# **Supporting Information**

## Multiple CH…O Interactions involving Glycol Chains as Driving Force for the Self-Assembly of Amphiphilic Pd(II) Complexes

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#### 1. Nucleation-Elongation model for Cooperative Supramolecular Polymerizations

The new Nucleation-Elongation model recently developed by Ten Eikelder, Markvoort and Meijer<sup>1,2</sup> describes the equilibrium between the monomer pool and supramolecular polymers, and the cooperative growth of the latter. 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.

Symmetric Supramolecular Polymerization. Due to the fact that supramolecular polymerization occurs via a cooperative mechanism, the process can be divided in a nucleation and an elongation phase in which a nucleus size of 2 is assumed. The values  $T_e$ ,  $\Delta H^\circ_{nucl}$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  can be found by a non-linear least-square analysis of the experimental melting curves. The equilibrium constants associated to the nucleation and elongation phases can be calculated using equations 1 and 2:

Nucleation step: 
$$K_n = e^{\left(\frac{-(\Delta H^o - \Delta H^o_{nucl}) - T\Delta S^o}{RT}\right)}$$
 (1)

Elongation step: 
$$K = e^{\left(\frac{-(\Delta H^O - T\Delta S^O)}{RT}\right)}$$
 (2)

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

$$\sigma = \frac{K_n}{K_e} = e^{\left(\frac{\Delta H_{nucl}^o}{RT}\right)}$$
(3)

The cooling curves of **1** in MeOH and in the MeOH/DCM (88:12) mixture were obtained by plotting the fraction of aggregated species  $\alpha_{agg}$  at 425 nm as a function of temperature *T*.

The  $\alpha_{agg}$  values can be calculated using equation 4:

$$\alpha_{agg} = 1 - \frac{\varepsilon - \varepsilon(agg)}{\varepsilon(mon) - \varepsilon(agg)}$$
(4)

<sup>[1]</sup> H. M. M. Ten Eikelder, A. J. Markwoort, T. F. A. De Greef, P. A. J. Hilbers, *J. Phys. Chem. B* 2012, *116*, 5291-5301.
[2] A. J. Maarkvort, H. M. M. Ten Eikelder, P. J. J. Hilbers, T. F. A. De Greef, E. W Meijer, *Nat. Commun.* 2011, *2*, 509-517.

## 2. Supplementary Figures



*Fig. S1* Solvent-dependent UV/Vis experiments of **1** (3.1 x  $10^{-4}$  M - 3.2 x  $10^{-4}$  M) at room temperature.



*Fig. S2* <sup>1</sup>H NMR spectra of **1** in CD<sub>3</sub>OD after measurement of the melting curve from 312-270 K (400 MHz,  $3.60 \times 10^{-4}$  M).



*Fig. S3* UV/Vis spectra of **1** (MeOH/DCM (88:12),  $3.51 \times 10^{-3}$  M) at 25 °C before and after the corresponding temperature-dependent UV/Vis experiments from 305-271 K (see Fig. 2 a).

**Table S1.** Corresponding thermodynamic parameters  $K_2$ , K,  $\sigma$ ,  $T_e$ ,  $\Delta H^{\circ}$ ,  $\Delta H^{\circ}_{nucl}$  and  $\Delta S^{\circ}$  obtained for **1** in MeOH/DCM (88:12) on the basis of the cooperative model.

Conc. [M]	∆H° <sub>nucl</sub> [kJmol <sup>-1</sup> ]	$\Delta H^{\circ} [kJmol^{-1}]$	⊿S° [kJmol <sup>-1</sup> K <sup>-1</sup> ]	<i>T</i> <sub>e</sub> [K]	$K_2$ [M <sup>-1</sup> ]	$K$ $[M^{-1}]$	σ
1.64 x 10 <sup>-3</sup>	-14.6 ± 0.3	-64.2 ± 1.5	-0.1696 ± 0.0052	288.0 ± 0.1	1.37	$6.1 \\ x \ 10^2$	2.3 x 10 <sup>-3</sup>
2.32 x 10 <sup>-3</sup>	-18.2 ± 0.1	-55.8 ± 0.3	-0.1405 ± 0.0009	292.4 ± 0.02	0.24	$\begin{array}{c} 4.3 \\ x \ 10^2 \end{array}$	0.6 x 10 <sup>-3</sup>
2.92 x 10 <sup>-3</sup>	-16.5 ± 0.1	-61.1 ± 0.3	-0.1594 ± 0.0012	$\begin{array}{c} 293.8 \\ \pm \ 0.03 \end{array}$	0.40	$3.4 \\ x 10^2$	1.2 x 10 <sup>-3</sup>
3.53 x 10 <sup>-3</sup>	-17.1 ± 0.2	-67.2 ± 0.4	-0.1796 ± 0.0014	$\begin{array}{c} 296.5 \\ \pm \ 0.04 \end{array}$	0.28	$2.8 \\ x 10^2$	1.0 x 10 <sup>-3</sup>



*Fig. S4* Van't Hoff plot of the elongation constants *K* of **1** in MeOH/DCM (88:12) (R = 0.97463). *K* and  $T_e$  values were determined by temperature-dependent UV/Vis studies at four different concentrations (3.53 to 1.64 x 10<sup>-3</sup> M) (see Fig. 2b and Table S1).

*Table S2* Thermodynamic parameters associated to the self-assembly process of **1** in MeOH/DCM (88:12) at 298 K.

$\Delta H^{o[a]}$	$\Delta S^{o[a]}$	$\Delta G^{\alpha^{(b)}}$		
[kJmol <sup>-1</sup> ]	[kJmol <sup>-1</sup> K <sup>-1</sup> ]	[kJmol <sup>-1</sup> ]		
-65.3±6.1	-0.1734±0.0207	-13.6±0.11		

[a] Van't Hoff equation:  $lnK = -\frac{\Delta H^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R}$ ; R = 8.3144621 JK<sup>-1</sup>mol<sup>-1</sup>. [b] Gibb's equation:  $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$ 



*Fig. S5* TEM image of **1** in water onto a carbon-coated copper grid revealing the morphology of a six weeks aged solution  $(5.1 \times 10^{-4} \text{ M})$  showing short worm-like structures with a length of 20-30 nm.



*Fig. S6* a) Hydrogel of **1** at  $6.8 \times 10^{-4}$  M in water formed after an aging time of twelve weeks and b) TEM images of the hydrogel onto a carbon-coated copper grid demonstrating the gradual elongation of the self-assembled structures to up to 120 nm with aging.



*Fig. S7* AFM height (a, c, e) and phase (d, f) images of a gel of **1** in water ( $6.8 \times 10^{-4}$  M). The samples were prepared by spin-coating a drop of the hydrogel onto mica with 5000 rpm. Image (b) shows the cross section analysis along the yellow line in image (a). The height (diameter) of fibers was measured to be  $3.0\pm0.2$  nm, the length could be defined to be up to 120 nm.



*Fig. S8* a, b) Gelation studies of **1** at  $9.3-10.2 \times 10^{-3}$  M in organic media (left to right: DMF, MeCN, EtOH, *n*-BuOH), showing the "stable-to-inversion of the test tube" method in b).



*Fig. S9* AFM height images of a diluted gel of 1 in ethanol. The samples were prepared by drop casting a diluted gel solution in ethanol onto mica. Image (c) depicts the cross-section analysis along the yellow line 1-1' in image (a). Z scale is 5 nm. The height (diameter) of fibers was measured to be  $2.4\pm0.5$  nm.



*Fig. S10* SEM images of a gel of **1** in ethanol on silicon wafer  $(10.2 \times 10^{-3} \text{ M})$ . The images show the surface of the gel bead dried in air.

*Table S3* Critical gelation concentration for the gels of **1** in EtOH and *n*-BuOH.

	EtOH	BuOH	
<b>Critical gelation</b>	6.71	6 17	
conc. [mg/ml]		0.17	

### 3. Crystal structure

Single crystal X-ray diffraction data for **1** were collected at 100 K on a Bruker X8Apex-II diffractometer with a CCD area detector and multi-layer mirror monochromated  $Mo_{K\alpha}$  radiation. The structures were solved using direct methods, expanded with Fourier techniques and refined with the Shelx software package.<sup>[3]</sup> All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculation on geometrically idealized positions.

Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre, deposition number CCDC 1018057. These data can be obtained free of charge from The CCD centre via www.ccdc.cam.ac.uk/data\_request/cif.

Parameter	
Formula	$C_{84}H_{110}Cl_2N_2O_{24}Pd$
Mr	1709.03
Crystal system	triclinic
Space group	$P\overline{1}$
T(K)	100
<i>a</i> (Å)	12.7142(5)
<i>b</i> (Å)	13.0337(5)
<i>c</i> (Å)	14.4284(5)
α (°)	64.8840(11)
β (°)	83.6590(12)
γ (°)	81.0220(12)
$V(\text{\AA}^3)$	2135.77(14)
Ζ	1
density (calc, g/cm <sup>-3</sup> )	1.329
wavelength (Å)	0.71073
abs. coef (mm <sup>-1</sup> )	0.354
<i>F</i> (000)	900
crystal size (mm <sup>-3</sup> )	0.18 x 0.12 x 0.12
theta range for data collection	3.167 - 26.407
index ranges	-15 < h < 15
	-16 < k < 16
	-18 < 1 < 18
reflections collected	28964
independent reflections	8699
refinement method	full-matrix least-squares on $F^2$
data/restraints/parameters	8699/0/514
goodness of fit on $F^2$	1.024
final R indices	$R_1 = 0.0296$
[I>2σ(I)]	$wR_2 = 0.0651$
largest diff peak and hole [eÅ-3]	0.439 and -0.590

Table S3.	Crystallographic	data	for	1.
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[3] G. M. Sheldrick, Acta Crystallogr. A 2008, 64, 112-122.



*Fig. S11* Molecular structure of **1** in the solid state. Hydrogen atoms have been omitted for clarity. Atomic displacement ellipsoids are drawn at 50 % probability.



*Fig. S12* Packing of 1 characterized by numerous intermolecular contacts (< sum of van der Waals radii). Hydrogen atoms have been omitted for clarity, with exception of those integrated in the network of weak intermolecular interactions. Atomic displacement ellipsoids are drawn at 50 % probability. Magnification of the "handshake-like" intertwining (colored in blue and orange) represented as spacefill model.



*Fig. S13* One-dimensional double-strands (colored in blue and orange) of **1** arranged in a parallel fashion. Atomic displacement ellipsoids are drawn at 50 % probability.

#### 4. ROESY measurements



*Fig. S14* Selected areas of the 600 MHz ROESY spectrum of **1** in MeOD/DCM (80:20) at  $3.35 \times 10^{-3}$  M (293 K) representing the intermolecular through-space coupling signals between a) aromatic protons and b) aromatic protons and protons of the glycol chains. c) Model of the molecular arrangement highlighting the coupling protons in a) on the basis of the ROESY experiment.

### 5. Experimental Section

**General.** All solvents were dried according to standard procedures. Reagents were used as purchased. All air-sensitive reactions were carried out under argon atmosphere. Flash chromatography was performed using silica gel (Merck Silica 60, particle size 0.04-0.063 nm). Analytical thin layer chromatography (TLC) was performed on Fluka silica gel 60  $F_{254}$  coated aluminum foil. NMR spectra were recorded on a Bruker Avance 400 (<sup>1</sup>H: 400 MHz; <sup>13</sup>C: 100.6 MHz) or Bruker DMX 600 MHz spectrometer using partially deuterated solvents as internal standards. Coupling constants (*J*) are denoted in Hz and chemical shifts ( $\delta$ ) in ppm. Multiplicities are denoted as follows: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. MALDI-TOF mass spectrometry was performed on an autoflex II instrument (Bruker Daltronik GmbH) in positive mode with a DCTB matrix. A microTOF focus instrument (Bruker Daltronik GmbH) was used to perform high resolution ESI-TOF mass spectrometry in positive mode.

**UV/Vis Absorption Spectroscopy**. For all spectroscopic measurements, spectroscopic grade solvents (Uvasol) from Merck were used. UV/Vis spectra were recorded on a JASCO V-670 Spectrophotometer with a spectral bandwidth of 1.0 nm and a scan rate of 200 nmmin<sup>-1</sup>. For temperature-dependent experiments a Julabo Temperature Programmer F 250 was used.

**Transmission electron microscope (TEM)**. TEM measurements were performed on a Siemens Elmiskop 101 Electron Microscope, operating at an acceleration voltage of 80-100 kV. For the observation of aggregates, a drop of sample solution was placed on 300-mesh formvar copper grids coated with carbon. Negative staining was performed by addition of a drop of uranyl acetate aqueous solution (0.5 %) onto the copper grid.

Atomic Force Microscopy (AFM). The AFM images were recorded on a Multimode<sup>®</sup> with Nanoscope IV controller (Bruker AXS) by using an E-scanner with a maximum scan area of 15 x 15  $\mu$ m. Silicon cantilevers with a nominal spring constant of 41.0 Nm<sup>-1</sup> and with resonant frequency of 300 kHz, and a typical tip radius of 7 nm (OMCL-AC160TS, Olympus) were employed.

**Scanning Electron Microscopy (SEM)**. SEM imaging was performed on a Carl Zeiss Microscope Ultra plus field emission scanning electron microscope (FESEM) equipped with a GEMINI® e-Beam column (Carl Zeiss NTS GmbH) operating at an accelerating voltage of 3 kV. The sample was prepared by placing a drop of the gel solution of **1** onto silicon wafer and drying at room temperature.

**ESI mass spectra experiments.** The ESI-TOF mass spectra described above were performed with a Bruker Daltonics micrOTOF focus mass spectrometer equipped with an APCI ion source (Agilent G1947-60101). A stainless steel spraying capillary and as transfer capillary a nickel-coated glass capillary with an inner diameter of 500  $\mu$ m was utilized.

The ions were generated continuously by introducing 5  $\mu$ M solutions in a chloroform or acetontril/chloroform (v/v 1:1) by use of a syringe pump (Cole Palmer Instruments 789100C) and a flow rate of 100  $\mu$ l.min-1 into the ion source.

The calibration standard was introduced after or before the sample measurement. Calibration was performed as internal calibration with a 1:100 dilution of APCI/APPI Tuning Mix (G2432A; Agilent) in acetontrile.

For calculation of the respective mass values of the isotopic distribution, the software modul "Bruker Daltonics IsotopePattern" of the software Compass 1.1 from Bruker Daltonik GmbH, Bremen was used.

#### 6. Synthetic details and characterization



Scheme 1. Synthesis of the Pd(II) complex 1.

4-((4-((3,4,5-tris(2-(2-(2-methoxy)ethoxy)ethoxy)pthoy)pthoy)pthyl)pthyl)pthyl)pthyl)pthyl)pyridine ( $C_{42}H_{55}NO_{12}$ ) **2** was prepared following the reported synthetic procedure and showed identical spectroscopic properties to the compound reported therein.<sup>[4]</sup>



4-((4-((3,4,5-tris(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)phenyl)ethynyl)phenyl)ethynyl)pyridine **2** (315 mg, 0.41 mmol) was dissolved in 30 ml dichloromethane and subjected to five vacuum/argon cycles. Similarly, a solution of dichlorobis(benzonitrile)palladium(II) (79 mg, 0.21 mmol) in dichloromethane (65 ml) was prepared, subjected to five vacuum/argon cycles and added dropwise (over 1 hour) to the solution of **2** while stirring under argon at room temperature. The next day, the solvent was evaporated under reduced pressure and the compound was purified by repeated precipitation of the solid using dichloromethane and hexane affording **1** as a yellow solid (281 mg, 0.16 mmol, yield: 80 %).

<sup>[4]</sup> C. Rest, M. J. Mayoral, K. Fucke, J. Schellheimer, V. Stepanenko, G. Fernandez, Angew. Chem. Int. Ed. 2014, 53, 700-705.

<sup>1</sup>**H-NMR** (**400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K**):  $\delta$  (in ppm) = 8.79 (d, J = 6.80 Hz, 4 H, H<sub>a</sub>), 7.56 (m, 8 H, H<sub>c</sub>), 7.43 (d, J = 6.80 Hz, 4 H, H<sub>b</sub>), 6.81 (s, 4 H, H<sub>d</sub>), 4.16 (m, 12 H, H<sub>e</sub>), 3.48 – 3.85 (m, 60 H, H<sub>f-j</sub>), 3.32 (s, 18 H; H<sub>k</sub>).



<sup>13</sup>**C-NMR (150.9 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K):** δ (in ppm): 153.3, 153.0, 140.0, 134.7, 132.6, 132.0, 127.1, 125.4, 121.3, 117.8, 111.3, 97.8, 92.7, 88.1, 87.4, 72.9, 72.3, 71.2, 71.0, 70.9, 70.8, 70.0, 69.3, 59.0.



**HRMS (ESI, pos. Mode), (dichloromethane/methanol 1:1):** m/z: calculated for [X+6] of  $C_{84}H_{110}Cl_2N_2O_{24}Pd+NH_4^+([X+6] of [M+NH_4]^+)$ : 1726.62152; found: 1726.62253.

Due to the isotopic distribution over a broad m/z region caused by Chlorine and Palladium the signal of the monoisotopic signal was too small for some compounds in intensity for an accurate mass measurement. Therefore, the most intense signal (X+6) of this isotopic distribution was taken as described and compared with the respective calculated value.

HRMS (ESI pos) calculated for [X+6] of  $[C_{84}H_{110}Cl_2N_2O_{24}Pd+NH_4]^+$  1726.62152; found 1726.62253.



*Fig. S15* ESI-MS of **1**  $[M+NH_4]^+$  with the corresponding isotopic pattern, showing m/z 1726 as the most intense signal.

**Elemental analysis:** calculated for  $C_{84}H_{110}Cl_2N_2O_{24}Pd$ : C 59.03; H 6.49; N 1.64; found: C 58.90; H 6.61; N 1.59.