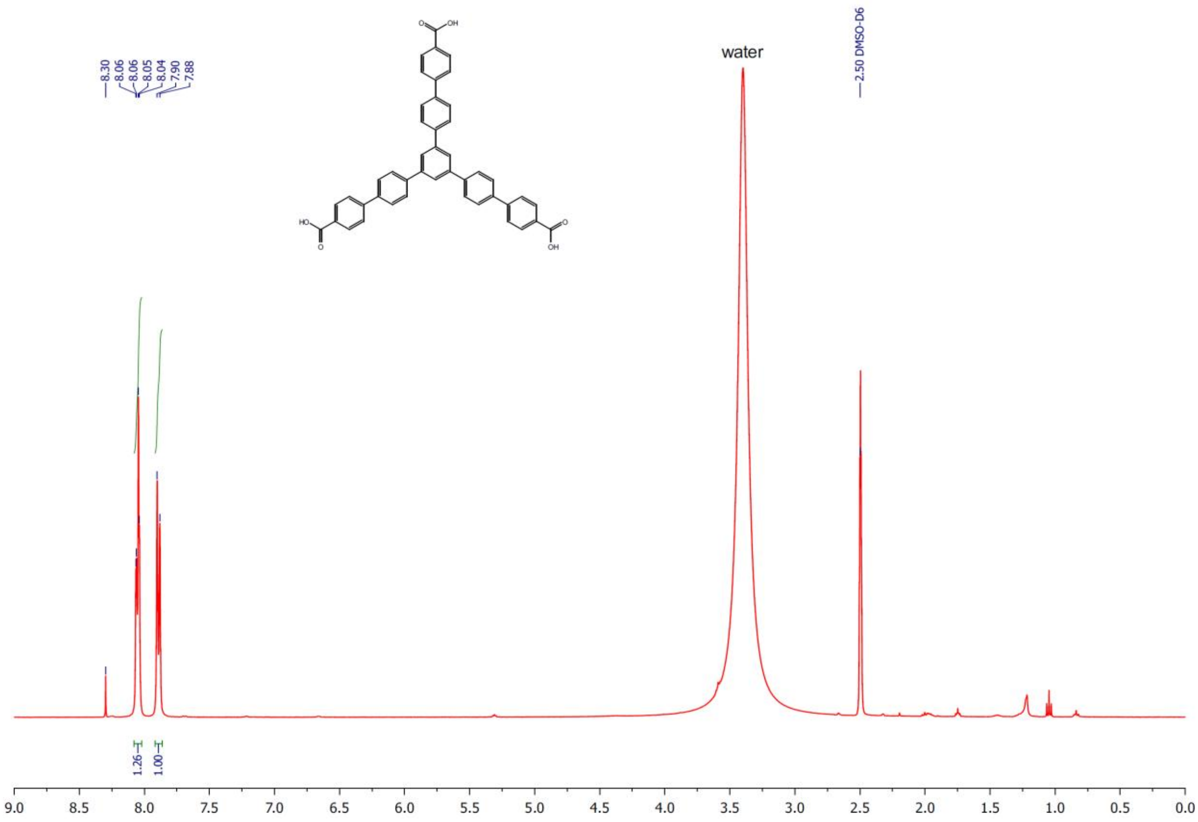


Fig S2. ^{1}H NMR spectrum of TBB **2** (400 MHz, DMSO-d6).

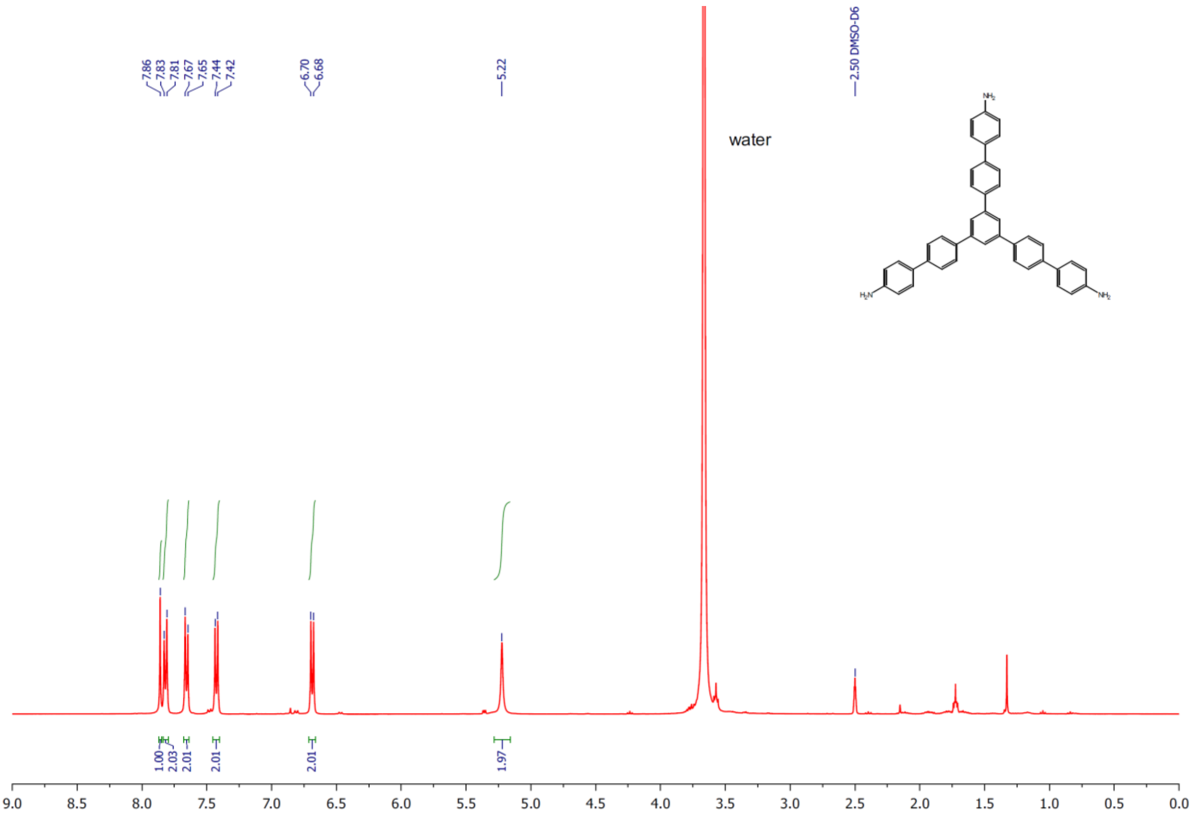


Fig S3. ^{1}H NMR spectrum of TBB **3** (400 MHz, DMSO-d6).

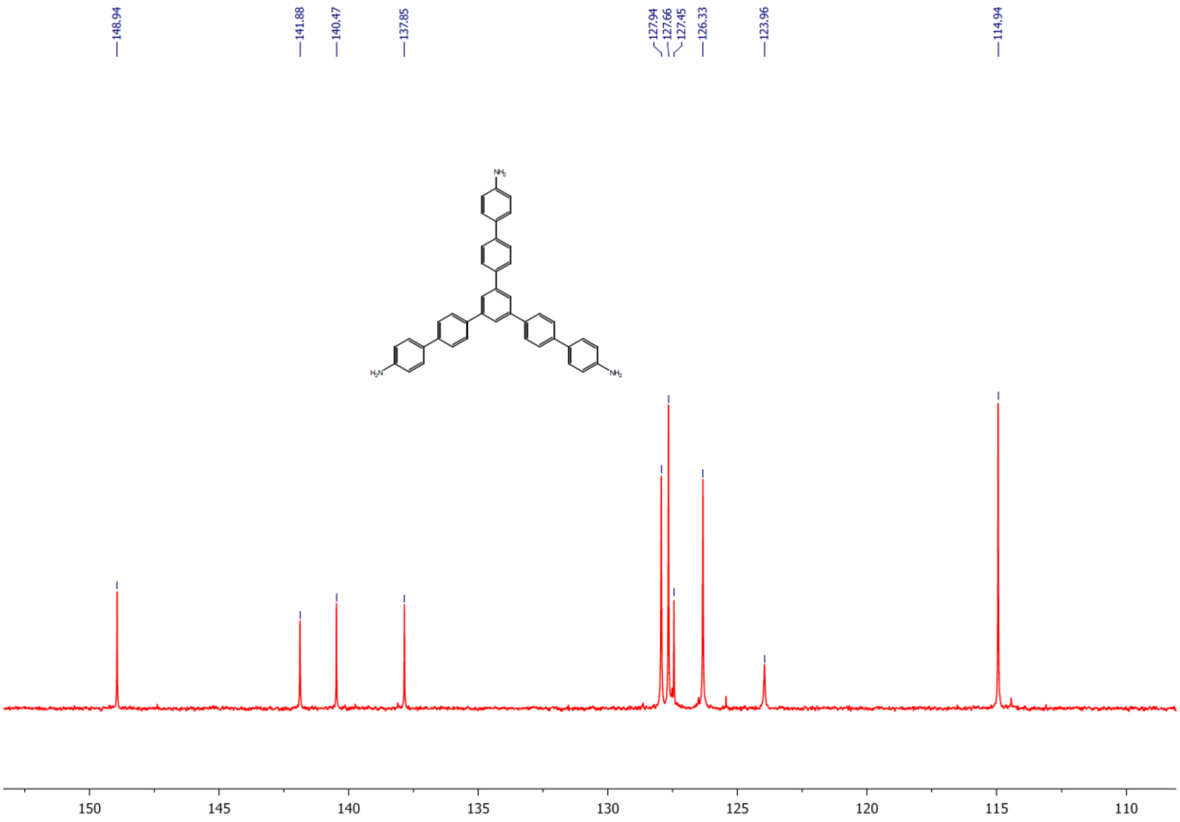


Fig. S4. ^{13}C NMR spectrum of TBB **3** (100 MHz, DMSO-d6).

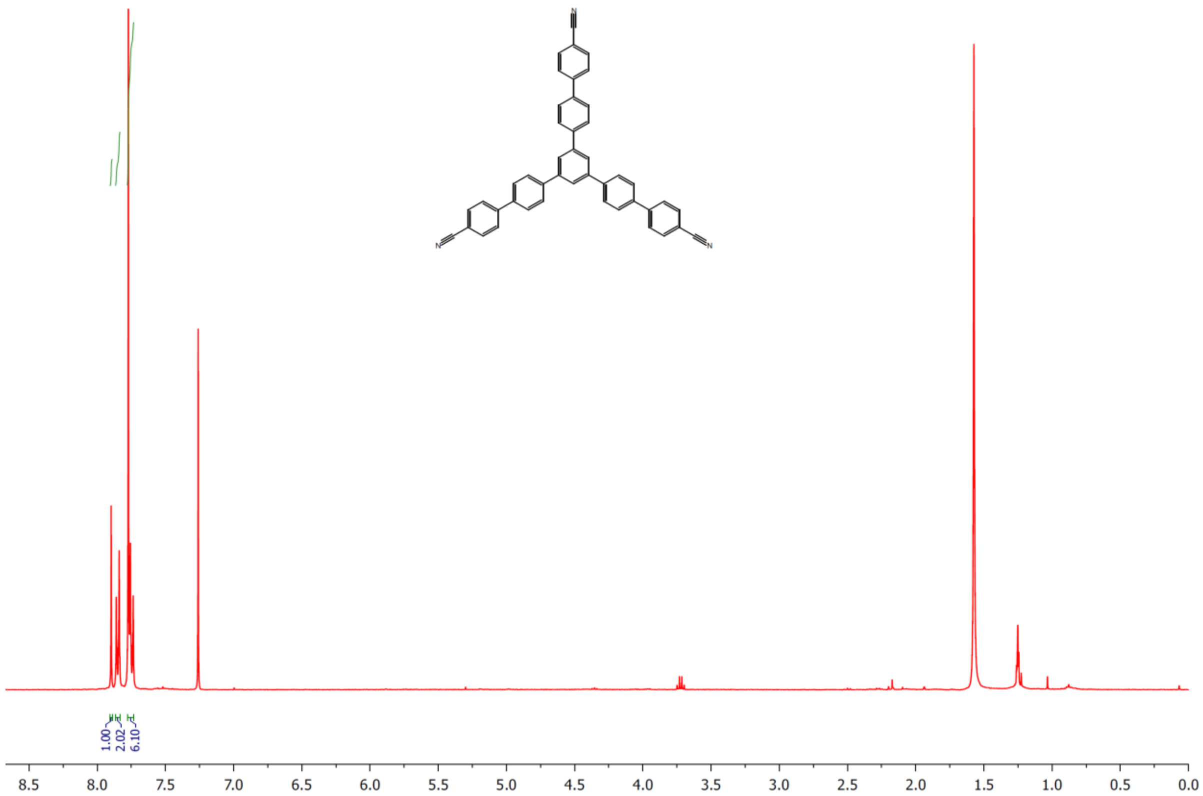


Fig. S5. ^{1}H NMR spectrum of TBB **4** (400 MHz, $CDCl_3$).

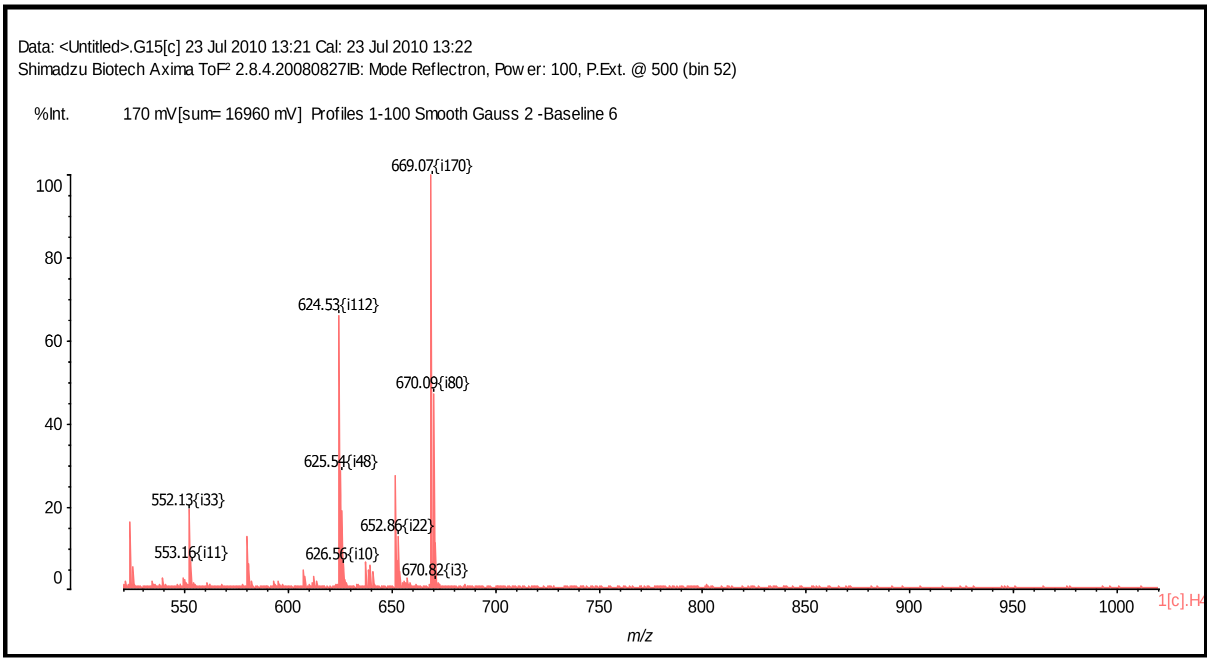


Fig. S6. MALDI TOF Mass spectra of TBB **2**.

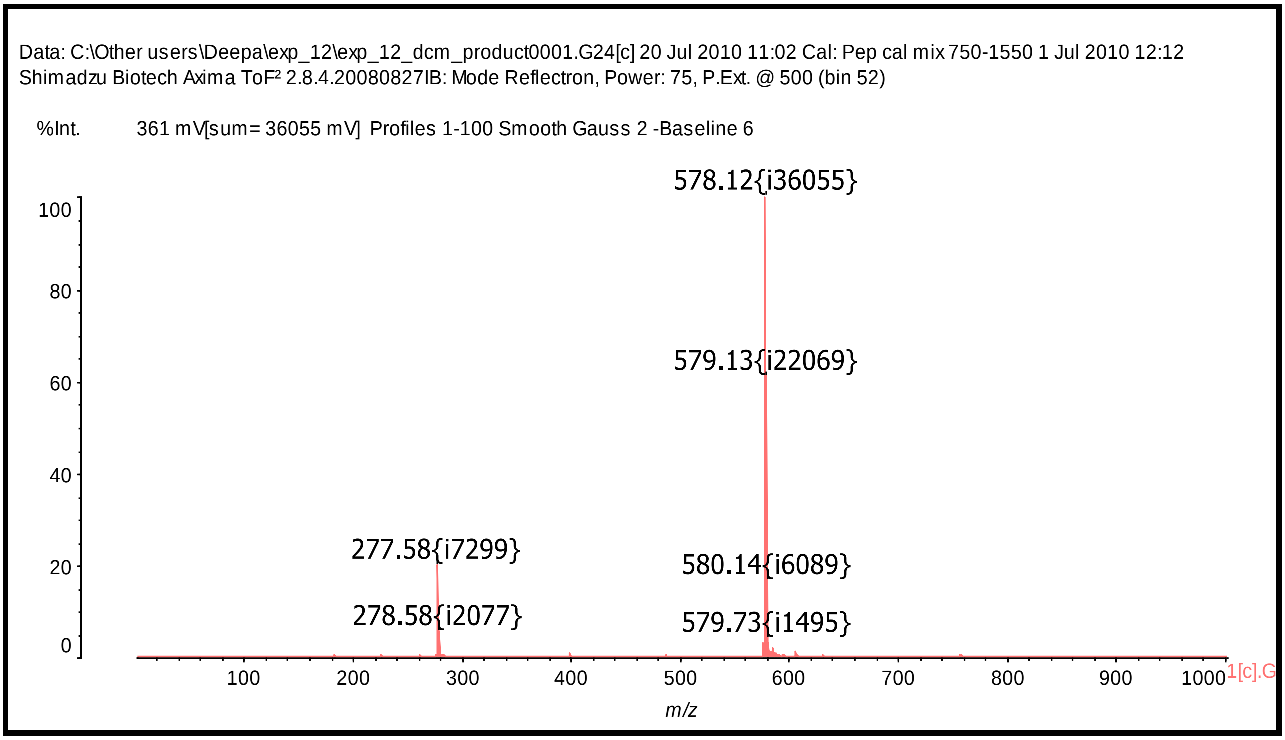
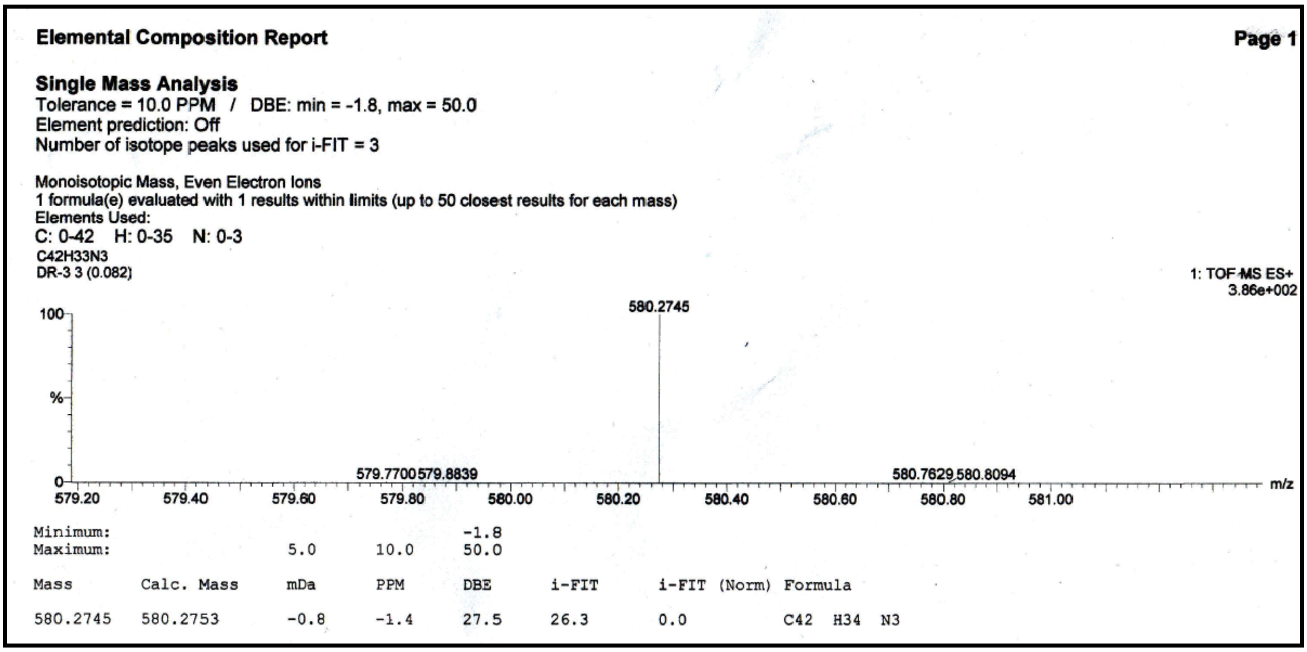


Fig. S7. MALDI TOF Mass spectra of TBB **3**.



Elemental Composition Report

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Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.8, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
1 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-42 H: 0-35 N: 0-3
C42H33N3
DR-3 3 (0.082)

```
Minimum:                                -1.8
Maximum:                 5.0     10.0   50.0

Mass      Calc. Mass    mDa    PPM     DBE     i-FIT    i-FIT (Norm) Formula

580.2745  580.2753      -0.8   -1.4    27.5    26.3     0.0          C42  H34  N3
```

Fig. S8. High Resolution Mass spectra TBB **3**.

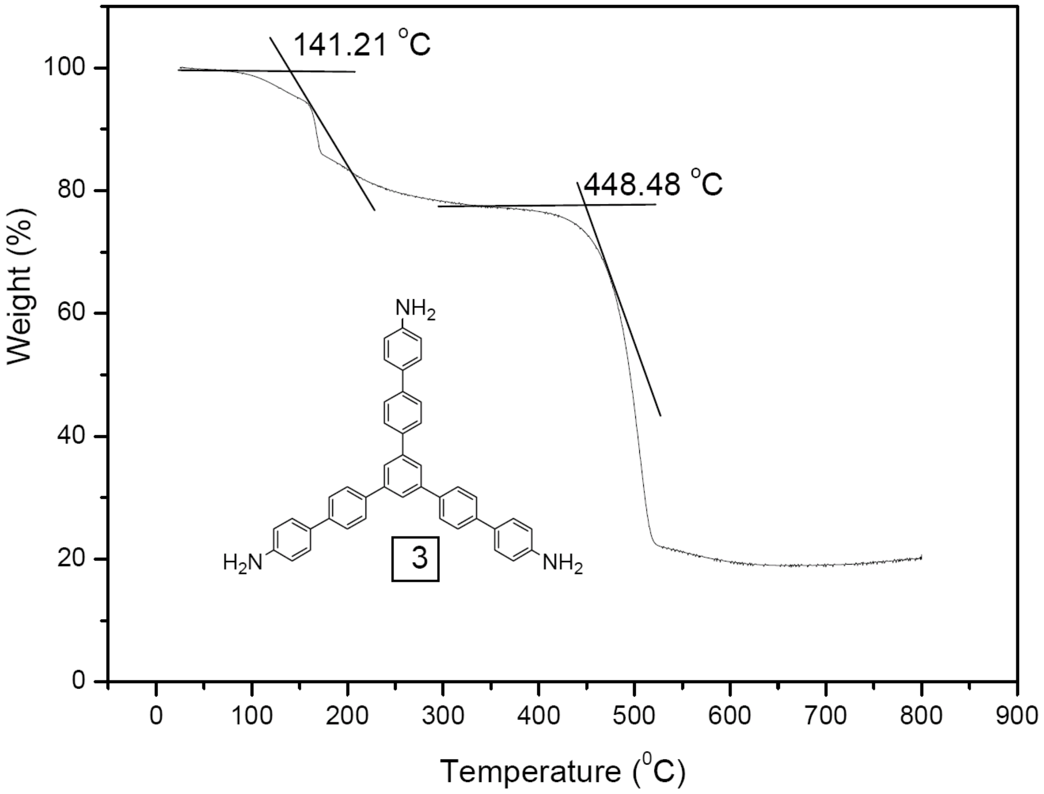

Fig. S9. Thermo gravimetric analysis (TGA) of TBB **3**.

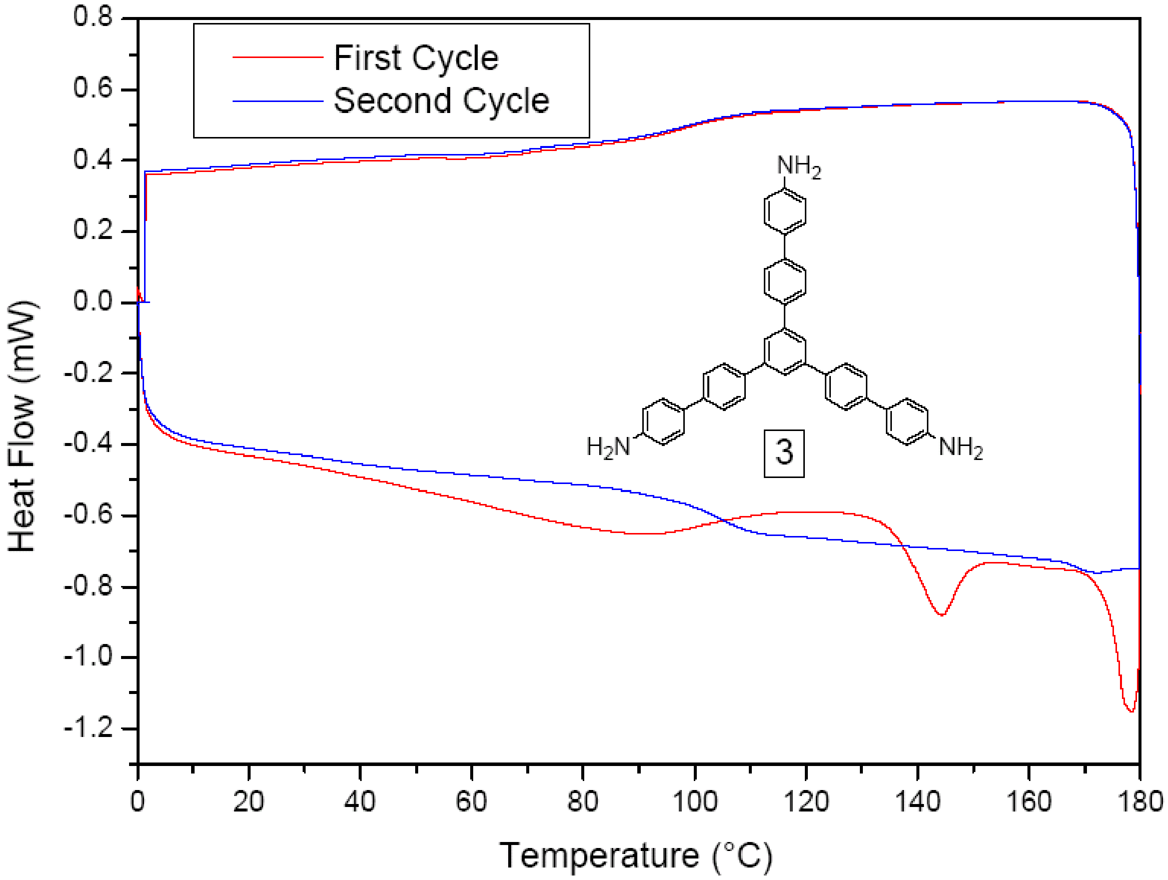

Fig. S10. Differential scanning calorimetry (DSC) data of TBB **3**.

UV-visible absorption and emission spectra of TBB 1-4

Room temperature UV–visible absorption and photoluminescence (PL) spectra of TBBs **1-4** recorded in tetrahydrofuran (THF) and in the solid state are presented in Fig. 1. The UV–Vis absorption maxima in THF solution of trigonal oligomers TBB **1,** TBB **2,** TBB **3** and TBB **4**, were observed at 299, 291, 294 and 299 nm respectively, which are due to the π–π* transition of aromatic ring, while the maxima of the photoluminescence spectrum were observed at 354, 353, 362 and 423 nm respectively. Thin solid film fluorescence spectra of the TBBs **1-4** were largely red-shifted by 45, 44 and 65 nm relative to their corresponding monomeric spectra obtained from the dilute solutions. The observed red-shift and broadening of the emission spectra of **1**, **2** and **4** in solid state support the formation of intermolecular hydrogen bonds.

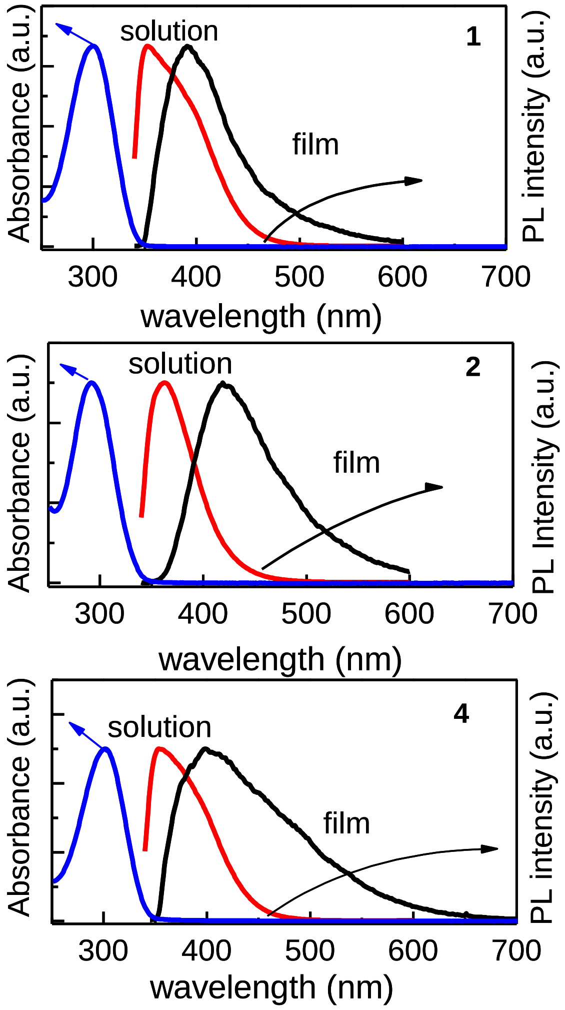

Fig. S11. UV–visible absorption spectra (blue lines) and normalized fluorescence spectra of **1**, **2** and **4** in dilute (1×10^{-6} M) Tetrahydrofuran (THF) solutions (red lines) and in the solid state (black lines). For these three TBB oligomers there is a clear red-shift in emission spectrum from solution to solid state.

However, the emission of TBB **3** in solid film is almost identical with that of the dilute solution, except for some broadening which confirms the negligible intermolecular interactions of **3** in solid film. To further confirm this behaviour we have performed low temperature photoluminescence measurements in solid thin films. From Fig. 6, it is clear that no major shift in the photoluminescence peak was observed with increasing the temperature, which should be due to very small radius and large binding energy of Frenkel excitons in the organic molecules. However, the full width at half-maximum (FWHM) in photoluminescence spectra of TBB **3** in the solid state became broadened by 0.189 eV with increasing the temperature from 10 to 300 K.

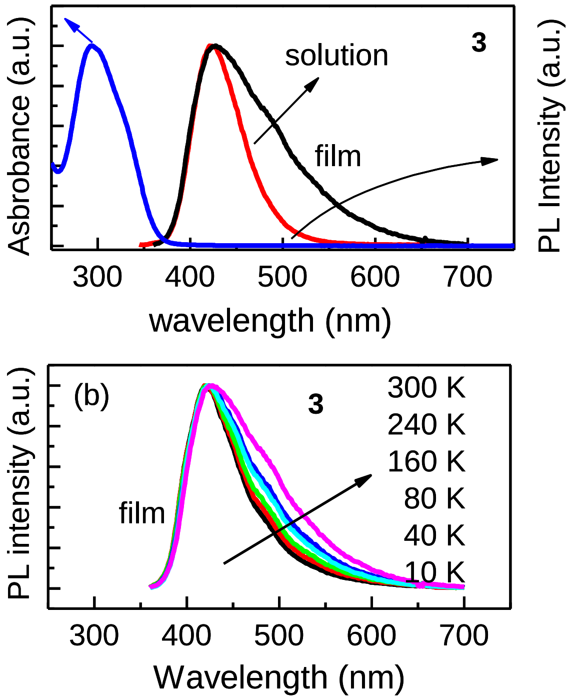

Fig. S12. a) UV–Vis absorption spectra (blue lines) and normalized fluorescence spectra of TBB **3** in dilute (1×10^{-6} M) THF solutions (red lines) and in thin solid film (black lines) b) Temperature dependent PL spectra from 10 K (black lines) to 300 K (pink line) of TBB **3**, showing an increase in FWHM from 0.475 eV to 0.664 eV on increasing temperature.

In summary, the temperature dependence of PL in the solid state has been performed for the TBB **3**. It is observed that full width at half-maximum becomes narrower with decreasing the temperature from 300 K to 10 K, showing the aggregations of molecules with decreasing temperature which is obvious for the molecules with hydrogen bonding sites, although we have not observed any significant red shift in emission as expected. This may be due to the fact that this low temperature PL measurement was performed in solid thin films not in solution.

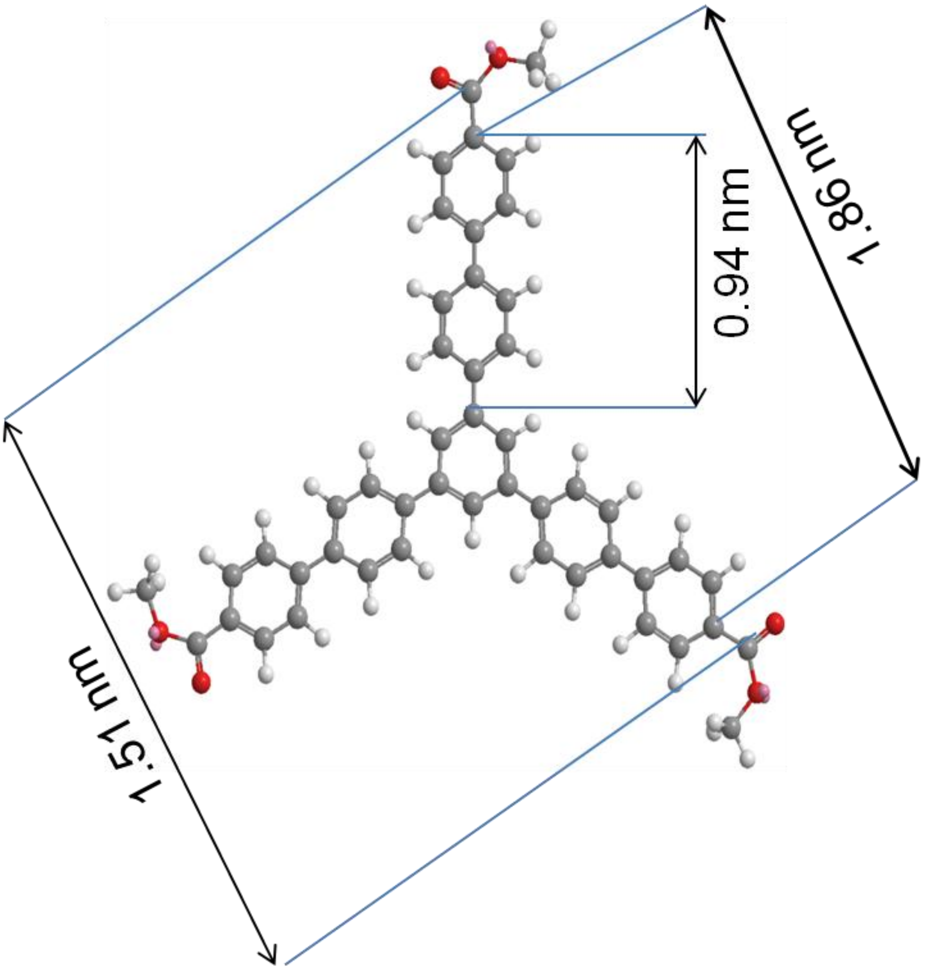

Fig. S13. Chem 3D model of TBB **1**.