Cooperative Supramolecular Polymerization Driven by Metallophilic Pd···Pd Interactions

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Ⓢ *Supporting Information*

ABSTRACT: A new oligophenyleneethynylene (OPE)-based Pd(II) pyridyl complex has been synthesized, and its self-assembly has been investigated in solution, in the bulk state, and on surfaces. Detailed analysis of concentration- and temperature-dependent UV–vis studies in methylcyclohexane supported by DFT calculations demonstrate for the first time that cooperative supramolecular polymerization processes can be driven by metallophilic interactions.

The concept and assessment of cooperativity[1] is a topic of high relevance for understanding the hierarchical organization of molecular and macromolecular systems in chemistry, biology, or materials science.[2] Typical examples of cooperative systems in nature are the binding of oxygen to hemoglobin[3] or the supramolecular polymerization pathways in actin,[4] flagellin,[5] or virus assemblies.[6] Efforts to unveil the complexity of these natural systems have been devoted to the detailed investigation of the mechanisms involved in the self-assembly of different synthetic counterparts.[7] The most common approach exploits the strength and directionality of hydrogen bonding in combination with secondary π–π and/or hydrophobic interactions.[8] Other strategies have made use of dipolar interactions[9] or the combination of metal–ligand coordination and π-stacking interactions to induce cooperativity.[10] Yet, little is known about the influence of metal–metal bonding on self-assembly pathways despite the fact that metallophilic interactions involving d^{10} ions,[11] d^8 ions,[11d,12] or the combination of both in heterometallic systems[13] have been often observed to play a key role in the crystalline packing of different metal complexes[11–13] and the construction of self-assembled structures in solution[14–16] or the liquid crystal state.[17]

Herein, we demonstrate that metallophilic interactions can efficiently induce the cooperative supramolecular polymerization of a new oligophenyleneethynylene (OPE)[18]-based Pd(II) pyridyl complex (**2**). **2** has been synthesized by the reaction of a pyridine-substituted OPE-based ligand (**1**) with [PdCl$_2$(PhCN)$_2$] in CH$_2$Cl$_2$ (Scheme 1) and fully characterized by NMR, IR, HRMS-ESI, UV–vis, fluorescence, and elemental analysis (Supporting Information (SI)).

Pd(II) complex **2** is highly soluble in CH$_2$Cl$_2$, CHCl$_3$ and THF, whereas its solubility in nonpolar solvents such as hexane or methylcyclohexane (MCH) is moderate at rt. However, when an initially greenish suspension (1 mg mL^{-1}) of **2** in MCH is

Scheme 1. Structures of OPE-Based Derivatives 1–3
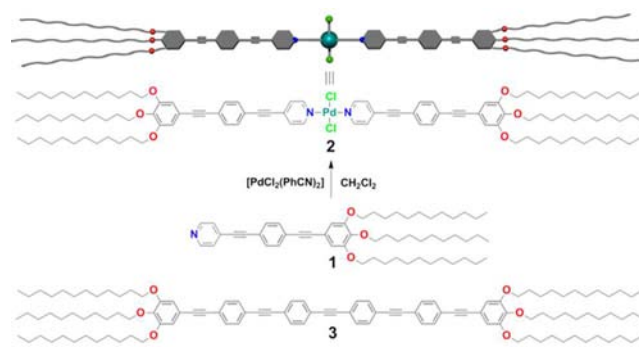
slightly heated up to 50 °C a colorless solution is immediately formed. Surprisingly, on cooling the solution back to rt a remarkable color change from colorless to greenish yellow takes place, which ultimately leads to a thermoreversible gelation process at sufficiently high concentration (2 mg mL^{-1}, Figure 1a). Both phenomena suggest a fully reversible transition between monomeric and aggregated species.

The supramolecular polymerization of **2** has been analyzed in detail through temperature-dependent UV–vis experiments. Solutions of **2** in MCH at four different concentrations (2.2 × 10^{-4}–9 × 10^{-5} M; Figure S1) were slowly cooled down from 343 to 278 K at a rate of 0.5 K min^{-1} to ensure that the process takes place under thermodynamic control. Above 313 K, **2** exhibits a sharp transition with a maximum at ∼350 nm that can be assigned to a molecularly dissolved state.[7] On cooling the solution, depletion of the absorption maximum at 350 nm is accompanied by the emergence of a new red-shifted transition centered at 371 nm that spreads into the visible region up to ∼470 nm (Figure 1a). This behavior can be attributed to the formation of self-assembled structures facilitated by the interaction of the axial d$_{z^2}$ orbitals of the central Pd(II) atoms of neighboring molecules[19] along with a small contribution of π-stacking interactions between the OPE units. The appearance of three isosbestic points at 289, 312, and 363 nm is indicative of equilibrium between well-defined species. The cooling curve obtained by plotting the fraction of aggregated species (α_{agg}) against temperature at 415 nm is clearly nonsigmoidal, which is evidence that the supramolecular polymerization of **2** is a
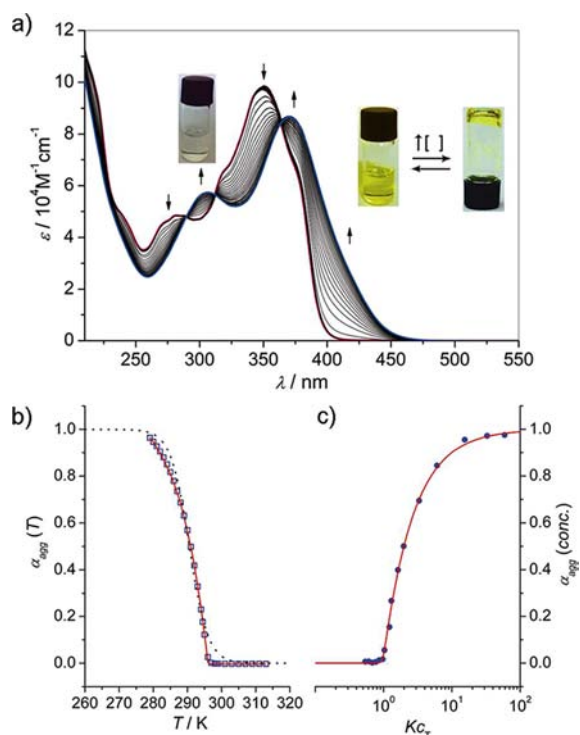
Figure 1. (a) Temperature-dependent UV–Vis experiments of **2** (MCH, 1.6×10^{-4} M, 343–278 K). Arrows indicate the spectral changes upon decreasing temperature. Fitting of the spectral changes to the (b) ten Eikelder–Markvoort–Meijer model and (c) Goldstein–Stryer model at 415 nm. Blue squares (b) and blue circles (c) represent the experimental data of 2 from temperature- and concentration-dependent UV–Vis experiments, respectively. The dotted line in (b) represents the fit to the isodesmic model.

cooperative process (Figures 1b and S2). The spectral changes have been analyzed by applying a nucleation–elongation model recently developed by ten Eikelder, Markvoort, Meijer and co-workers.[20] This mechanism assumes that after an initial thermodynamically unfavorable dimerization process (nucleation) described by an association constant K_2, a highly favorable cooperative growth (elongation) with a much larger binding constant (K) takes place. Application of this model to our experimental data enables the calculation of the thermodynamic parameters of the supramolecular polymerization of **2** (for details, see SI). The enthalpy of elongation (ΔH_e) was calculated to be ~ -87 kJ mol^{-1} and the dimerization (K_2) and elongation (K) constants are 0.64 and $\sim 8 \times 10^3$ M^{-1}, respectively, whereas the cooperativity factor (σ), described as $\sigma = K_2/K$, was 3.5×10^{-5} (Tables 1 and S1). This low value of σ indicates that the self-assembly of **2** in MCH is a highly cooperative process.

Concentration-dependent UV–vis studies (298 K, 2×10^{-3}–4×10^{-5} M, MCH) are reminiscent of those observed by temperature-dependent studies (Figure S3). The spectral changes at 415 nm have been fitted manually to the general

nucleation–elongation model of Goldstein and Stryer[21] for the best match (Figure 1c). The best fits were obtained for a nucleus size (s) of 2 molecules, a degree of cooperativity (σ) of 5.0×10^{-5}, and dimerization (K_2) and elongation (K) constants of ~ 0.65 and 1.3×10^4 M^{-1}, respectively, in good agreement with temperature-dependent experiments (Table 1).

To examine the quantitative contribution of metallophilic Pd$\cdots$Pd interactions to the supramolecular polymerization of **2**, we have compared the self-assembly behavior of **2** with that of an analogous OPE derivative **3** with identical size and shape in which the central Pd(II) ion has been replaced by a triple bond (Scheme 1). At temperatures higher than 313 K, the UV–vis spectrum of **3** (5.5×10^{-5} M, MCH) bears close resemblance to that of **2**, showing a transition centered at 355 nm that can be assigned to monomeric species (Figure S4). However, and in contrast to Pd(II) complex **2**, the transition from monomeric to aggregated species is accompanied by only a minor red shift of the absorption maximum from 355 to 361 nm upon decreasing temperature (Figure S4a). The sharp differences observed in the aggregation behavior of **2** and **3** clearly indicate that the intense red-shifted aggregate band observed for **2** below 313 K can only be originated from intermolecular interactions between the Pd(II) centers within the aggregate. Interestingly, the cooling curve of **3** at 410 nm is sigmoidal in shape, characteristic of a noncooperative (isodesmic) aggregation mechanism (Figure S4b). Application of this model to the spectral changes of **3** affords an excellent fit, and a binding constant of 1.6×10^4 M^{-1} at rt can be calculated (Figure S4; Table S3). Accordingly, the fact that OPE **3** self-assembles in a noncooperative fashion whereas the supramolecular polymerization of **2** is a highly cooperative process demonstrates that metallophilic Pd$\cdots$Pd interactions are the origin of the cooperativity.

Density functional theory (DFT) calculations have been performed to shed some light on the aggregation mechanism. The ground state DFT-optimized structure of **2** at the B3LYP/6-31G*/LANL2DZ level predicts the expected N–Pd–N bond angle (179.7°) for a complex with square-planar geometry (Figure 2a), which is also in good accordance with the crystalline packing of related Pd(II)-pyridyl complexes.[10] During the dimerization process, rotation around the metal–nitrogen bonds occurs to maximize the π-stacking between the two monomers (Figures 2b, S5; Table S4). Simultaneously, the Cl–

Table 1. Thermodynamic Parameters s, σ, K_2, and K Obtained from Temperature and Concentration-Dependent UV–vis Experiments of 2 in MCH

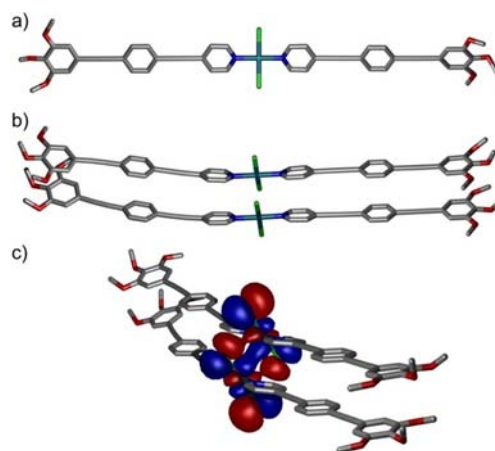| experiment	s	K_2/M^{-1}	K/M^{-1}	σ
temp	2	0.64	7.7×10^3	3.5×10^{-5}
concn	2	0.65	1.3×10^4	5.0×10^{-5}

Figure 2. DFT-optimized geometry of the monomer (a) and dimer (b) and electron density of the HOMO−2 for the dimer of **2** (c) (B3LYP/6-31G*/LANL2DZ level).

Pd−Cl bond angle changes from 179.7° in the monomer to 171.5° and 170.8° in the dimer, as a result of electrostatic repulsions between Cl-atoms of different monomers. The energetic penalty associated with these conformational changes suggests that the dimerization of **2** is an unfavorable process. This is also in accordance with the small dimerization constant value (0.6 M^{-1}) calculated by UV−vis studies. The electron density of the HOMO−2 (Highest Occupied Molecular Orbital) reveals that a chemical bond takes place between Pd(II) of one monomer and one of the Cl-atoms of another monomer (d_{Cl-Pd} = 3.56−3.58 Å; Figure 2c). This strong interaction between Pd and Cl of different monomers plays an important role in the self-assembly process of **2**, since two such bonds are simultaneously formed in each binding event. Additionally, the molecular orbital represented in Figure 2c clearly shows a σ-bond between the Pd centers (d_{Pd-Pd} = 3.51 Å), leading to a stable conformation through metallophilic interactions (Figures 2b,c; Table S4). The theoretical distance of 3.51 Å often becomes shorter for larger aggregates[22] and is in good accordance with the Pd(II)−Pd(II) distances observed in the crystalline structures of related complexes[23] and slightly larger than the smallest ones found in Pd(III)−Pd(III) systems (∼2.7−2.8 Å).[24] Upon dimer formation, the addition of subsequent monomeric units to the polymer chain does not require such significant structural changes compared to the initial dimerization process, which explains why the elongation is experimentally found to be the most favorable step.

Time-dependent DFT (TD-DFT) calculations at the same theoretical level show that the lowest-energy electronic transition S$_1$←S$_0$ has a strong metal-centered (MC) character for the monomer and a metal-to-metal charge transfer (MMCT) character for the dimer (Figure S6, Tables S5 and S6), the latter involving charge transfer from one Pd(II) center to the other one. The calculations show that, upon dimerization, the lowest-energy excited singlet state is red-shifted (Figure S6), and the HOMO−LUMO energy gaps calculated for the monomer and dimer decrease from 3.20 to 2.90 eV, respectively, in agreement with the red shift experimentally observed in the absorption spectra (Figure S7). The DFT and TD-DFT results strongly suggest that intermolecular Pd···Cl and Pd···Pd interactions take place in the aggregates of **2**.

The molecular arrangement of **2** in the liquid crystal state is also in good agreement with that predicted by DFT calculations. Complex **2** forms a columnar hexagonal mesophase (Col$_h$), as demonstrated by polarized optical microscopy (POM) and small-angle X-ray scattering (SAXS) studies (Figures S8−S10; Table S7). Notably, the SAXS patterns show a sharp reflection at 2θ = 25.7° that corresponds to π-stacking interactions between the molecules of **2** within the columns with a uniform distance of 3.5 Å, which exactly matches the distance predicted by DFT calculations.

Final evidence supporting the formation of extended supramolecular associates was provided by atomic force microscopy (AFM) experiments. The images of a diluted gel of **2** (8×10^{-4} M, MCH) spin-coated onto highly-oriented pyrolytic graphite (HOPG) reveal the formation of individual fibrillar assemblies that resemble DNA strands with lengths of several microns and a regular diameter of 5.1 ± 0.3 nm (Figures 3a,b, S11 and S12). These dimensions are in accordance with the hydrodynamic radii (∼1000 nm) obtained from DLS experiments (Figure S13) and demonstrate the formation of 1-D associates with a single-molecule width through cooperative Pd···Pd and π-stacking interactions (Figure 3c). In sharp contrast, AFM studies of **3** ($8 \times$
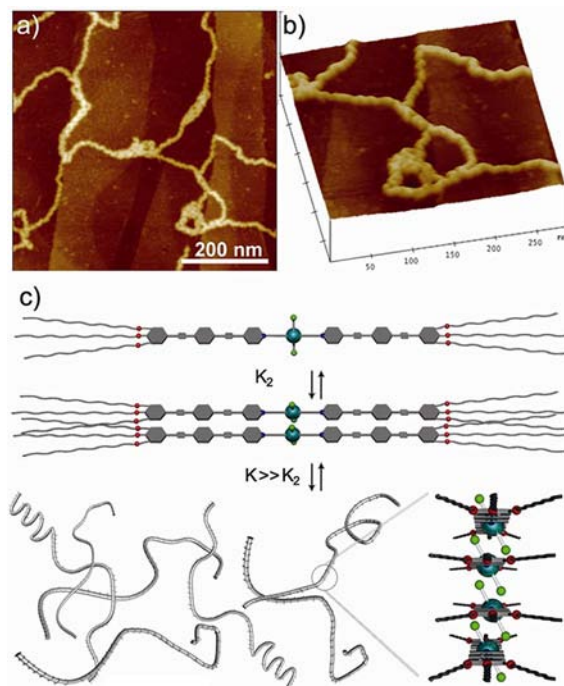

Figure 3. Height (a,b) and 3D (b) AFM images obtained upon spin-coating a solution of **2** (MCH, 8×10^{-4} M) on HOPG. (c) Cartoon of the proposed self-assembly pathway of **2** in MCH solution.

10^{-4} M, MCH) under identical conditions show the presence of considerably smaller rod-like aggregates (20−70 nm) whose cross section analysis yields a diameter of 5.5 ± 0.3 nm (Figure S14). As expected for a system that self-assembles primarily through π-stacking without the assistance of additional cooperative interactions, isodesmic supramolecular structures with a lower degree of internal order are formed.[2a]

In conclusion, we have described the self-assembly in solution, on solid substrates, and in the liquid crystal state of an OPE-based Pd(II) complex **2** driven by cooperative $\pi-\pi$ and metal−metal interactions, as revealed by temperature- and concentration-dependent UV−vis experiments, DLS, AFM, and SAXS and supported by DFT calculations. Besides being one of the first examples of supramolecular polymers based on Pd···Pd interactions, our unprecedented studies demonstrate that metallophilic interactions can efficiently drive cooperative supramolecular polymerization processes. This concept represents a fundamentally new approach to the organization of metallosupramolecular systems with relevance to the field of self-assembled materials and potential application in optoelectronics. The investigation of related systems based on Pd(II) and other transition metal ions is currently underway.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information
Mathematical models for supramolecular polymerization, DFT calculations, UV−Vis, melting curves, POM, DSC, SAXS, AFM, DLS and experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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