“Bottom-up” Self-assembly and “Cold Crystallization” of Butterfly Shaped Tetrabenzofluorene Molecules**

Srinivasan Sampath,a,b,* A. A. Boopathia and A. B. Mandala,c,*

a. Polymer laboratory, Council of Scientific and Industrial Research (CSIR)-Central Leather Research Institute (CLRI), Adyar, Chennai 600020, INDIA.
b. Academy of Scientific and Innovative Research (AcSIR), Rafi Marg, New Delhi 110001, INDIA.
c. Chemical laboratory, Council of Scientific and Industrial Research (CSIR)-Central Leather Research Institute (CLRI), Adyar, Chennai 600020, INDIA

* sampathsrinivasan@yahoo.com, ssrinivasan@clri.res.in; abmandal@hotmail.com, abmandal@clri.res.in

[**] This research was financially supported by DST–INSPIRE Faculty Award (IFA13-CH130). S.S and A.A.B acknowledge DST for the fellowship. We thank Dr. N. Somanathan, Dr. T. Narasimhaswamy and Dr. S. N. Jaisankar for the fruitful discussion. We thank Chemical Physics, Bio-physics, Chemical and Organic laboratories in CSIR-CLRI and CSIF in CSIR-CLRI, IIT-Madras and Madras University for sample analysis. We thank Dr. E. Bhoje Gowd, NIIST-Trivandrum for variable temperature PXRD analysis.

Experimental Details

Supplementary Information
Table of Contents

Section A. NMR studies of 1 and 2  S4

Fig. S1. $^1$H NMR spectrum of 1 in CDCl$_3$
Fig. S2. $^{13}$C NMR spectrum of 1 in CDCl$_3$
Fig. S3. $^1$H-$^1$H DQF COSY NMR spectrum of 1 in CDCl$_3$
Fig. S4. $^1$H-$^{13}$C HSQC NMR spectrum of 1 in CDCl$_3$
Fig. S5. $^1$H NMR spectrum of 2 in CDCl$_3$
Fig. S6. $^{13}$C NMR spectrum of 2 in CDCl$_3$
Fig. S7. $^1$H-$^1$H DQF COSY NMR spectrum of 2 in CDCl$_3$
Fig. S8. $^1$H-$^{13}$C HSQC NMR spectrum of 2 in CDCl$_3$

Section B. Single crystal X-ray structure of 1  S10

Fig. S9. Crystal structure of 1 and hydrogen bonding interactions
Table S1. Hydrogen bond geometry for 1
Fig. S10. Crystal structure of 1 showing intermolecular π-π stacking
Fig. S11. Crystal structure of 1 showing the molecular packing

Section C. Powder X-ray diffraction spectra of 1 and 2  S13

Fig. S12. Powder X-ray diffraction spectra of 1 and 2
Fig. S13. PXRD spectra of 1 after heating and cooling cycle in DSC

Section D. Thermogravimetric analysis (TGA) spectra of 1 and 2 (Fig. S14)  S14

Section E. Differential scanning calorimetric (DSC) spectra and
Hot-stage polarising microscopy (HOPM) images of 1 and 2  S15

Fig. S15. DSC trace and HOPM images of 1 at first heating and cooling
Fig. S16. DSC trace and HOPM images of 1 at second heating and cooling
Fig. S17. DSC trace of 2 at first heating cycle
Fig. S18. DSC spectra of 1 as a function of heating rate

Table S2. DSC spectra details of 1 as a function of heating rate

Fig. S19. DSC spectra of 1 as a function of cooling rate

Fig. S20. DSC spectra of 1 as a function of sample weight

Section F. NMR studies of 1 after DSC experiment

Fig. S21. ¹H NMR spectrum of 1 in CDCl₃ after heating and cooling cycle in DSC

Fig. S22. ¹³C NMR spectrum of 1 in CDCl₃ after heating and cooling cycle in DSC

Section G. Optical studies of 1 and 2

Fig. S23. Absorption and Fluorescence spectra of 1 in different solvents

Fig. S24. Absorption and Fluorescence spectra of 2 in different solvents

Fig. S25. Absorption and Fluorescence spectra of 2 in water-THF mixtures

Fig. S26. Fluorescence decay curves of 1 and 2 in THF solution

Table S3. Photophysical properties of 1 in various solvents

Table S4. Photophysical properties of 2 in various solvents

Table S5. Photophysical properties of 1 and 2 in THF solution

Section H. Dynamic light scattering spectra of 1 and 2

Fig. S27. DLS spectra of 1 in THF and water-THF mixtures

Fig. S28. DLS spectra of 2 in THF and water-THF mixtures

Section I. Microscopic images of 1 and 2

Fig. S29. HRTEM images of 1 and particle size distribution graph

Fig. S30. HRTEM images of 1 at various location and magnification

Fig. S31. FESEM images of 1 and 2 from water-THF mixture

Fig. S32. AFM images of 1 from water-THF mixture

Fig. S33. AFM images of 1 from toluene

Fig. S34. FESEM images of 1 and 2 from toluene

Section J. References
Section A. NMR studies of 1 and 2

**Fig. S1.** $^1$H NMR spectrum of 1 in CDCl$_3$ at 298 K. x: water and acetone

**Fig. S2.** $^{13}$C NMR spectrum of 1 in CDCl$_3$ at 298 K.
Fig. S3. $^1$H-$^1$H DQF COSY NMR spectrum of 1 in CDCl$_3$ at 298 K.
Fig. S4. $^1$H–$^{13}$C HSQC NMR spectrum of 1 in CDCl$_3$ at 298 K.
Fig. S5. \(^1\)H NMR spectrum of 2 in CDCl\(_3\) at 298 K. x: dichloromethane and acetone.

Fig. S6. \(^{13}\)C NMR spectrum of 2 in CDCl\(_3\) at 298 K.
Fig. S7. $^1$H-$^1$H DQF COSY NMR spectrum of 2 in CDCl$_3$ at 298 K.
Fig. S8. $^1$H-$^13$C HSQC NMR spectrum of 1 in CDCl$_3$ at 298 K.
Section B. Single crystal X-ray structure of 1

Fig. S9. Single crystal X-ray structure of 1 a) and b) shows the labelling of carbon atoms. c) shows the distance between C29 and H32, d) shows the intermolecular distance between C7 and H27 and e) shows the distance between O1 and H9.

Table S1. Hydrogen bond geometry for 1.

<table>
<thead>
<tr>
<th>S. No</th>
<th>D–H····A</th>
<th>D–H (Å)</th>
<th>H····A (Å)</th>
<th>D····A (Å)</th>
<th>D–H····A (°)</th>
<th>Symmetry code: (i)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C27–H27····C7</td>
<td>0.981</td>
<td>2.855</td>
<td>3.654</td>
<td>139.19</td>
<td>1-x,3-y,1-z</td>
</tr>
<tr>
<td>2</td>
<td>C9–H9····O1</td>
<td>0.930</td>
<td>2.674</td>
<td>3.536</td>
<td>154.45</td>
<td>x, -1+y, z</td>
</tr>
<tr>
<td>3</td>
<td>C32–H32····C29</td>
<td>0.930</td>
<td>2.878</td>
<td>3.356</td>
<td>113.29</td>
<td>x, y, z</td>
</tr>
</tbody>
</table>
Fig. S10. Single crystal X-ray structure of 1 a) and b) shows the intermolecular π-π stacking.
Fig. S11. Single crystal X-ray structure of 1 a) shows the molecular packing and b) shows the intermolecular distance between the planes of C40 to C45 alkyl chain.
Section C. Powder X-ray Diffraction spectra of 1 and 2

Fig. S12. Powder X-ray diffraction spectra of a) 1 and b) 2.
Fig. S14. TGA curves of 1 and 2 at heating rate of 10 °C/min under N\textsubscript{2} atmosphere.
Section E. DSC spectra and HOPM images of 1 and 2

**Fig. S15.** DSC trace of 1 at heating and cooling cycle at 5 °C/min under N$_2$ atmosphere (first cycle). The inset shows the HOPM images at respective transition temperature in both heating and cooling cycle. HOPM images were recorded by placing the sample between glass covers on a temperature controlled hot stage.
Fig. S16. DSC trace of 1 at heating and cooling cycle at 5 °C/min under N$_2$ atmosphere (second cycle). The inset shows the HOPM images at respective transition temperature in both heating and cooling cycle. HOPM images were recorded by placing the sample between glass covers on a temperature controlled hot stage.
**Fig. S17.** DSC trace of 2 at heating and cooling cycle at 5 °C/min under N₂ atmosphere (first cycle).

**Fig. S18.** The effect of heating rate on the cooling traces of 1 are studied by keeping the cooling rate constant (10 °C/min) and varying the previous step heating rates. a) Heating traces of 1 with varying heating rates while the cooling rate is kept constant at 10 °C/min.a) All cooling traces at a cooling rate of 10 °C/min, however, the different color curves indicate their earlier step’s heating rate.
Table S2. DSC spectra details of 1 as a function of heating rate.

<table>
<thead>
<tr>
<th>S. No</th>
<th>( \lambda ) (K/min)</th>
<th>( T_p ) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>371.8</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>385.2</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>397.8</td>
</tr>
<tr>
<td>4</td>
<td>20</td>
<td>409.3</td>
</tr>
<tr>
<td>5</td>
<td>30</td>
<td>416.3</td>
</tr>
<tr>
<td>6</td>
<td>40</td>
<td>421.2</td>
</tr>
<tr>
<td>7</td>
<td>50</td>
<td>425.4</td>
</tr>
</tbody>
</table>

Kissinger equation:\(^1\)

\[
\ln\left(\frac{\lambda}{T_p^2}\right) = -\frac{E_a}{RT_p} + C \quad \ldots \quad 1
\]

Where \( R \) is gas constant, \( T_p \) is crystallization peak temperature, \( \lambda \) is DSC heating rate, \( E_a \) is the crystallization activation energy and \( C \) is a constant.\(^1\) The slope of \( \ln(\lambda/T_p^2) \) vs \( 1/T_p \) gives the value for \( E_a/R \). The calculated \( E_a \) is 71 ± 0.8 kJ/mol \( (R^2 = 0.999) \).

Fig. S19. The effect of cooling rate on the heating traces of 1 are studied by keeping the heating rate constant (10 °C/min) and varying the previous step’s cooling rates. a) All heating traces at a heating rate of 10 °C/min, however, the different color curves indicate their earlier step’s cooling rate. b) Cooling traces of 1 with varying cooling rates while the heating rate is kept constant at 10 °C/min.
Fig. S20. DSC trace of 1 at heating and cooling cycle at 10 °C/min under N₂ atmosphere with different sample weight in the range of 1.2 mg to 4.5 mg (second cycle). The peak positions have negligible changes or trend with increase in the sample weight in the above analysed weight range.

Section F. NMR studies of 1 after DSC experiment

Fig. S21. ¹H NMR spectrum of 1 in CDCl₃ at 298 K. Sample preparation for ¹H NMR after DSC experiment, 1 was first subjected to heating up to 210 °C and subsequent cooling back to 25 °C with heating and cooling rate of 5 °C/min under N₂ atmosphere and then dissolved in CDCl₃.
Fig. S22. $^{13}$C NMR spectrum of 1 in CDCl$_3$ at 298 K. Sample preparation for $^{13}$C NMR after DSC experiment, 1 was first subjected to heating up to 210 °C and subsequent cooling back to 25 °C with heating and cooling rate of 5 °C/min under N$_2$ atmosphere and then dissolved in CDCl$_3$.

Section G. Optical studies of 1 and 2

Fig. S23. a) Absorption and b) Fluorescence spectra of 1 in dichloromethane (DCM), tetrahydrofuran (THF), hexane, cyclohexane, toluene and dimethylformamide (DMF) at 25 °C. $\lambda_{ex}=360$ nm ($l = 1$ cm, $c = 1 \times 10^{-5}$M).
Fig. S24. a) Absorption and b) Fluorescence spectra of 2 in dichloromethane (DCM), tetrahydrofuran (THF), toluene and dimethylformamide (DMF) at 25 °C. $\lambda_{ex}=360$ nm ($l = 1$ cm, $c = 1 \times 10^{-5}$M).

Fig. S25. a) Absorption and b) Fluorescence spectra of 2 in various tetrahydrofuran (THF) water mixture ratio (From 0 % water to 70 % water in THF) at 25 °C. $\lambda_{ex}=360$ nm ($l = 1$ cm, $c = 1 \times 10^{-5}$M).
Fig. S26. Fluorescence decay curves of 1 and 2 in THF solution, emission monitored at 430 nm, $\lambda_{ex} = 375$ nm at 25 °C. ($l = 1$ cm, $c = 1 \times 10^{-5}$M). Bottom panel shows the residual traces of fluorescence decay curves fitting along with their corresponding $\chi^2$ values.
Table S3. Optical properties of 1 in various solvents.

<table>
<thead>
<tr>
<th>S. No</th>
<th>Solvent</th>
<th>Absorption Maxima ( \lambda_{\text{abs}} ) (nm)</th>
<th>Emission Maximum ( \lambda_{\text{em}} ) (nm)</th>
<th>Stokes Shift ( \Delta \nu_{\text{St}} ) cm(^{-1} )</th>
<th>Molar extinction coefficient ( (\varepsilon) \times 10^4 ) M(^{-1})cm(^{-1} )</th>
<th>Quantum Yield ( (\Phi_f) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>DCM</td>
<td>368, 382</td>
<td>431</td>
<td>3971</td>
<td>5.33</td>
<td>0.32</td>
</tr>
<tr>
<td>2</td>
<td>THF</td>
<td>368, 382</td>
<td>431</td>
<td>3971</td>
<td>3.78</td>
<td>0.33</td>
</tr>
<tr>
<td>3</td>
<td>Hexane</td>
<td>366, 380</td>
<td>427</td>
<td>3903</td>
<td>3.05</td>
<td>0.35</td>
</tr>
<tr>
<td>4</td>
<td>Cyclohexane</td>
<td>366, 382</td>
<td>427</td>
<td>3903</td>
<td>3.06</td>
<td>0.33</td>
</tr>
<tr>
<td>5</td>
<td>Toluene</td>
<td>370, 384</td>
<td>430</td>
<td>3772</td>
<td>2.63</td>
<td>0.31</td>
</tr>
<tr>
<td>6</td>
<td>DMF</td>
<td>368, 382</td>
<td>432</td>
<td>4025</td>
<td>2.22</td>
<td>0.33</td>
</tr>
</tbody>
</table>

[a] \( \Delta \nu_{\text{St}} = \lambda_{\text{abs}} - \lambda_{\text{em}} \), and is the difference in absorption and emission frequencies, or the Stokes shift. \( \lambda_{\text{ex}} = 360 \) nm. Quinine sulphate in 0.5M H\(_2\)SO\(_4\) used as quantum yield reference. Fluorescence quantum yields (±5% error) were determined using quinine sulfate as the standard \((\Phi_f = 0.546 \) in 0.1 N H\(_2\)SO\(_4\)).

Table S4. Optical properties of 2 in various solvents.

<table>
<thead>
<tr>
<th>S.No</th>
<th>Solvent</th>
<th>Absorption Maxima ( \lambda_{\text{abs}} ) (nm)</th>
<th>Emission Maximum ( \lambda_{\text{em}} ) (nm)</th>
<th>Stokes Shift ( \Delta \nu_{\text{St}} ) cm(^{-1} )</th>
<th>Molar extinction coefficient ( (\varepsilon) \times 10^4 ) M(^{-1})cm(^{-1} )</th>
<th>Quantum Yield ( (\Phi_f) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>DCM</td>
<td>368, 378</td>
<td>426</td>
<td>3699</td>
<td>6.04</td>
<td>0.39</td>
</tr>
<tr>
<td>2</td>
<td>THF</td>
<td>367, 381</td>
<td>427</td>
<td>3828</td>
<td>3.94</td>
<td>0.38</td>
</tr>
<tr>
<td>3</td>
<td>Toluene</td>
<td>368, 380</td>
<td>427</td>
<td>3754</td>
<td>3.26</td>
<td>0.38</td>
</tr>
<tr>
<td>4</td>
<td>DMF</td>
<td>366, 380</td>
<td>425</td>
<td>3793</td>
<td>2.16</td>
<td>0.39</td>
</tr>
</tbody>
</table>

[a] \( \Delta \nu_{\text{St}} = \lambda_{\text{abs}} - \lambda_{\text{em}} \), and is the difference in absorption and emission frequencies, or the Stokes shift. \( \lambda_{\text{ex}} = 360 \) nm. Quinine sulphate in 0.5M H\(_2\)SO\(_4\) used as quantum yield reference. Fluorescence quantum yields (±5% error) were determined using quinine sulfate as the standard \((\Phi_f = 0.546 \) in 0.1 N H\(_2\)SO\(_4\)).

Table S5. Optical properties of 1 and 2 in THF solution.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Quantum Yield ( (\Phi_f) )</th>
<th>Lifetime ( \tau ) (ns)</th>
<th>Average Lifetime ( \tau_{\text{av}} ) (ns)</th>
<th>( k_r ) (s(^{-1}))</th>
<th>( k_d ) (s(^{-1}))</th>
<th>( k_r/k_d )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.33</td>
<td>1.26 (35 %) 2.85 (65 %)</td>
<td>2.54</td>
<td>1.3 x 10(^8)</td>
<td>2.6 x 10(^8)</td>
<td>0.50</td>
</tr>
<tr>
<td>2</td>
<td>0.38</td>
<td>2.55 (100 %)</td>
<td>-</td>
<td>1.5 x 10(^8)</td>
<td>2.4 x 10(^8)</td>
<td>0.63</td>
</tr>
</tbody>
</table>

The average lifetime \( (\tau_{\text{av}}) \) of the biexponential decay was calculated based on the equation \( \tau_{\text{av}} = (a_1 \tau_1^2 + a_2 \tau_2^2)/(a_1 \tau_1 + a_2 \tau_2) \), where ‘a’ is the amplitude and ‘\( \tau \)’ is the corresponding lifetime of the decay components.
Section H. DLS spectra of 1 and 2

Fig. S27. Dynamic light scattering (DLS) spectra of 1 in a) THF, b) 10, c) 30 and d) 50% water:THF mixture at 25 °C (l = 1 cm, c = 1 x 10⁻⁵M).
**Fig. S28.** Dynamic light scattering (DLS) spectra of 2 in 1 in a) THF, b) 10 and c) 30% water:THF mixture at 25 °C ($l = 1$ cm, $c = 1 \times 10^{-5}$M).
Section I. Microscopic images of 1 and 2

Fig. S29. a) HRTEM images of 1 drop casted from 1x10^-4 M water:THF (30:70) solution mixture, b) Particle size distribution bar diagram of 1 obtained by analysing the particle size from HRTEM image of 1.

Fig. S30. a)-d) HRTEM images of 1 drop casted from 1x10^-4 M water:THF (30:70) solution mixture at various location and magnification. The sample is drop casted on carbon-coated TEM grids and solvents are removed by keeping the samples under vacuum at room temperature for 24 hours.
Fig. S31. FESEM images of a) 1 drop casted from 1x10^{-4} M water:THF (30:70) solution mixture, b) 2 drop casted from 1x10^{-4} M water:THF (30:70) solution mixture.

Fig. S32. a)-c) AFM images of 1 drop casted from 1x10^{-4} M water:THF (30:70) solution mixture at various magnification. The sample is drop casted on freshly cleaved mica surface and solvents are removed by keeping the samples under vacuum at room temperature for 24 hours.

Fig. S33. a) AFM height images of 1 drop casted from 1x10^{-4} M toluene solution. b) the height profile of line shown in (a). The sample is drop casted on freshly cleaved mica surface and solvent was removed by keeping the samples under vacuum at room temperature for 24 hours.
Fig. S34. a) and b) FESEM images of 1 drop casted from $1 \times 10^{-4}$ M toluene solution at different magnification. c) and d) FESEM images of 2 drop casted from $1 \times 10^{-4}$ M toluene solution at various location and magnification. The samples are drop casted on aluminum foil and solvent was removed by keeping the samples under vacuum at room temperature for 24 hours.

Section J. References