Electronic Supplementary Information

Structurally directed thienylenevinylene self–assembly for improved charge carrier mobility: 2D sheets vs 1D fibers

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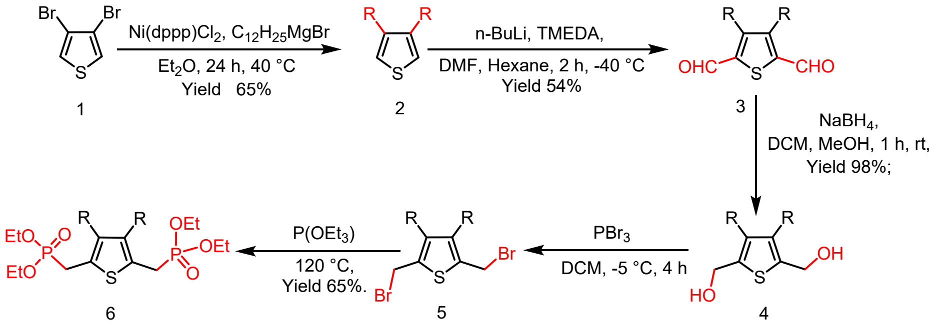
1. Materials and methods

Unless otherwise stated, all starting materials and reagents were purchased from commercial suppliers (Sigma–Aldrich, Alfa Aesar, Tokyo Chemical Industry and Sisco Research Laboratories) and used without further purification. All organic extracts were dried over sodium sulfate (Na_2SO_4) powder to remove the water, and solvents were evaporated under reduced pressure using rotary evaporator BUCHI R–210. Solvents required were dried according to standard literature procedures. Column chromatography was performed by using 100–200 mesh silica gel. Spectroscopic grade solvents were used for precipitation and optical studies.

^1H and ^{13}C NMR spectra were recorded on a 500 MHz Bruker Avance DPX spectrometer using TMS (0 ppm for ^1H) and $CDCl_3$ (77 ppm for ^{13}C) as the internal standard, respectively. FT–IR spectra were recorded on a Nicolet Impact 400D infrared spectrometer. Matrix–assisted laser desorption ionization time–of–flight (MALDI–TOF) mass spectra were obtained on AXIMA–CFR PLUS (SHIMADZU) MALDI–TOF mass spectrometer.

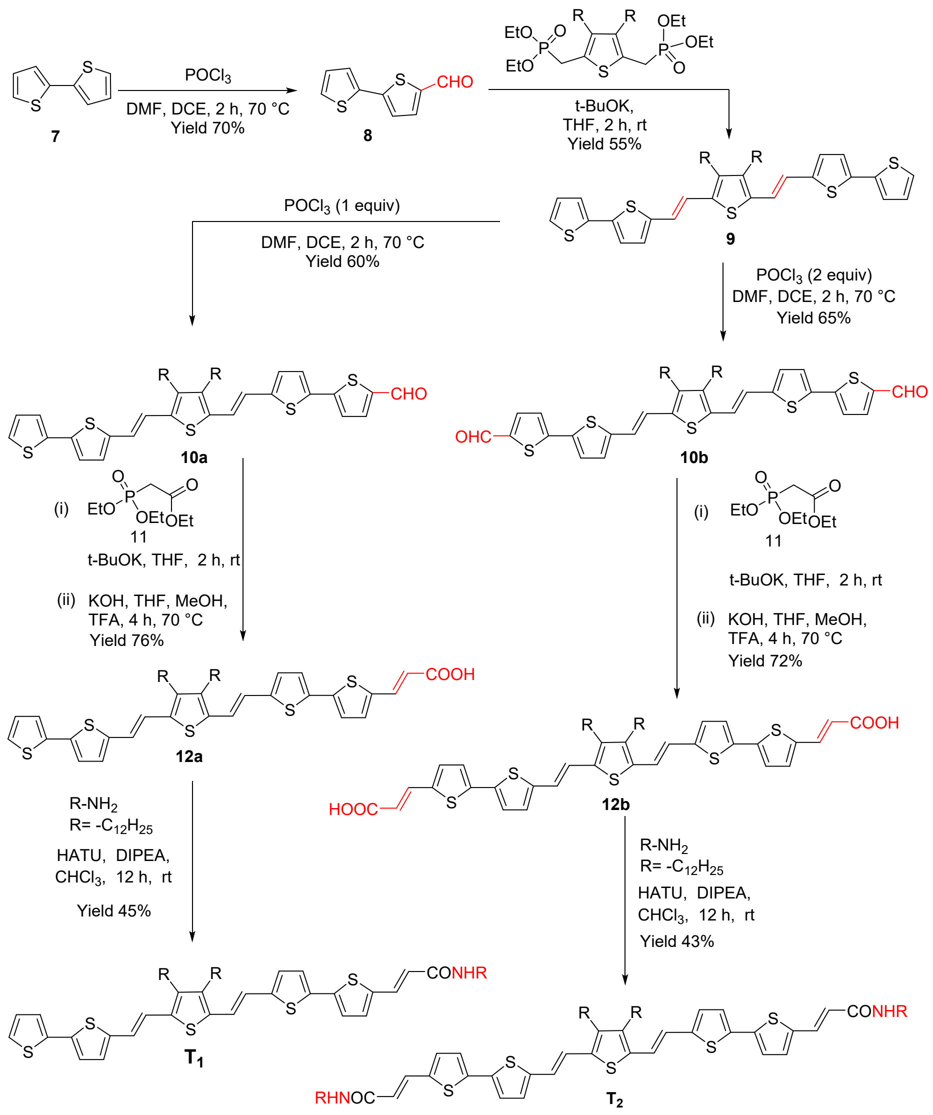
2. Synthesis and Characterization



Scheme S1 The schematic representation of the synthetic strategy for the precursor compound **6**.

Synthesis of 1-6

The synthetic strategy for the preparation of precursor of **T1** and **T2** is illustrated in Scheme S1 adopted from the previous reports.[1,2]



Scheme S2 Synthetic scheme for the preparation of **T1** and **T2**.

Synthesis of 8

Compound (**7**) was prepared by Vilsmeier formylation of 2,2′ bithiophene (**7**) (1 g, 6.02 mmol), using DMF (3 mL, 36 mmol) and $POCl_3$ (2.2 mL, 24 mmol) in dry 20 mL of 1,2 dichloroethane. The reaction mixture was reflux for 2 h. After cooling of the reaction mixture, 1 M sodium acetate was added for neutralization. The mixture was then stirred for 1h and the solution was extracted with DCM. The organic layer was separated out and dried over Na_2SO_4. The solvent was removed and purified by Column chromatography (silicagel-40% DCM/Hexane) (Yield: 70%).

^{1}**H NMR** ($CDCl_3$, 500 MHZ) δ(ppm) = 9.78 (s, 1H), 7.60 (d,1H), 7.28 (m,2H), 7.18 (d,1H), 7.00 (m, 1H) ppm.

FAB-MS (m/z) : 193.96; (calculated = 194.27)

Synthesis of 9

Compound **9** was synthesized by Wittig-Horner olefination of compound **6** and **8**. To a mixture of **6** (200 mg, 1.03 mmol) and **8** (104 mg, 2.10 mmol) in 30 mL of dry THF, t-BuOK (618 mg 5.15 mmol) was added portion wise under nitrogen atmosphere. The reaction mixture was then stirred for 3 h. After removal of the solvent under reduced pressure, the residue was dissolved in CH_2Cl_2 and washed with water. After extraction, the organic layer was separated out and dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (neutral alumina - 5% ethyl acetate /hexane) (Yield: 55%).

^{1}**H NMR** ($CDCl_3$, 500 MHz) δ(ppm) = 7.22-7.18 (m, 4H), 7.07-7.06 (m, 2H), 7.04-7.01 (t, 2H), 6.98 (s, 2H), 6.93-6.90 (m, 4H), 2.58 (t, 4H), 1.57-1.25 (m, 44H), 0.87-0.85 (m, 6H).

^{13}**C NMR (**$CDCl_3$, 125 MHz) δ(ppm) = 142.07, 142.04, 137.53, 135.84, 134.79, 127.89, 126.86, 124.43, 124.26, 123.64, 120.70, 120.05, 31.94, 31.28, 29.74, 29.70, 29.63, 29.44, 29.38, 27.01, 22.70, 14.13.

MALDI-TOF (m/z) : 801.51; (calculated = 801.35).

Synthesis of 10a

Compound (**10a**) was prepared by Vilsmeier formylation of **9** (130 mg, 0.16 mmol), using DMF (0.076 mL, 1 mmol) and $POCl_3$ (0.062 mL, 0.66 mmol) in dry 40 mL of 1,2 dichloroethane. The reaction mixture was refluxed for 2 h. After cooling the reaction mixture, 1 M sodium acetate (20 mL) was added for neutralization. The mixture was then stirred for 1 h and the solution was extracted with DCM. The organic layer was separated out and dried over Na_2SO_4. The solvent was removed and purified by column chromatography (neutral alumina – 15% ethyl acetate /hexane) (Yield: 60%).

^{1}**H NMR** ($CDCl_3$, 500 MHz) δ(ppm) = 9.85(s, 1H), 7.67–7.66 (m, 1H), 7.24 (d, 1H), 7.22 (m, 1H) , 7.21 (m, 1H), 7.19 (m, 1H), 7.08–7.01 (m, 2H), 6.98–6.97 (m, 2H), 6.94 (s, 1H), 6.93–6.89 (m, 2H), 2.58 (t, 4H), 1.52–1.25 (m, 45H), 0.88–0.85 (t, 6H);

^{13}**C NMR (**$CDCl_3$, 125 MHz) δ(ppm) =181.30, 146.15, 144.04, 141.87,141.05, 140.85, 140.38, 136.45, 136.35, 134.56, 133.34, 132.94, 126.88, 12.04, 125.95, 125.92, 123.47, 123.23, 122.89, 122.66, 120.49, 120.07, 118.90, 118.86, 30.91, 30.31,30.25, 28.73, 28.68, 28.62, 28.41, 28.36, 26.02, 25.97, 21.68, 14.11.

MALDI–TOF (m/z): 830.36; (calculated = 829.36).

Synthesis of 10b

Compound **10b** was prepared by Vilsmeier formylation of **9** (130 g, 0.16 mmol), using DMF (0.15 mL, 2 mmol) and $POCl_3$ (0.12 mL, 0.13 mmol) in dry 40 mL of 1,2 dichloroethane. The reaction mixture was refluxed for 2 h. After cooling the reaction mixture, 1 M sodium acetate (20 mL) was added for neutralization. The mixture was then stirred for 1 h and the solution was extracted with dichloromethane. The organic layer was separated out and dried over Na_2SO_4. The solvent was removed and purified by column chromatography (Yield: 65%).

^{1}H NMR ($CDCl_3$, 500 MHz) δ(ppm) = 9.86 (s, 2H), 7.68–7.67 (m, 4H), 7.09(s, 1H), 7.04(s, 1H), 6.99–6.95(m, 3H), 6.90(s, 1H), 2.60(m, 4H), 1.24(m, 42H), 0.85(t, 6H).

^{13}C NMR ($CDCl_3$, 125 MHZ) δ(ppm) = 182.37, 147.10, 144.88, 142.94, 141.51, 137.37, 135.09, 134.19, 127.18, 126.96, 124.00, 121.40, 120.36, 31.92, 31.31, 29.73, 29.68, 29.62, 29.42, 29.37, 27.04, 22.69, 14.14.

MALDI–TOF (m/z): 857.24; (calculated = 857.37)

Synthesis of 12a

The compound **12a** was synthesized by Wittig-Horner olefination of compound **10a** and ethyl 2-(diethoxyphosphoryl) acetate. To a mixture of **10a** (60 mg, 0.072 mmol) and ethyl 2-(diethoxyphosphoryl) acetate (**11**) (32 mg, 0.14 mmol) in 30 mL of dry THF, t-BuOK (33 mg, 0.30 mmol) was added in portions under nitrogen atmosphere. The reaction mixture was washed with water and extracted using chloroform. The residue was dissolved in THF and 40 mg (1 mmol) NaOH in 10 mL methanol was added. The reaction mixture was stirred under reflux for 2 h. After the removal of the solvent the crude mixture was dissolved in THF and trifluroacetic acid was added drop by drop for the neutralization. After extraction, the organic layer was separated out and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure. The crude product was purified by precipitation from chloroform/methanol mixture (Yield: 62%).

^{1}H NMR (THF-d_8, 500 MHz) δ(ppm) = 10.91 (s, 1H), 7.71 (s, 1H), 7.61-7.58 (d, 1H), 7.22-7.21 (m, 1H), 7.16-7.15 (m,1H), 7.13-7.01 (m, 2H), 7.03-6.99 (m, 2H), 6.96-6.89 (m, 4H), 6.86 (s, 1H), 6.07-6.04 (d, 2H), 2.55 (t, 4H), 1.44-1.42 (m, 4H), 1.21(m, 36H), 0.77 (t, 6H).

^{13}C NMR (THF-d_8, 125 MHZ) δ(ppm) = 164.56, 145.90, 141.28, 141.02, 140.33, 139.96, 139.90, 136.63, 136.49, 135.40, 135.26, 134.15, 134.00, 133.40, 133.15, 132.90, 132.73, 125.85, 125.36, 123.61, 123.36, 122.46, 121.89, 118.43, 118.39, 30.91, 30.04, 30.01, 29.43, 27.87, 27.81, 27.59, 27.36, 24.73, 20.74, 14.10.

MALDI-TOF (m/z) : 871.86; (calculated = 871.39).

Synthesis of 12b

The compound **12b** was Synthesized by Wittig-Horner olefination of compound **10b** and ethyl 2-(diethoxyphosphoryl) acetate, (**11**). To a mixture of **10b** (60 mg, 0.070 mmol) and ethyl 2-(diethoxyphosphoryl) acetate (**11**) (62 mg, 0.28 mmol) in 30 mL of dry THF, t-BuOK (62 mg, 0.56 mmol) was added in portions under nitrogen atmosphere. The reaction mixture was washed with water and extracted using chloroform. The product was precipitated in chloroform/methanol system and filtered. The residue (**12b**) was dissolved in THF and 40 mg (1 mmol) NaOH in 10 mL methanol was added. The reaction mixture was stirred under reflux for 2 h. After the removal of the solvent, the crude mixture was dissolved in THF and trifluroacetic acid was added drop by drop for the neutralization. After extraction, the organic layer was separated out and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure. The crude product was purified by precipitation from chloroform methanol mixture (Yield: 72%).

^{1}H NMR (THF-d_8, 500 MHz) δ (ppm) = 10.91 (s, 2H), 7.60-7.58 (d, 2H), 7.13 -7.11 (m, 2H), 7.03-7.00 (m, 2H), 6.95-6.94 (m, 2H), 6.83-6.82 (m, 2H), 6.80-6.71 (m, 4H), 6.48-6.47 (m, 2H), 2.64 (m, 4H), 1.62-1.10 (m, 44H), 0.76 (m, 6H).

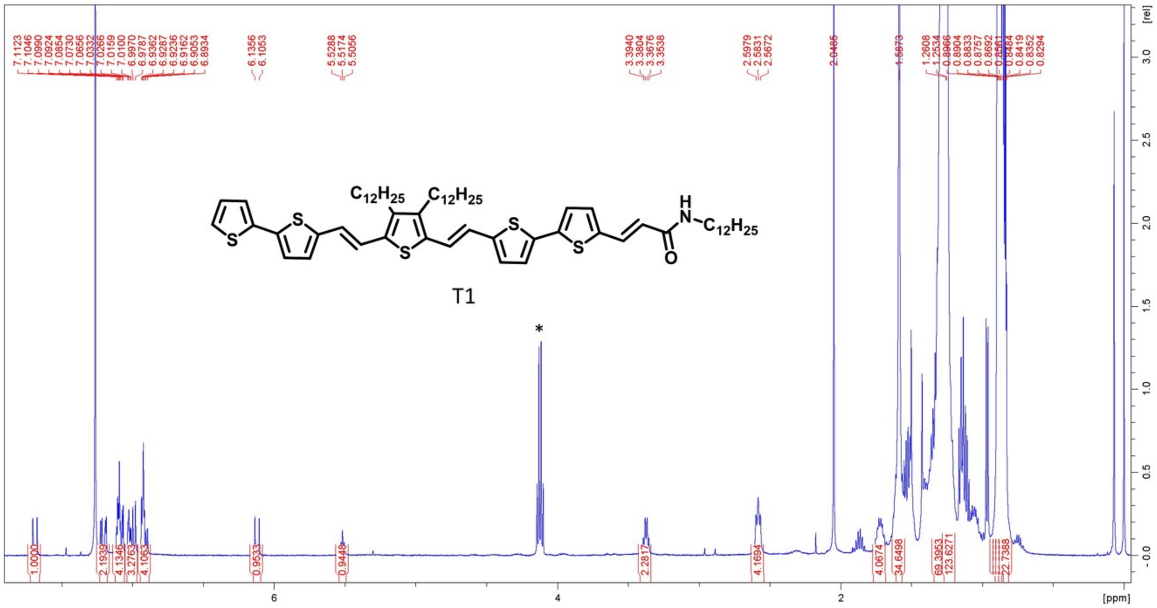
^{13}C NMR (THF-d$_8$, 125 MHZ) δ (ppm) = 164.53, 150.09, 149.8, 142.94, 141.58, 137.42, 135.48, 135.18, 133.24, 130.92, 125.98, 123.05, 122.55, 120.61, 118.54, 32.31, 32.25, 27.99, 27.64, 27.87, 27.82, 27.72, 25.61, 14.12.

MALDI-TOF (m/z) : 941.81; (calculated = 941.44)

Synthesis of T1

To an ice cooled solution of **12a** (50 mg, 0.057 mmol), in dry chloroform (30 mL), dodecylamine (11 mg, 0.06 mmol) and HATU (46 mg, 0.12 mmol). Then *N,N*–diisopropylethylamine (0.056 g, 0.4 mmol) was added drop wise to the mixture and stirred at room temperature for 12 h. After removal of the solvent, the residue was dissolved in chloroform and the organic layer was washed with water. After extraction, the organic layer was separated and dried over Na_2SO_4. Solvent was evaporated under vacuum. The crude product was purified by column chromatography (Basic Alumina–Hexane/Ethyl acetate 9:1) gave pure dark red solid compound (m.p.141–142 °C) (Yield : 45%).

^{1}H NMR (CDCl$_3$, 500 MHZ) δ (ppm) = 7.70–7.67 (d, 1H), 7.22–7.18 (m, 2H), 7.11–7.07 (m, 4H) 7.03 (m, 3H), 6.94–6.89 (m, 4H), 6.13–6.10 (d, 1H), 5.49(t, 1H), 3.38–3.37 (m, 2H), 2.58 (t, 4H) ,1.29–1.25 (m, 62H), 0.88–0.87 (m, 12H).



* residual solvente peak of ethyl acetate.

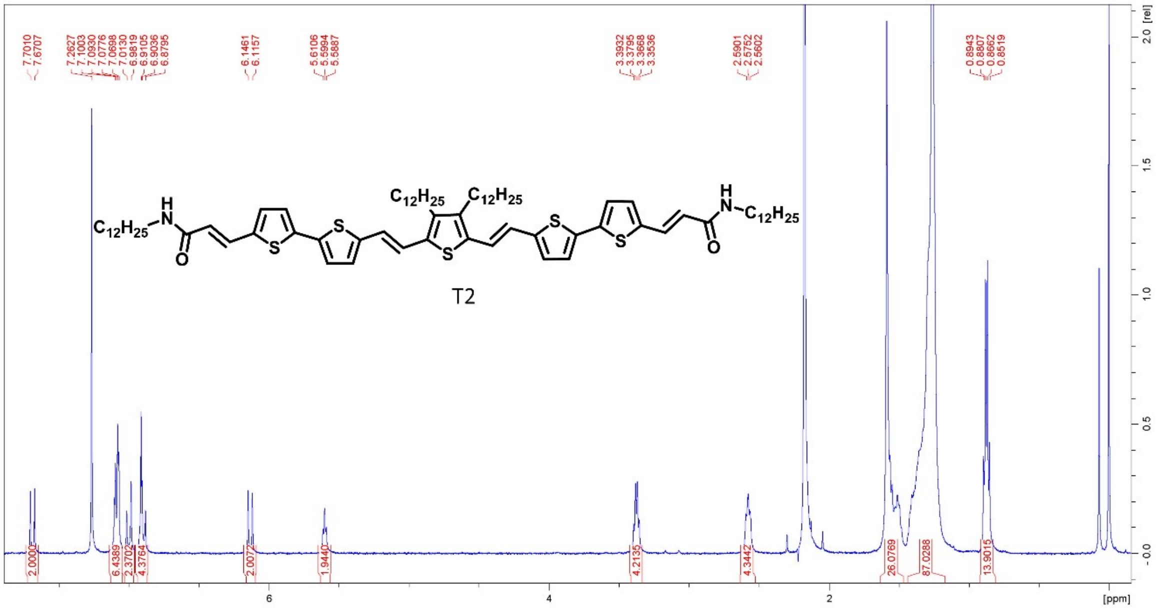
^{13}C NMR (CDCl$_3$, 125 MHZ) δ (ppm) = 165.53, 143.11, 142.40, 142.08, 141.96, 139.09, 138.68, 137.51, 135.93, 135.13, 134.63, 133.39, 131.53, 127.50, 126.95, 125.11, 124.46, 124.25, 124.15, 123.65, 120.61, 120.35, 119.97, 119.31, 39.87, 31.94, 31.29, 29.75, 29.71, 29.65, 29.57, 29.44, 29.39, 26.99, 22.70, 14.14.

MALDI–TOF (m/z) : 1039.04; (calculated = 1038.73)

Synthesis of T2

The compound **T2** was synthesized from **12b** (50 mg, 0.053 mmol), using a similar procedure described for **T1.** The crude product was purified by column chromatography (Basic Alumina, (Hexane/Ethyl acetate 8:2) to give a pure red solid compound (m.p. = 147–149 °C) (Yield : 45%).

^{1}H NMR (CDCl$_3$, 300 MHZ) δ (ppm) =7.70–7.67 (d, 2H), 7.11–7.08 (m, 6H), 7.02–6.99 (m,3H), 6.92–6.89 (m,5H), 6.14–6.11 (d, 2H), 5.55 (t, 2H) ,3.39–3.35 (q, 4H), 2.60–5.56 (t, 4H), 1.26–1.25 (m, 66H) , 0.88–0.87 (m, 12H).



^{13}C NMR ($CDCl_3$, 125 MHZ) δ(ppm) = 165.98, 143.16, 142.25, 141.15, 139.13, 137.57, 135.11, 133.92, 131.75, 130.41, 128.62, 123.92, 121.24, 120.34, 118.55, 39.94, 31.88, 31.13, 29.68, 29.38, 29.29, 29.22, 29.05, 28.97, 25.89, 22.71, 14.13;

MALDI–TOF (m/z) : 1276.45; (calculated = 1276.11).

3. Description on Experimental Techniques

3.1. Optical Measurements

Electronic absorption spectra of **T1** and **T2** were recorded on a Shimadzu UV–3101 PC NIR scanning spectrophotometer. Temperature dependent studies were carried out either in a 0.1cm or 1 cm quartz cuvette with a thermistor directly attached to the wall of the cuvette holder at a heating and cooling rate of 2 °C /min.

3.2. General procedure for gelation

The gelation studies were carried out as per reported procedures.[1,2] A definite amount of **T2** was added to 1 mL of a required solvent in a glass vial and heated to dissolve the gelator. After cooling to ambient temperature, the vessel was turned upside down to verify the gel formation. The reversibility of the gelation was confirmed by repeated heating, and cooling. The critical gelator concentration (CGC) of **T2** were determined from the minimum amount of gelator required for the formation of gel at room temperature. The xerogels were prepared by removing the solvents under reduced pressure at room temperature.

3.3. Transmission Electron Microscopy (TEM)

TEM images were obtained on a FEI Tecnai G2 30 EDAX microscope with an accelerating voltage of 100 kV and 300 kV respectively. Samples were prepared by drop casting *n*–decane solutions of **T1** and **T2** on to carbon coated copper grids at the required concentrations and dried under ambient conditions. TEM images were obtained without staining.

3.4. Atomic Force Microscopy (AFM)

Atomic Force Microscopy images were recorded under ambient conditions using a NTEGRA (NT–MDT) operating with tapping mode regime. Micro–fabricated TiN cantilever tips (NSG10) with a resonance frequency of 299 kHz and a spring constant of 20–80 $\mathrm{Nm^{-1}}$ were used. Samples for the imaging were prepared by drop casting *n*–decane solutions of **T1** and **T2** solutions on freshly cleaved mica surface at the required concentrations and dried under ambient conditions.

3.4. Wide–angle X–ray Diffraction (WAXD)

Wide–angle X–ray diffraction measurements were examined out on a XEUSS 2D SAXS/WAXS system using a Genix microsource from Xenocs operated at 50 kV and 0.3 mA. The Cu Kα radiation (λ = 1.54 Å) was collimated with a FOX2D mirror and two pairs of scatterless slits from Xenocs. For WAXD measurement, self–assembled aggregates of **T1** and **T2** was processed from *n*–decane/chloroform (1:1 v/v) and dried under vacuum, then placed directly in the sample holder.

3.5. Flash Photolysis–Time Resolved Microwave Conductivity (FP–TRMC)

Transient charge carriers were generated through photoexcitation by laser pulses of third harmonic generation (λ = 355 nm) from a Spectra Physics INDI–HG Nd:YAG laser with a pulse duration of 5–8 ns at the photon density of 4.6×10^{15} photon $\mathrm{cm^{-2}}$. The frequency and power of probing microwave were set at around 9.1 GHz and 3 mW, respectively, so that the electric field of the microwave was sufficiently small not to disturb the motion of charge carriers. Photoconductivity transients, demodulated through a GaAs crystal–diode with Schottky–barriers (rise time < 1 ns), were monitored by a Tektronix model TDS3032B digital oscilloscope. Time constant (τ) of the present TRMC system was then determined by the Q–value of microwave cavity (Q = 2000), leading to $\tau = Q/2f \sim 100$ ns. The observed conductivities were normalized, given by a photocarrier generation yield (ϕ) multiplied by sum of the carrier mobilities of electron/hole ($\Sigma\mu$), according to the equation,

$$\phi\Sigma\mu = \mathrm{A}\Delta\mathrm{P_R}/\mathrm{eI_0F_LP_R}$$

where, e, A, I_0, F_L, P_R and ΔP_R are elementary charge, sensitivity factor (S cm^{-1}), incident photon density of the excitation laser (photon cm^{-2}), correction factor (cm^{-1}) for overlapping between special distribution of photo–generated charge carriers and electromagnetic field strength of probing microwave in the cavity, and reflected microwave power and its transient change, respectively.

A white light continuum from a Xe lamp was used as a probe light for TAS. The probe light was guided into a wide–dynamic–range streak camera (Hamamatsu C7700) which collects two–dimensional image of the spectrum and time profiles of light intensity. All the experiments were carried out at room temperature.

In order to estimate the ϕ, *N*,*N′*–bis(di–nonyl)–3,4,9,10–perylenedicarboximide (PDI) was used as an acceptor and 20 wt% PDI was mixed with **T1** and **T2**. Self–assembled and non–assembled films of **T1/PDI** and **T2/PDI** were processed from chloroform and *n*–decane/chloroform (1:1 v/v) respectively and drop–cast over quartz plate and dried under vacuum at 40 °C. The anion radical of PDI was observed around 650–800.

3.6. Structural Optimization

Geometry optimization of **T1** and **T2** was carried out using density functional theory (DFT), where B3LYP used as a function and 6−31G* as the basis set in the Gaussian09 suite (Revision D.01).[3]

4. Additional Figures

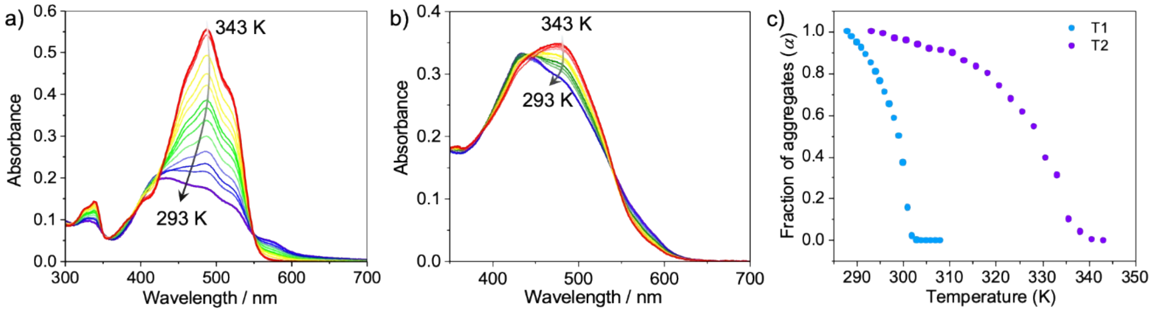


Fig. S1 Temperature dependent absorption spectra of a) **T1** and b) **T2** in *n*–decane. (c) Experimental cooling curve of **T1** and **T2** monitored at respective absorption maxima.

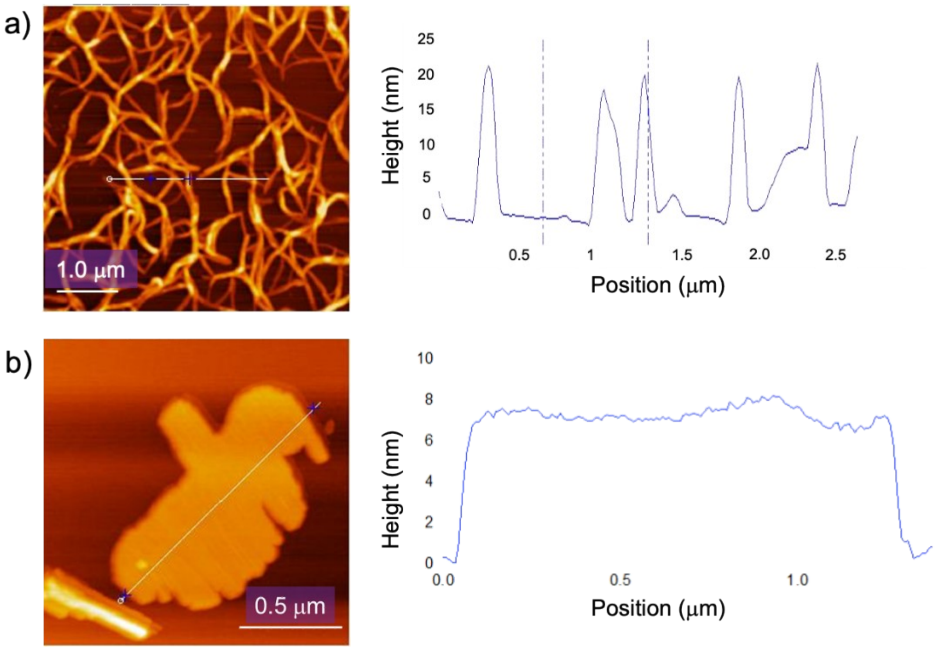


Fig. S2 AFM images of the self–assembled a) **T1** and b) **T2** with corresponding height profiles.

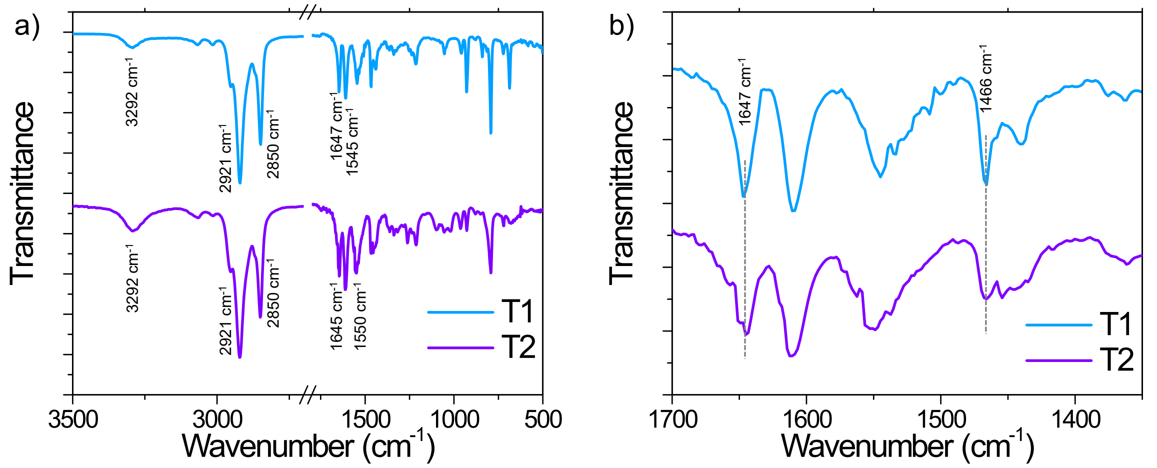


Fig. S3 FT–IR spectra of the self–assembled **T1** and **T2** processed from *n*–decane a) complete spectra b) selected region of interest.

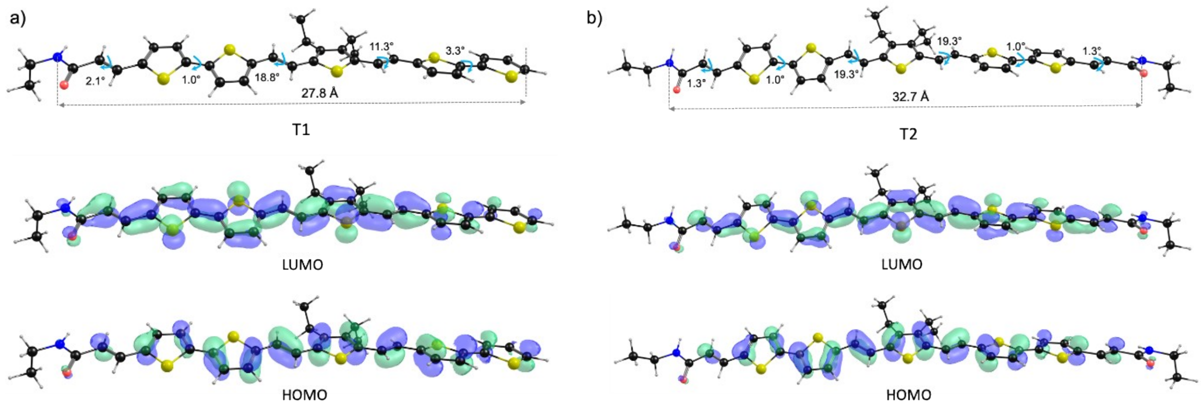


Fig. S4. Geometry optimized structures of a) **T1** and b) **T2** with corresponding HOMO and LUMO, having isosurface (0.03) of the electron density. Long alkyl chains were replaced with ethyl groups to reduce the calculation time and computational cost.

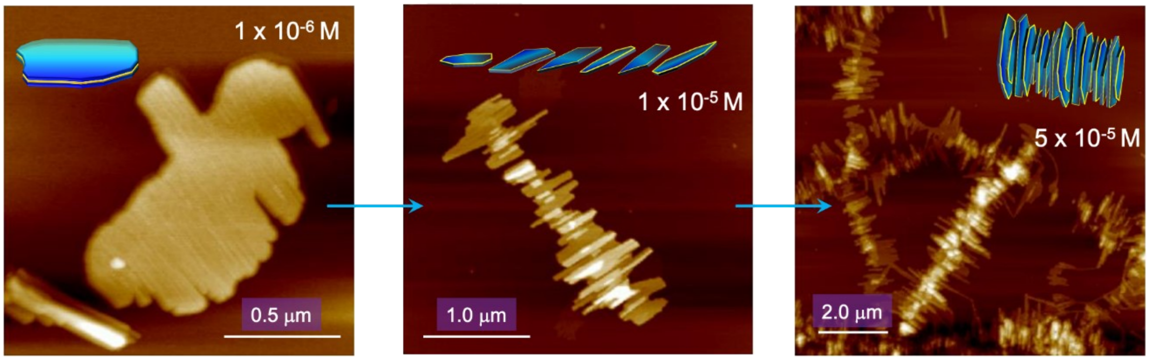


Fig. S5 Sequential AFM images of the self-assembled **T1** with the corresponding pictorial representation as inset showing the process of hierarchical assembly formation with the increase in concentration.

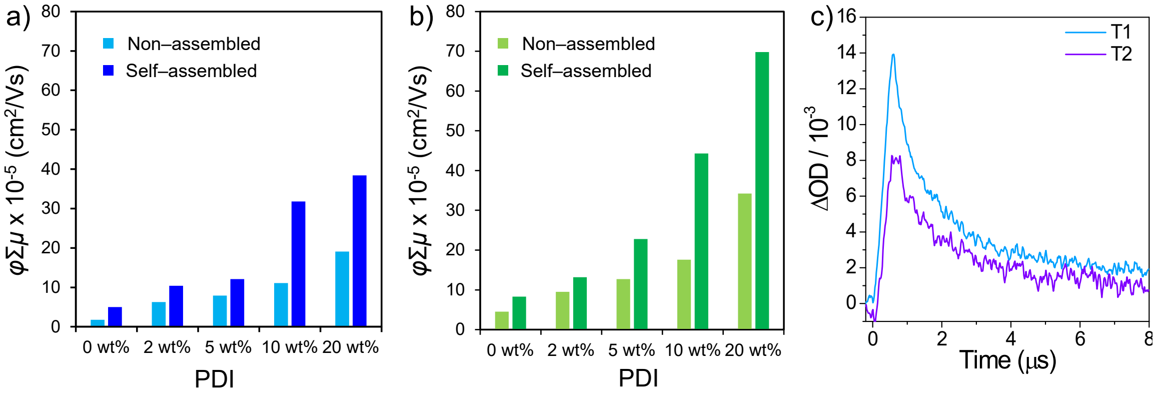


Fig. S6 Photoconductivity of self–assembled and non–assembled films of (a) **T1** and (b) **T2** with the increase in concentration of PDI. (c) Transient absorption decay profile of PDI anion radical at 715 nm in the self–assembled films of **T1** and **T2** consisting of 20 wt% PDI.

Table S1 Gelation studies of **T2** in polar and non–polar solvents

Solvents	**Nature of gel**	**CGC**(mM) **2**
Decane	G	0.35
Cyclohexane	G	0.41
Benzene	G	0.59
Toluene	G	0.68
Chloroform	S	-
Methanol	NS	-
DMSO	NS	-

In parenthesis, G = gel, S = Soluble, and NS = Not Soluble at room temperature.

9. Supplementary Information References

(1) S. Prasanthkumar, A. Saeki, S. Seki and A. Ajayaghosh, *J. Am. Chem. Soc.* 2010, **132**, 8866−8867.

(2) S. Prasanthkumar, A. Gopal and A. Ajayaghosh, *J. Am. Chem. Soc.* 2010, **132**, 13206–13207.

(3) Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.