Supporting Information

Consequences of Hidden Kinetic Pathways on Supramolecular Polymerization
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Summary of Contents

1. Nucleation-Elongation Model for cooperative Supramolecular Polymerizations .......................................2
2. Denaturation Model for Cooperative Supramolecular Polymerizations ..........................................................3
3. Thermodynamic Parameters ........................................................................................................................4
4. Supplementary Figures ................................................................................................................................5
5. Calculation of the molar fraction of Agg I and Monomer vs. Temperature ..................................................17
6. Experimental Part .......................................................................................................................................18
   6.1. Materials and Methods ........................................................................................................................18
   6.2. Synthesis and Characterization .............................................................................................................20
1. Nucleation-Elongation Model for cooperative Supramolecular Polymerizations

The equilibrium between the monomeric and supramolecular polymer species can be described in a cooperative process with the Nucleation-Elongation model which was developed by Ten Eikelder, Markvoort and Meijer\textsuperscript{1,2}. This model is used to describe the aggregation of 1 which exhibits a non-sigmoidal cooling curve as shown in temperature dependent UV-Vis experiments. The model extends nucleation-elongation based equilibrium models for growth of supramolecular homopolymers to the case of two monomer and aggregate types and can be applied to symmetric supramolecular copolymerizations, as well as to the more general case of nonsymmetric supramolecular copolymerizations.

In a cooperative process the polymerization occurs via two steps: a nucleation step, where a nucleus, which is assumed to have a size of 2 molecules, is formed and a following elongation step. The values $T_e$, $\Delta H^\circ_{\text{nuc}}$, $\Delta H^\circ$ and $\Delta S^\circ$ can be found by a non-linear least-square analysis of the experimental melting curves. The equilibrium constants associated with the nucleation and elongation phases can be calculated using the following equations:

Nucleation step: $K_n = e^\left(-\frac{\left(\Delta H^\circ - \Delta H^\circ_{\text{nuc}}\right)}{RT}\right)$

Elongation step: $K = e^\left(-\frac{\Delta H^\circ}{RT}\right)$

Furthermore, the cooperativity factor ($\sigma$) is given by:

$$\sigma = \frac{K_n}{K_e} = e^\left(-\frac{\Delta H^\circ_{\text{nuc}}}{RT}\right)$$

\textsuperscript{1} H. M. M. Ten Eikelder, A. J. Markwoort, T. F. A. De Greef, and P. A. J. Hilbers, \textit{J. Phys. Chem. B} 2012, 116, 5291-5301.

\textsuperscript{2} A. J. Markvoort, H. M. Ten Eikelder, P. J. J. Hilbers, T. F. A. De Greef and E. W. Meijer, \textit{Nat. Commun.} 2011, 2, 509-517.
2. Denaturation Model for Cooperative Supramolecular Polymerizations

The denaturation model is based on the concentration-dependent supramolecular polymerization equilibrium model by Goldstein, where the polymerization is described as a sequence of monomer addition equilibria.

\[
[P_n] = K_n[P_{n-1}][X]
\]

\[
[P_{n+1}] = K_e[P_n][X]
\]

\[
[P_i] = K_e[P_{i-1}][X]
\]

For the cooperative model \( K_n < K_e \) and for isodesmic process \( K_n = K_e \). The concentration for each species \( P_i \) is given by \( [P_i] = K^{i-1}e [X] \) for \( i \leq n \) and \( [P_i] = K^n e [K^{n-1}][X]^i \) for \( i > n \).

The dimensionless mass balance is obtained by inserting the dimensionless concentration, the monomer concentration \( x = K_e[X] \) and the concentration of each species \( P_i \) (for \( i \leq n \): \( p_i = \sigma^{i-1}x^i \) and for \( i > n \): \( p_i = \sigma^{n-1}x^i \)).

\[
x_{tot} = \sigma^{-1} \sum_{i=1}^{n} i(\sigma x)^i + \sigma^{n-1} \sum_{i=n+1}^{\infty} ix^i
\]

Both sums are evaluated by using standard expressions for converging series:

\[
x_{tot} = \left( \frac{(\sigma x)^{n+1}(n\sigma x - n - 1)}{(\sigma x - 1)^2} + \frac{\sigma x}{(\sigma x - 1)^2} - \sigma^{n-1} \left( \frac{x^{n+1}(nx - n - 1)}{(x - 1)^2} \right) \right)
\]

With \( x_{tot} = c_{tot}K_e \) and \( c_{tot} \): total monomer concentration.

The sum solved by standard numerical methods (Matlabfzerosolver) yields the dimensionless monomer concentration \( x \). Considering that every species with \( i > 1 \) is defined as aggregate, the degree of aggregation results in:

\[
\alpha_{A gg} = \frac{x_{tot} - x}{x_{tot}}
\]

Via \( K_e = \exp(-\Delta G_0^0/RT) \), the denaturation curves can be obtained with \( f \) defined as volume fraction of good solvent:

\[
\Delta G_0^0 = \Delta G^0 + m f
\]

It is assumed that the cooperativity factor \( \sigma \) is independent on the volume fraction and the \( m \) value for the elongation regime equals the \( m \) value for nucleation.

The denaturation data needs to be transformed into the normalized degree of aggregation, if fitted to the supramolecular polymerization equilibrium model:

---

1. P. A. Korevaar, C. Schaefer, T. F. A. de Greef, E. W. Meijer, *J. Am. Chem. Soc.*, 2012, 134, 13482-13491.
2. R. F. Goldstein and L. Stryer *Biophys. J.*, 1986, 50, 583-599.
\[ f = \frac{A(f) - A(f = 0)}{A(f = 1) - A(f = 0)} \]

The optimization of the four needed parameters (\(\Delta G_0, m, \sigma \) and \(p\)) to fit the equilibrium model to the experimental data (normalized degree vs. \(f\)) is done by the non-linear least-squares analysis using Matlab (lsqnonlin solver). The data is then fitted with the non-linear least squared regression (Levenberg-Marquardt algorithm).

### 3. Thermodynamic Parameters

The thermodynamic Parameters (Table S1+S2) were obtained fitting respective experimental data to the nucleation-elongation model or the denaturation model. VT fits were obtained by simultaneously fitting multiple concentrations (\textbf{Agg I}: 3, 4, 5 \(\mu\)M; \textbf{Agg II}: 2.5, 5, 7.5, 10 \(\mu\)M).

**Table S1**: Thermodynamic parameters obtained for \textbf{Agg I}

| \(c^a\) | \(\Delta H_0^b\) | \(\Delta S_0^c\) | \(\Delta H_{NP}^b\) | \(T_{ed}\) | \(\Delta G_{298}^b\) | \(K_{ee}\) | \(K_{nucle}\) | \(\sigma\) |
|---|---|---|---|---|---|---|---|---|
| EQ model | 3, 4, 5 | -106.8 | -190.0 | -24.8 | 361.0 (3 \(\mu\)M) | -50.1 | 3.3 x 10\(^5\) | 87.3 | 2.6 x 10\(^5\) |
| VT-fit | 363.9 (4 \(\mu\)M) | 366.2 (5 \(\mu\)M) |
| Denat. fit | 5 | -51.5 | | | | | 6.6 x 10\(^2\) |

\(a\) in \(\mu\)M; \(b\) in \(\text{kJmol}^{-1}\); \(c\) in \(\text{JK}^{-1}\text{mol}^{-1}\); \(d\) in \(K\), the values in parentheses correspond to the utilized concentration; \(e\) in \(M^{-1}\)

**Table S2**: Thermodynamic parameters obtained for \textbf{Agg II}

| \(c^a\) | \(\Delta H_0^b\) | \(\Delta S_0^c\) | \(\Delta H_{NP}^b\) | \(T_{ed}\) | \(\Delta G_{298}^b\) | \(K_{ee}\) | \(K_{nucle}\) | \(\sigma\) |
|---|---|---|---|---|---|---|---|---|
| EQ model | 2.5, 5, 7.5, 10 | -286.2 | 743.0 | -8.9 | 336.5 (5 \(\mu\)M) | -64.6 | 4.0 x 10\(^5\) | 1.7 x 10\(^4\) | 4.2 x 10\(^2\) |
| VT-fit | 338.8 (7.5 \(\mu\)M) | 340.1 (10 \(\mu\)M) | 341.1 (12.5 \(\mu\)M) |
| Denat. fit | 5 | -41.6 | | | | | 1.1 x 10\(^2\) |

\(a\) in \(\mu\)M; \(b\) in \(\text{kJmol}^{-1}\); \(c\) in \(\text{JK}^{-1}\text{mol}^{-1}\); \(d\) in \(K\), the value in parentheses correspond to the utilized concentration; \(e\) in \(M^{-1}\)
4. Supplementary Figures

Figure S1: UV-Vis spectra of free ligand (black, c $= 1 \times 10^{-5}$ M) monomer (red, c $= 5 \times 10^{-6}$ M), Agg I (blue, c $= 5 \times 10^{-6}$ M) and Agg II (cyan, c $= 5 \times 10^{-6}$ M) prepared by a) thermal quenching, b) solvophobic quenching. CD spectra of Agg I (c) and Agg II (d) for (R)- and (S)-enantiomer (c $= 5 \times 10^{-6}$ M, for all $\alpha = 1$), showing that both enantiomers form identical aggregates. Time dependent CD-spectra of Agg II for (R)-1 (e) and (S)-1 (f).

The slight difference in the intensity of the spectra of Agg II (d) originates from the high sensitivity of the CD measurements towards further growth/clustering of Agg II which results in a strong LD signal affecting the CD intensities (see Fig. S5). As these processes occur very quickly after quenching, the intensity depends strongly on the exact point in time when the spectra are measured (see time dependent spectra (e)+(f)). Nevertheless, the spectral features are almost identical, which proves that both enantiomers form the same supramolecular polymers, but with inverse CD signals.
**Figure S2:** VT UV-Vis spectra obtained upon cooling solutions of \((R)-1\) (a-c) and \((S)-1\) (d-f) at different cooling rates \((c = 5 \times 10^{-6} \text{ M})\).

**Figure S3:** Top panel: absorption (a) and emission spectra (b: \(\lambda_{\text{exc}} = 321 \text{ nm}\), c: \(\lambda_{\text{exc}} = 375 \text{ nm}\)) of free \((R)\)-chiral ligand \((c = 1 \times 10^{-5} \text{ M, black})\) and monomeric complex \((R)-1\) \((c = 1 \times 10^{-5} \text{ M, 368 K, red})\) in MCH. Bottom panel: corresponding excitation spectra recorded at the emission maxima (d: \(\lambda_{\text{em}} = 371 \text{ nm}\), e: \(\lambda_{\text{exc}} = 390 \text{ nm}\) and f: \(\lambda_{\text{exc}} = 422 \text{ nm}\)).

The red-shift and loss of vibronic fine structure of the absorption of the complex with respect to the free ligand and the similarity of the fluorescence spectra of both compounds, regardless of the excitation wavelength, indicate that the absorption of the complex originates from ligand-centered \(^1\text{IL} (\pi \rightarrow \pi^*)\) transitions with possible \(^1\text{MLCT}\) contributions. The similarity between the excitation spectra of complex and ligand confirms the contributions of ligand centered transitions. Excitation at 375 nm where the
complex absorbs strongly, but the ligand only poorly, again yields very similar fluorescence spectra. This indicates that the absorption of the complex at this wavelength does not solely originate from the IL transitions which exhibit fluorescence, but include non-fluorescent MLCT contributions. The corresponding excitation spectra recorded at 422 nm (f) confirm this assumption.

**Figure S4:** Top panel (a-d): AFM images of mixtures of both aggregates of (R)-1 obtained upon thermal quenching (small structures: **Agg I**, big structures: **Agg II**). Bottom panel: additional AFM images of **Agg I** (e+f) and **Agg II/IIc** (g+h).

**Figure S5:** Linear dichroism of (R)-1 evolving after the formation of **Agg II** (c = 5 x 10⁻⁶ M).
**Figure S6:** a) Development of the absorbance at 399 nm upon formation of *Agg II* over a time span of 180 min (*c* = 5 x 10^{-6} M). b) Zoom-in of the steady-state regime (2-15 min) corresponding to fully assembled *Agg II* and the time span where clustering to *Agg IIc* takes place (c).

**Figure S7:** UV-Vis spectra of solutions (a) and thin films (b) of (R)-1 showing the equivalence of in-solution and solid-state structures. Conditions: d = 0.1 mm, CHCl_3 for monomer (*c* = 0.5 x 10^{-3} M), MCH + 10% CHCl_3 for *Agg I*, MCH + 1% CHCl_3 for *Agg II*.

**Figure S8:** a) Repeated cycles of clustering over time and dissolution of the superstructures by shaking, visualized at 399 nm, showing the reversibility of the hierarchical step (*c* = 5 x 10^{-6} M). b) Corresponding UV-Vis spectra recorded after shaking (at peaks in a).
Figure S9: UV-Vis spectra of (R)-1 recorded of the solutions used for NMR spectroscopic studies to determine the packing of Agg I upon varying the MCH-d_{14} volume fraction of the solution (c = 2 x 10^{-3} M).
Figure S10: 2D ROESY NMR spectrum of (R)-1 (Agg I, c = 1 x 10^{-2} M, 1:1 CDCl$_3$:MCH-$d_{14}$) and zoomed-in regions showing the correlation signals in the aliphatic and aromatic region, respectively.
The lack of through-space couplings of protons of the peripheral alkoxy chains with the aromatic core can be attributed to a parallel arrangement of the chromophores. Only the second CH$_2$ group of the solubilizing chains shows a weak coupling with the gallic C-H proton, which is possible in the proposed packing. The other cross peaks (black box) arise from interactions with the MCH-$d_{14}$ solvent. In the aromatic region, a multitude of cross peaks is observed, however most of them originate from intramolecular couplings (blue circles). The through-space contacts are marked with red circles and their origin can be extracted from the schematic packing shown below the spectra.

**Figure S11**: Partial thin-film FT-IR spectra of both aggregates of (R)-1 in the spectral region characteristic of a) the C$_{aryl}$-OR band (1260-1160 cm$^{-1}$) and b) the meta-substituted ring vibration (1100-1000 cm$^{-1}$).

**Figure S12**: Time-dependent evolution of both Agg I (a) and Agg II (b) of (R)-1 over a time span of six months ($c = 5 \times 10^{-6}$ M).
**Figure S13:** Experimental data points extracted for the disassembly of Agg II (c = 5 x 10^{-6} M) at \( \lambda = 399 \) nm and fit to the nucleation-elongation model showing the cooperative character of the transition.

**Figure S14:** a) Solvent-dependent UV-Vis studies of (R)-1 (Agg II) monitoring the disassembly via an increase in the volume fraction of good solvent at a constant concentration (c = 5 x 10^{-6} M) and corresponding cooperative fit using the denaturation model (b).

**Figure S15:** a) Solvent-dependent UV-Vis studies of (R)-1 (Agg I) monitoring the disassembly via an increase in the volume fraction good solvent at a constant concentration (c = 5 x 10^{-6} M) and corresponding cooperative fit using the denaturation model (b).
Figure S16: Solvent-dependent CD studies of (R)-1 (Agg II) monitoring the disassembly via an increase in the volume fraction of good solvent at a constant concentration (c = 5 x 10⁻⁶ M) showing the intermediate formation of Agg I (blue spectrum).

Figure S17: UV-Vis (a) and CD (b) spectrum of (R)-1 showing the characteristic features of Agg I which was obtained during disassembly of Agg II at a chloroform volume fraction of 11.5 % (c = 5 x 10⁻⁶ M). The spectra were recorded 12 hours after addition of 11.5 % v/v chloroform to the MCH solution of Agg II, showing that Agg I is a persistent intermediate in the disassembly process of Agg II rather than a transient species.
**Figure S18:** Time-dependent evolution of the UV-Vis spectra of (R)-1 (Agg I (a) and Agg II (b)) upon annealing solutions (c = 5 x 10^{-6} M) of both polymorphs at 333 K. In the case of Agg I no changes occur, whereas Agg II transforms to Agg I.

**Figure S19:** UV-Vis spectra of (R)-1 recorded upon annealing solutions of freshly prepared Agg II at 333 K at different concentrations.
Figure S20: UV-Vis (a,b,c) and CD spectra (d,e,f) of (R)-1 obtained after annealing solutions of freshly prepared Agg II at a,d) 313 K, b,e) 323 K and c,f) 333 K, showing the conversion to Agg I (c = 5 x 10^{-6} M).

Figure S21: UV-Vis spectra of (R)-1 recorded upon probing seeded supramolecular polymerization (ratio Agg I_{seed}:Agg II 1:1, c = 5 x 10^{-6} M) stirring at 1000 rpm (a,b,c) or without stirring (d,e,f). c,f) Plot of absorbance at 399 nm vs. time showing a rapid decay of absorbance. The results show that the supramolecular polymerization of 1 cannot proceed in a living manner. The spectral changes can be attributed to a lowering of the concentration of Agg II in solution due to cluster formation (a,d), which after shaking are re-dissolved, thus recovering the initial spectra (b,e). As obvious from the slower and more uniform decrease in absorbance in the experiments with stirring (top), the mechanical agitation slows down/hinders cluster formation to some extent, however not sufficiently to cancel its impact preventing seeded supramolecular polymerization.
Figure S22: Cooling curves of Agg I (c = 5 x 10^{-6} M) for different cooling rates showing a slight increase of the thermal hysteresis. However, even at the fastest rate (10 Kmin^{-1}, highest kinetic influence), the onset of Agg I elongation never falls below the elongation temperature necessary to initiate the kinetic Agg II polymerization.
5. Calculation of the molar fraction of Agg I and Monomer vs. Temperature

The heating experiments of Agg II and the thermally induced transitions from Agg II to Agg I exhibited an isosbestic point and no intermediate appearance of the monomer spectra could be detected. This suggests a direct incorporation of every monomer which is released in the disassembly of Agg II, into Agg I. Consequently, the molar fraction of the monomer can be estimated by subtracting the degree of aggregation $\alpha_{Agg II}$ obtained for Agg I in heating experiments of Agg I:

$$\alpha_{Mono} = 1 - \alpha'_{Agg I}$$ (1)

Furthermore, the sum of the molar fractions of all species ($\alpha_{total}$) in multi-species processes is constant (= 1), which can be reorganized to give $\alpha_{Agg I}$:

$$\alpha_{total} = 1 = \alpha_{Mono} + \alpha_{Agg I} + \alpha_{Agg II}$$ (2)

$$\rightarrow \alpha_{Agg I} = 1 - \alpha_{Mono} - \alpha_{Agg II}$$ (3)

As the degree of aggregation $\alpha_{Agg II}$ is known from the heating experiments of Agg II ($\alpha_{Agg II} = \alpha'_{Agg II}$), the molar fraction of Agg I in the same experiment can thus be estimated via equation (4) which results from substitution of eq. (1) and $\alpha_{Agg II} = \alpha'_{Agg II}$ into eq. (3):

$$\rightarrow \alpha_{Agg I} = 1 - \alpha_{Mono} - \alpha_{Agg}$$ (4)

The data used for this estimation of the molar fraction of the different species was the data obtained by the fits of the corresponding heating curves.
6. Experimental Part

6.1. Materials and Methods

General Procedures
All solvents were dried according to standard procedures. Reagents were used as purchased. All air-sensitive reactions were carried out under argon or nitrogen atmosphere. For all spectroscopic measurements, spectroscopic grade solvents were used.

Column Chromatography
Preparative column chromatography was conducted in self-packed glass columns of different sizes with silica gel (Merck Silica 60, particle size 0.04–0.063 nm).

NMR measurements
\(^1\)H and \(^{13}\)C NMR spectra were recorded on a Bruker Avance 400 (\(^1\)H: 400 MHz; \(^{13}\)C: 100.6 MHz) and a Bruker AV300 (\(^1\)H: 300 MHz; \(^{13}\)C: 100.6 MHz). Additional 1D \(^1\)H as well as 2D H,H COSY and 2D H,H ROESY spectra were recorded on an Agilent DD2 500 (\(^1\)H: 500 MHz) and an Agilent DD2 600 (\(^1\)H: 600 MHz) at a standard temperature of 298 K in deuterated solvents. The recorded spectra were referenced to the remaining resonance signals of the deuterated solvents. The coupling constant \(J\) of the measured spin multiplets is given in Hertz (Hz) and the chemical shifts \(\delta\) are given in reference to the chemical shift of trimethylsilane (0 ppm). Multiplicities for proton signals are abbreviated as s, d, t, q and m for singlet, doublet, triplet, quadruplet and multiplet, respectively.

Mass spectrometry (MS)
MALDI mass spectra were recorded on a Bruker Daltronics Ultraflex ToF/ToF or a Bruker Daltronics Autoflex Speed with a SmartBeamTM NdYAF-Laser with a wavelength of 335 nm. ESI mass spectra were measured on a Bruker MicrOTOF system. The signals are described by their mass/charge ratio (m/z) in u.

UV-Vis spectroscopy
UV-Vis absorption spectra were recorded on a JASCO V-770 or a JASCO V-750 with a spectral bandwidth of 1.0 nm and a scan rate of 400 nm min\(^{-1}\) or on an Agilent Cary 4000 with a spectral bandwidth of 2 nm at a scan rate of 600 nm min\(^{-1}\). Glass cuvettes with an optical length of 1 cm, 1 mm and 0.1 mm were used. All measurements were conducted in commercially available solvents in spectroscopic grade.

Fluorescence spectroscopy
Fluorescence and excitation spectra were recorded on a JASCO Spectrofluorometer FP-8500 in quartz cuvettes (SUPRASIL®, Hellma) with an optical length of 1 cm.

FT-IR spectroscopy
Solution and solid-state measurements were carried out using a JASCO-FT-IR-6800 equipped with a CaF\(_2\) cell with a path length of 0.1 mm.
Atomic force microscopy (AFM)
The AFM images were recorded on a Multimode®8 SPM System manufactured by Bruker AXS. The used cantilevers were AC200TS by Oxford Instruments with an average spring constant of 9 N m\(^{-1}\), an average frequency of 150 kHz, an average length of 200 µm, an average width of 40 µm and an average tip radius of 7 nm. All samples were spin-coated from freshly prepared solutions onto an HOPG surface at a spin velocity between 2000 and 4000 rpm.

Dynamic Light Scattering (DLS)
DLS spectra were been recorded on a CGS-3 Compact Goniometer System manufactured by ALV GmbH, equipped with a HeNe laser with a wavelength of 632.8 nm (22 mW) and an ALV/LSE-5004 Digital Correlator by ALV GmbH.

Gel permeation chromatography (GPC)
Gel permeation chromatography was performed on a Shimadzu prominence GPC system equipped with two Tosoh TSKgel columns (G2500H XL; 7.8 mm I.D. x 30 cm, 5 µm; Part. No. 0016135) with CH\(_2\)Cl\(_2\) as eluent. The solvent flow was set to be 1 mL/min. Detection was carried out via a Shimadzu prominence SPD-M20A diode array detector (DAD).

Elemental Analysis
Elemental analyses were carried out on a Vario EL III Element Analyzer by elementar Analysensysteme GmbH.
6.2. Synthesis and Characterization

Scheme S1: Synthesis route to obtain final compound (R)-1.

3,4,5-Tris(((R)-3,7-dimethyloctyl)oxy)-N-(4-iodophenyl)benzamide (2)5 and 4-((4-ethynylphenyl)-ethynyl)pyridine (3)6 were prepared following reported synthetic procedures and showed identical spectroscopic properties to those reported therein.

3,4,5-Tris(((R)-3,7-dimethyloctyl)oxy)-N-(4-((4-(pyridine-4-y1ethylene)phenyl)ethylene) phenyl)benzamide (4)

3,4,5-Tris(((R)-3,7-dimethyloctyl)oxy)-N-(4-iodophenyl)benzamide (2) (0.95 g, 1.20 mmol, 1 eq) tetrakis(triphenylphosphine)palladium(0) (81.71 mg, 0.071 mmol, 0.05 eq) and copper(I) iodide (13.47 mg, 0.071 mmol, 0.05 eq) were dissolved in a 1:1 mixture of degassed THF:NEt3 (5 mL). The solution was stirred at 50 °C for 30 minutes. A solution of 4-((4-ethynylphenyl)-ethynyl)pyridine (3) (244 mg, 1.20 mmol, 1 eq) in a 1:1 mixture of degassed THF:NEt3 (5 mL) was added dropwise. The solution was stirred at 70 °C for 12 hours. The solvents were removed in vacuo and the residue was dissolved in DCM and filtered over a thin layer (2 cm) of Celite 545®. The solvent was removed in vacuo and the crude product was purified by column chromatography (DCM:EtOAc 6:1) and several precipitation steps (DCM/MeOH + 1 % NEt3) yielding the product as a colorless solid (0.93 g, 1.07 mmol, 89 %).

5 F. Wang, M.A.J. Gillissen, P.J.M. Stals, A.R.A. Palmans and E.W. Meijer, Chem. Eur. J., 2012, 18, 11761-11770.
6 A. Langenstroer, K. K. Kartha, Y. Dorca, J. Droste, V. Stepanenko, A. Rodrigo Q., M. R. Hansen, L. Sánchez and G. Fernández, J. Am. Chem. Soc., 2019, 141, 5192-5200.
$^1$H NMR (CDCl$_3$, 500 MHz): $\delta = 8.62$ (AA’XX’, 2H, H$_1$), 7.78 (s, 1H, H$_7$), 7.68-7.64 (m, 2H, H$_6$), 7.57-7.53 (m, 2H, H$_5$), 7.53 (s, 4H, H$_{3+4}$), 7.39 (AA’XX’, 2H, H$_2$), 7.06 (s, 2H, H$_8$), 4.06 (m, 6H, H$_9$), 1.93-1.79 (m, 4H, H$_{10}$), 1.77-1.67 (m, 3H, H$_{11}$), 1.66-1.58 (m, 2H, H$_{10}$), 1.57-1.49 (m, 3H, H$_{16}$), 1.40-1.10 (m, 18H, H$_{13-15}$), 0.95 (d, 6H, $^3$$J_{HH} = 6.6$ Hz, H$_{12}$), 0.93 (d, 3H, $^3$$J_{HH} = 6.6$ Hz, H$_{12}$), 0.87 (d, 18 H, $^3$$J_{HH} = 6.7$ Hz, H$_{17}$).

$^{13}$C NMR (CDCl$_3$, 126 MHz) $\delta$ (ppm) = 165.73, 153.50, 149.98, 141.95, 138.50, 132.73, 131.99, 131.72, 131.39, 129.77, 125.66, 124.42, 121.85, 119.91, 118.77, 106.01, 93.74, 91.80, 88.87, 88.47, 71.99, 68.01, 39.52, 39.42, 37.65, 37.50, 36.53, 30.01, 29.82, 28.14, 24.87, 22.86, 22.77, 19.75, 19.72.

HR-MS (MALDI-TOF, dithranol): calculated for C$_{58}$H$_{79}$N$_2$O$_4$ [M+H]$: 867.6034, found: 867.6025

Figure S23: $^1$H NMR (CDCl$_3$, 500 MHz) spectrum of compound 4.
Figure S24: $^{13}$C NMR (CDCl$_3$, 126 MHz) spectrum of compound 4.

Palladium(II) Complex [PdL$_2$]Cl$_2$ (\((R)-1\))

3,4,5-tris((\((R)-3,7\)-dimethyloctyl)oxy)-N-(4-((4-(pyridin-4-ylethynyl)phenyl)ethynyl)phenyl)- benzamide (4) (50 mg, 57.56 μmol, 2.00 eq) was dissolved in 5 mL anhydrous, degassed DCM. A solution of bis(benzonitrile)palladium(II) dichloride (11.06 mg, 28.83 μmol, 1.00 eq) in 1 mL anhydrous, degassed DCM was added dropwise. The solution was heated to 35 °C and stirred for 48 hours. The solution was filtered through Celite 545$^*$ and rinsed with DCM. The solvent was removed in vacuo and the residue was dissolved in as few DCM as possible and precipitated with methanol. The process was repeated various times. The resulting yellow solid was subjected to gel permeation chromatography (GPC) to yield the pure product as a pale yellow solid (36.50 mg, 19.09 μmol, 66%).
\( ^{1}H \) NMR (CDCl\(_3\), 500 MHz) \( \delta \) (ppm) = 8.52 (\( AA'XX' \), 4H, H\(_{1}\)), 8.1 (s, 2H, H\(_{7}\)), 7.66-7.64 (m, 4H, H\(_{3}\)), 7.49-7.46 (m, 8H, H\(_{3+4}\)), 7.44-7.42 (m, 4H, H\(_{6}\)), 7.25 (\( AA'XX' \), 4H, H\(_{2}\)), 7.12 (s, 4H, H\(_{8}\)), 4.11-4.01 (m, 12H, H\(_{9}\)), 1.91-1.79 (m, 8H, H\(_{10}\)), 1.75-1.65 (m, 6H, H\(_{11}\)), 1.64-1.56 (m, 4H, H\(_{10}\)), 1.55-1.48 (m, 6H, H\(_{16}\)), 1.40-1.10 (m, 36H, H\(_{13-15}\)), 0.97-0.91 (m, 18H, H\(_{12}\)), 0.87 (d, 36H, \( ^{3}J_{HH} = 6.6 \) Hz, H\(_{17}\)).

\( ^{13}C \) NMR (126 MHz, CDCl\(_{3}\)) \( \delta \) (ppm) = 165.65, 153.20, 152.46, 141.52, 138.63, 134.28, 132.44, 132.06, 131.46, 129.52, 126.59, 125.05, 120.60, 119.65, 118.27, 105.92, 97.85, 92.26, 88.53, 86.88, 71.77, 67.69, 39.35, 39.26, 37.51, 37.49, 37.36, 37.33, 36.35, 29.86, 29.71, 27.97, 24.73, 24.72, 24.70, 22.69, 22.61, 22.59, 19.61, 19.58, 19.57.

Elemental Analysis: calculated for C\(_{116}H_{156}N_4O_8\)Pd: C: 72.88, H: 8.22, N: 2.93 found: C: 72.51, H: 8.53, N: 2.79

Figure S25: \( ^{1}H \) NMR (CDCl\(_{3}\), 500 MHz) spectrum of compound (R)-1.
Figure S26: $^{13}$C NMR (CDCl$_3$, 500 MHz) spectrum of compound (R)-1.