Supporting Information to

Pathway Complexity in the Enantioselective Self-Assembly of Functional Carbonyl-Bridged Triarylamine Trisamides

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1. METHODS AND MATERIALS

Dry ortho-dichloro benzene (*o*-DCB) was purchased from SIGMA ALDRICH and used as received.

UV-vis measurements were performed on a JASCO V-650 Spectrophotometer, attached with a JASCO ETCR 762 sample holder for solution samples.

Photoluminescence and circular dichroism spectra were recorded on a JASCO J-815 CD Spectrometer equipped with a FMO-427S/15 emission monochromator and a JASCO PFD-425S/15 peltier temperature control.

TEM images were recorded on a LEO 922 Omega electron microscope operated at 200 kV in bright-field mode.

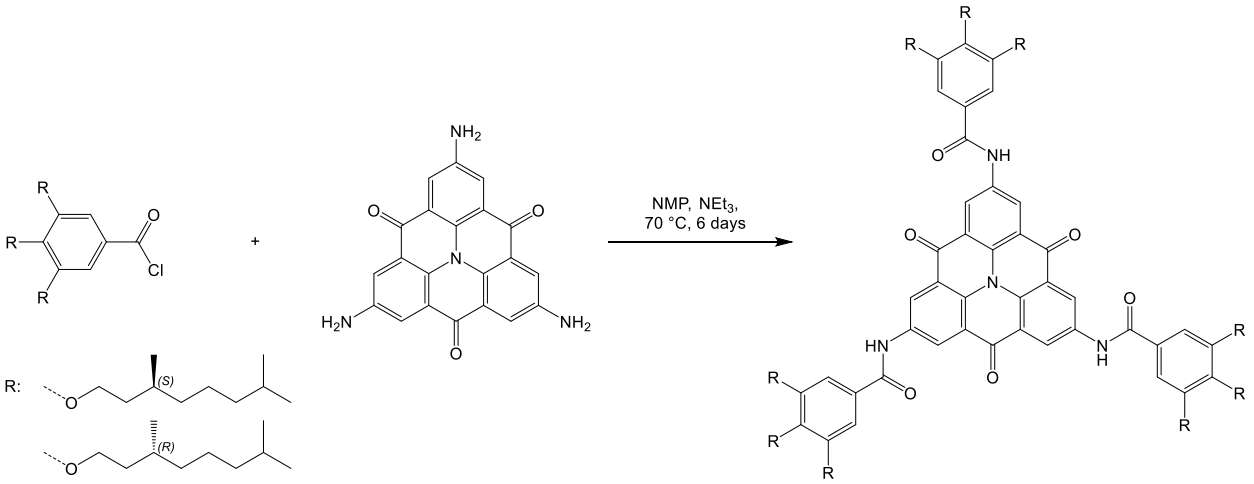
SAXS samples were mounted on V1 grade mica sheets 5-7 µm thick and measured using a SAXSLAB GANESHA system equipped with a GeniX-Cu ultralow divergence source producing X-ray photons with a wavelength of 1.54 Å and a flux of $1 \cdot 10^8$ phs^{-1}. 2D Scattering patterns were collected using a Pilatus 300K silicon pixel detector with a 487×619 pixel dimension and 172 μm^2 pixel size. The beam center and q range were calibrated using the diffraction peaks of silver behenate. Conversion of 2D images into 1D spectra was accomplished with Saxsgui software.

Atomic force microscopy (AFM) was conducted using a MFP-3D system (Asylum Research, Santa Barbara, CA) in non-contact tapping mode. Samples were prepared by spin-coating onto glass coverslips from a $3.5 \cdot 10^{-6}$ M solution in methylcyclohexane at 1000 RPM for 60 seconds. Images were processed using the IgorPRO MFP-3D and Gwyddion 2.45 software to determine feature sizes.

Circular polarization of luminescence (CPL) was measured on a home-built instrument using a photomultiplier array with 16-channels. The instrument uses a photoelastic modulator and digital photon counting. CPL spectra were measured with the emission detector in a direction perpendicular to the excitation beam. To avoid artifacts due to photoselection, the excitation light was linearly polarized in the plane spanned by excitation and emission beams.

2. SYNTHESIS OF COMPOUND **1** AND **2**

3,4,5-tri((*S/R*)-3,7-dimethyloctyloxy)benzoic acid chloride as peripheral building block and 2,6,10-triamino carbonyl-bridged triarylamine as core building block were synthesized following literature procedures.[1,2]



Scheme S1: Synthesis of compound **1** and **2** from 3,4,5-tri((*S/R*)-3,7-dimethyloctyloxy)benzoic acid chloride and 2,6,10-triamino carbonyl-bridged triarylamin.

Carbonyl-bridged triarylamine trisamide compound **1** and **2**:

Under dry conditions, 0.2 ml Pyridine (2.23 mmol, 6.5 eq.) and 126 mg 2,6,10-triamino carbonyl-bridged triarylamin (0.342 mmol, 1 eq.) were added at 0 °C to a solution of 1.33 mg 3,4,5-tri((S)-3,7-dimethyloctyloxy)benzoic acid chloride (2.23 mmol, 6.5 eq.) in 15 ml NMP. The reaction mixture was heated to 70 °C and stirred for 6 days. Then the solution was poured into ethanol/water and the precipitate was filtered off and subsequently washed with ethanol and diethylether. The crude product was first filtered over a short silica column with warm hexane/THF (1:1) and then recrystallized from DMF with a small amount of THF. The orange product was filtered and washed with dieethylether. The product was obtained as bright orange powder in 70.6 % yield (500 mg).

^{1}H-NMR (300.1 MHz, *o*-DCB-d_4/DMSO-d_6): δ = 0.81 (d, 54H, C*H*3), 0.96 (m, 27H, C*H*3), 1.09 (m, 27$H_{aliph.}$), 1.29 (m, 27$H_{aliph.}$), 1.44 (m, 9$H_{aliph.}$), 1.60 (m, 9$H_{aliph.}$), 1.77 (m, 9$H_{aliph.}$), 1.91 (m, 9$H_{aliph.}$), 4.15 (m, 18H, OC*H*$_2$CH$_2$), 7.67 (s, 6H, (CO)CC*H*C), 9.69 (s, 6H, CC*H*C), 10.73 (s, 3H, (CO)N*H*) ppm; ^{13}C-NMR (75.5 MHz, *o*DCB-d_4/DMSO-d_6): δ = 19.0, 19.1, 22.0, 22.2, 24.4,27.5, 29.2, 29.4, 36.2, 37.1, 37.2, 38.8, 38.9, 66.8, 70.8, 106.3, 122.9, 128.4, 131.2, 132.2, 137.3, 140.9, 152.5, 164.9, 175.3, ppm; IR (neat): ṽ = 3289 (m), 3074 (w), 2953 (s), 2925 (s), 2869 (s), 1662 (s), 1648 (s), 1601 (m), 1576 (m), 1532 (s), 1497 (s), 1461 (s), 1428 (s), 1383 (m), 1328 (s), 1227 (s), 1211 (s), 1108 (s), 1045 (w), 913 (m), 890 (m), 797 (m), 757 (m) cm^{-1} (s); MALDI-TOF-MS: m/z calcd for the Ag-adduct $C_{132}H_{204}AgN_4O_{15}$ [M]+ 2194.96 g/mol, found 2194.5 g/mol; thermally stable up to 300 °C, melting was not observed below decomposition temperature.

3. MOLECULAR MODELLING OF COMPOUND **1**

The energy minimized structure of compound **1** was calculated using a free copy of Avogadro Version 1.1.0 with an MMFF94s force field. The structure reveals a molecular radius of 2.2 nm in the case of ideally extended aliphatic side arms (Figure S1).

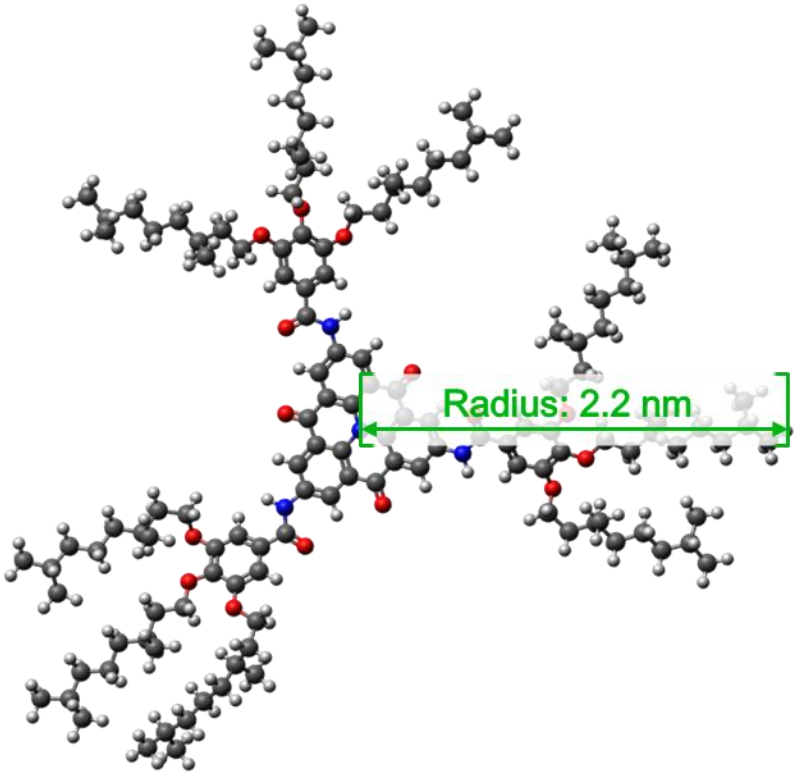


Figure S1: Molecular model of compound **1** with extended side arms.

4. SAXS MEASUREMENTS OF COMPOUND **1** IN BULK

SAXS samples were mounted on V1 grade mica sheets 5-7 µm thick and measured using a SAXSLAB GANESHA system equipped with a GeniX-Cu ultralow divergence source producing X-ray photons with a wavelength of 1.54 Å and a flux of 1 x 108 phs^{-1}. Scattering patterns were collected using a Pilatus 300K silicon pixel detector with a 487 x 619 pixel dimension and 172 μm^2 pixel size. The beam center and q range were calibrated using the diffraction peaks of silver behenate. Conversion of 2D images into 1D spectra was accomplished with Saxsgui software.

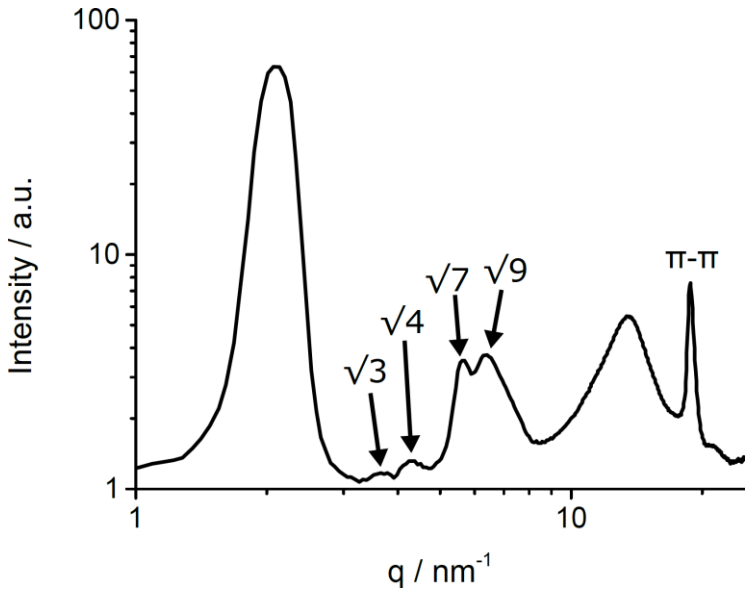


Figure S2: Small angle X-ray scattering (SAXS) of a powder sample of ***S*-CBT**. The locations of the higher order reflections correspond to a columnar hexagonal morphology and the scattering peak for the π-π stacking of the aromatic cores is indicated.

5. THERMODYNAMIC CHARACTERIZATION

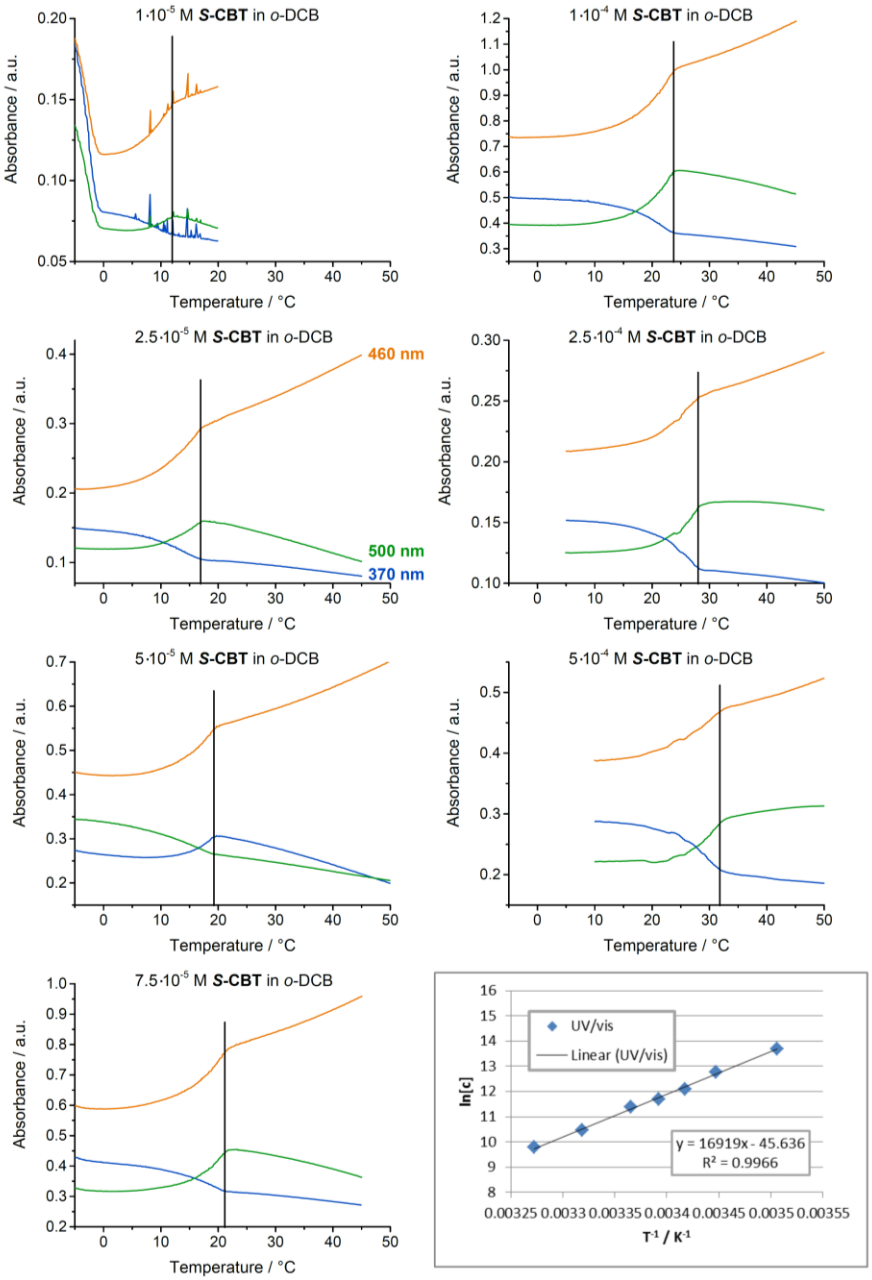


Figure S3.1: For seven different concentrations, ***S*-CBT** in *o*-DCB self-assembled in state **B** is heated with 0.1 $Kmin^{-1}$ and the absorbance at 370 nm, 460 nm, and 500 nm is monitored. At the elongation temperature T_e, spectroscopic features in the spectra that can be ascribed to state **B** vanish leaving only spectroscopic bands characteristic of state **A**. Plotting the concentration on a logarithmic scale versus the inverse elongation temperature (T_e) in a van't Hoff plot reveals a linear dependence. From these plots values for ΔH° and ΔS° of -141 kJ mol^{-1} and -379 J mol^{-1} K^{-1}, respectively, could be determined. The corresponding value for the elongation constant K_e at 273 K is $1.25 \cdot 10^7$ M^{-1}.

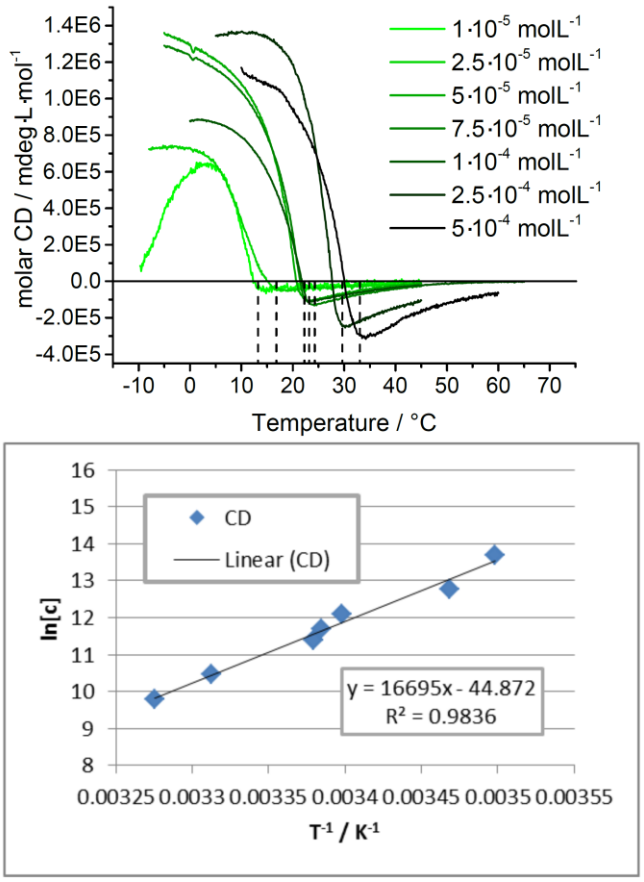


Figure S3.2: For seven different concentrations, ***S*-CBT** in *o*-DCB self-assembled in state **B** is heated with 0.1 $Kmin^{-1}$ and the CD-value at 490 nm is monitored. Plotting the logarithm of the concentration versus the inverse elongation temperature (T_e) in a van't Hoff plot reveals again a linear dependence. From these plots values for ΔH° and ΔS° of -139 kJ mol^{-1} and -373 J mol^{-1} K^{-1}, respectively, could be determined. The corresponding value for the elongation constant K_e at 273 K is $1.18 \cdot 10^7$ M^{-1}.