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Tuning the Molecular Packing of Self-Assembled Amphiphilic Pt(II) Complexes by Variation of the Hydrophilic Side Chain Length

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Abstract: Understanding the relationship between molecular design and packing modes constitutes one of the major challenges in selfassembly and is essential for the preparation of functional materials. Herein, we have achieved high precision control over the supramolecular packing of amphiphilic Pt(II) complexes by systematic variation of the hydrophilic side chain length. A novel approach of general applicability based on complementary X-ray diffraction and solid-state NMR spectroscopy has allowed us to establish a clear correlation between molecular features and supramolecular ordering: systematically increasing the side chain length gradually increases the steric demand and reduces the extent of aromatic interactions, inducing a gradual shift in the molecular packing from parallel to a long-slipped organization. Notably, our findings highlight the necessity of advanced solid-state NMR techniques to gain structural information for supramolecular systems where single-crystal growth is not possible. Our work further demonstrates a new molecular design strategy to modulate aromatic interaction strengths and packing arrangements, which may be useful for the engineering of functional materials based on Pt(II) and aromatic molecules.

Introduction

Self-assembled structures of π -conjugated systems have long been an area of active research in materials science, where molecular assemblies in solution, in the solid state as well as in the liquid crystalline state can be created.^[1] It is widely known that the functional properties of self-assembled structures are highly dependent on the molecular structure of the monomers and that minor changes in the molecular design can result in dramatic differences in the features and functionalities of the resulting materials.^[2] Therefore, tuning the balance of attractive noncovalent interactions (such as hydrogen bonding and aromatic interactions) and steric effects by molecular design is necessary to generate self-assembled materials with distinct properties.^[2] Besides purely organic compounds, the introduction of a metal ion like Pt(II) to π -conjugated molecules can further extend the range of possible intermolecular interactions and

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enable additional applications in optoelectronics and biomedicine.^[3] Hence, control of the resulting structures through molecular design is desirable.

As previously shown, tuning the length of peripheral alkyl chains -which are commonly used to achieve solubility of the compounds- can dramatically affect the self-assembly behavior of Pt(II) complexes. For instance, we reported the self-assembly of two oligophenyleneethynylene (OPE)-based Pt(II) complexes featuring terminal bispyridyldichlorido dodecyloxy vs. methoxy chains.^[4] We found that shortening the side chains causes a drastic change from a slipped arrangement of the molecules, both in solution and the solid state, to almost parallel π -stacks in the solid state with enhanced aromatic interactions and shortened Pt-Pt distances of \approx 4.4 Å. In another elegant example, Yam and co-workers showed that the hydrophobic tail length of amphiphilic Pt(II) complexes can alter the morphologies and emission behavior of self-assemblies in aqueous medium.^[5] Additionally, for different luminescent Pt(II) mesogens, it has been demonstrated that the variation of alkyl chains can be used to modulate the mesophases with regards to their stability and photophysical behavior.^[6] Interestingly, modification of the alkyl tail length for some of these compounds led to the emergence of multi-stimuli-responsive has polymorphism in the solid state, [6a,b] demonstrating the key impact of small structural changes (for instance, C₁₄ vs. C₁₆ chain^[6a]) on the final properties of the systems.

Apart from nonpolar alkyl chains, polar oligo- or polyethylene glycol chains (OEG, PEG) are commonly used as hydrophilic counterparts for achieving solubility in aqueous media.^[7] However, the effect of EG chain length variation on the self-assembly of Pt(II) complexes has been scarcely investigated.^[8] To the best of our knowledge, the only example of self-assembling Pt(II) complexes featuring PEG_n chains of different length was reported by the group of Manners.^[9] In this work, tetrazole-based tridentate Pt(II) complexes with ancillary ligands based on PEG_n were observed to form 1D fibers (n = 16) or 2D platelets (n = 7) in polar solvents, depending on the PEG chain length.

In this work, we demonstrate precise control over the supramolecular packing of amphiphilic Pt(II) complexes by systematic variation of the hydrophilic side chain length. This understanding may contribute to establishing a correlation between molecular design and packing modes, which remains one of the greatest challenges in the field of self-assembly.^[10] To this end, we herein investigated the solid-state structures of a series of rod-like bispyridyldichlorido Pt(II) complexes **1-4** featuring either three OEG chains on both termini, namely triethyleneglycol (TEG, **1**), diethyleneglycol (DEG, **2**), ethyleneglycol (EG, **3**), or methoxy groups (**4**, Scheme 1). **1-4** are smaller structural analogues of a previously reported Pt(II) complex **5** that was found to exhibit a unique molecular organization based on its crystal structure: the presence of voluminous TEG chains hinders a parallel molecular arrangement

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Scheme 1. Top left: synthesis of the Pt(II) complexes 1-4 and molecular structures of 1-5. Top right: representation of longitudinal and lateral shift of two stacked molecules. Bottom: schematic depiction of the side chain length-dependent packing modes of 1-4 in the solid state.

and ultimately enables the formation of a characteristic handshake motif, where the TEG groups of two adjacent Pt(II) units are in close contact through multiple CH…O interactions (see Scheme 1 and Fig. 1a).[11] To simplify our system, we shortened the aromatic backbone of the ligand to two rings (pyridine-ethynylphenylene) in order to reduce the amount of potential interactions, highlighting the influence of the glycol chains with identical π -surface. We envisioned that a gradual decrease of the EG chain length while keeping the aromatic surface of the molecules unchanged could progressively alleviate the steric demand of the chains and, consequently, reinforce the extent of π -overlap between the stacked molecules. This, in turn, is expected to lead to a gradual transformation from a more slipped to more parallel packing upon shortening the EG side chains. Thus, in this report, we focus on the self-assembly structures in the solid state, whereas investigations on the processes in solution are still ongoing.

Usually, the solid-state structure and molecular organization are determined by single-crystal X-ray diffraction, and we were able to obtain suitable single crystals for complexes **1** to **3**. Crystallization of complex **4**, however, resulted in polycrystalline powders unsuitable for X-ray analysis. Therefore, a complementary method was required for obtaining a systematic comparison of all compounds. To this end, we employed solid-state ¹H and ¹³C Magic-Angle Spinning (MAS) NMR in combination with two-dimensional, 'through-space' NMR correlation techniques based on the direct magnetic dipole-dipole (or dipolar) interaction between nuclear spins to elucidate the aggregation of the methoxy-functionalized complex **4**.^[12] Our approach consisted in identifying through-space ¹H-¹³C

comparing the ¹H and ¹³C MAS NMR results obtained from complexes **1** to **3** with the crystallographic data. On this basis, we are able to readily identify or exclude previously observed packing structures for this specific series of OPE-based Pt(II) complexes, filling in the missing structural information from crystallographic data.

Results and Discussion

Synthesis

Pt(II) complexes **1-4** were synthesized in moderate to good yields by complexation reaction of the precursor salt [PtCl₂(PhCN)₂] with the respective pyridine-based ligands in toluene at 100 °C (see Scheme 1 and Supporting Information). Complexes **1-3** resulted in crystalline solids upon concentration from Et₂O or pentanecontaining DCM as well as EtOAc solutions, whereas all other used solvents led to highly amorphous structures with soft texture. Compound **4**, however, could only be obtained as a powdery solid, which is poorly soluble in most organic solvents due to the short side chains. All complexes could be characterized by ¹H/¹³C NMR in solution, solid-state NMR, and gave good results for elemental analyses.

Crystal structure analysis

By slow vapor diffusion of Et_2O into solutions of **1-3** in EtOAc, pale yellow single crystals suitable for X-ray diffraction analysis could be grown. **1** and **2** both were solved and refined in the triclinic space group *P*-1, whereas **3** could be solved in the monoclinic

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space group $P2_1/n$ (for details of crystal structure determinations see the Supporting Information, Fig. S1-S6, Tables S1-S3). In the following, the arrangements of the stacked molecules in the solid state will be characterized in terms of a longitudinal shift along the molecular axis as well as by a lateral offset as depicted in Scheme 1. Figure 1 shows the obtained molecular structures and packing of complexes 1 to 3 in their crystal structures. For comparison, an excerpt of the crystal structure of previously reported analog 5 is also shown. Relevant close intermolecular contacts are highlighted. In the crystal structure of 1 (Fig. 1b), the packing can



Figure 1. Excerpts of the packing diagrams from the crystal structures of (a) 5, (b,c) 1, (d) 2, and (e) 3 showing the stacking of molecules and change from (c) handshake motif between adjacent amphiphilic molecules (1 and 5) to the more parallel stacking of molecules (2 and 3) caused by the gradual shortening of the attached hydrophilic side chains from TEG (1), DEG (2) to EG (3).

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be viewed as an arrangement of longitudinally shifted molecular units mainly stabilized by C-Harom. ···O (2.31 Å, 2.58 Å) interactions and a close Pt…H contact (2.91 Å) between the central Pt atom of one molecule and the proton of the inner glycol chain of a neighboring molecule. Such Pt...H interactions have been observed in earlier reports and can be explained by donation of electron density from the d_z^2 orbital of the Pt to the σ^* orbital of the C-H.^[13] Interestingly, no aromatic interactions are observed in the crystal structure of **1** (for a top view of the π -system illustrating the orientation of the aromatic rings see Fig. S2). Instead, the structure formation is dominated by the TEG chains, which form a large, bulky structure surrounding the neighboring aromatic backbone in a so-called handshake motif (Fig. 1c), similarly to that observed for complex 5 (Fig. 1a).^[11] The lack of close π - π contacts for 1 compared to the higher homolog 5 can be explained by the considerably larger aromatic surface for the latter (six vs. four aromatic rings), which enables a more efficient π -overlap of the OPE backbone in the crystal. The relatively short π -system of **1** must orient in a twisted manner with a torsion angle of the two aromatic rings (phenyl and pyridine) of 53.8° to form the present structure. Stabilization of the handshake motif is achieved by intermolecular C-Harom....O interactions exhibiting distances in the range of previously observed weak hydrogen bonding for such systems (2.41-2.56 Å).[11] The closest Pt-Pt distance that can be found in the packing of 1 is 9.854 Å, whereas the Pt-Pt distance illustrating the longitudinal shift of two molecules is 18.120 Å (Fig. 1b).

In the single crystal structure of 2, a distinct change in the arrangement compared to 1 is apparent (Fig. 1d). Although the molecules still arrange in a slipped manner, the change from TEG to DEG side chains facilitates a molecular stacking via π - π interactions, leading to an assembly with a decreased longitudinal molecular shift (inner stack Pt-Pt distance 8.126 Å vs. 18.120 Å in 1) and a slight lateral offset (see also Fig. S4). The parallel displaced *π*-stacking of two pyridine units has a distance of ~3.2 Å. In contrast to the structure of 1, where the Pt(II)Cl₂ fragment is surrounded by TEG chains, the Pt(II)Cl₂ moiety in 2 is located on top of the C=C bond of the next molecule in the stack. The structure is further stabilized by C-H_{glycol}…O (2.44 Å) as well as C-H_{glycol}····C_{arom.} (2.90 Å) interactions. Thus, instead of a handshake motif as in 1, the DEG side chains in 2 interdigitate with neighboring side chains (Fig. S4). Furthermore, an intermolecular weak C-H_{glycol}····Cl (2.84 Å) interaction is observed within adjacent stacks (Fig. S4).

A shortening of the glycol chains to one unit (EG) in **3** results in a similar molecular stacking to complex **2** (Fig. 1e) with a Pt-Pt distance that is even slightly shorter for **3** (7.339 Å) compared to **2** (8.126 Å). Parallel displaced π - π interactions of the pyridine rings with a distance of ~3.4 Å and C-H_{arom}...Cl (2.86 Å) interactions stabilize the molecular packing. Additional C-H_{glycol}...O (2.43 Å), C-H_{glycol}...C_{arom}. (2.41 Å) and C-H_{glycol}...C=C (2.87 Å) interactions of one stack with molecules of obliquely arranged neighboring stacks are also present (Fig. S6).

In contrast to compounds 1-3, single crystals of 4 could not be obtained. However, considering the trend followed by 1-3, we would expect a more parallel arrangement of the molecules in 4 (shorter Pt-Pt distances) and enhanced aromatic interactions compared to 1-3 due to the lack of any side chains. Due to no

available single crystal X-ray diffraction data for complex **4**, a complementary technique (solid-state NMR) was required to elucidate the molecular arrangement in the solid state.

Insights into the molecular packing from solid-state NMR

Our approach consisted in identifying intermolecular contacts characteristic for the packing motifs observed in 1-3 and 5. By comparing these contacts with those potentially observed (or alternatively not observed) for 4, a packing arrangement for this complex can be derived. All samples used for solid-state NMR measurements were powdered samples and were obtained under identical conditions as those used for the preparation of the single crystals discussed in the previous section (EtOAc/Et₂O solutions). We therefore assumed identical (or at the very least comparable) arrangements of the molecules in the samples for solid-state NMR studies and in the crystalline state. Additionally, we have conducted powder XRD analysis of 1-4 to further probe this assumption. A detailed summary and analysis of the XRD results can be found in the Supporting Information. Compound 1 shows the lowest crystallinity of all samples obtained by the precipitation protocol (Fig. S18). While the positions of the reflexes are in relatively good agreement with the predicted XRD pattern (based on the corresponding single-crystal data), the overall intensity is greatly diminished in particular for the range corresponding to the long-range order. The sterically demanding TEG chains, which adopt a highly ordered orientation in the single crystal, most likely prevent this long-range order in the powder sample; nevertheless, a similar short-range order could be confirmed. On the other hand, the higher crystallinity of 2 is reflected in the sharp reflexes, which match the predicted XRD pattern well (Fig. S19). Yet, the observation of some minor discrepancies, in particular for the immediate environment of the Pt(II) moiety, indicates that the high level of interdigitation of the DEG chains may not be perfectly transferred to the powdered sample used for the studies by solidstate NMR. Nevertheless, based on the reasonably good agreement between the experimental and predicted XRD patterns, we infer that the orientation within the 1D stack is largely preserved. For the sterically least demanding compound for which single-crystal analysis was possible (3), the predicted XRD reproduces the experimental results without pattern discrepancies (Fig. S20). This result is logical considering the absence of significant steric effects when the chains are reduced to EG units. On this basis, we infer that the molecular orientation in the bulk as well as in the single crystal matches. For compound 4 sharp reflexes could be appreciated as well, which suggests that the sample has a highly crystalline nature, which matches the observed trend for compounds 1-3 (Fig. S21).

Figure 2a summarizes the ¹H MAS NMR spectra of **1-4**. Overall, broad ¹H lines with few discernable details are observed due to the strong ¹H-¹H dipolar couplings present in the solid state. Nevertheless, apart from the broad peak around $\delta_{iso}(^{1}H) = 3.5$ ppm assigned to the protons of the EG moieties, two signals in the aromatic region are observed: while the signal at higher ppm values ($\delta_{iso}(^{1}H) = 9.1$ to 8.1 ppm) can be assigned to the aromatic protons adjacent to the pyridine nitrogen (H_a, position **Ha** in Fig. 2), the ¹H signal at lower values ($\delta_{iso}(^{1}H) = 7.8$

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Figure 2. (a) ¹H MAS NMR spectra of complexes 1 to 4, acquired at 11.7 T (500 MHz) using 29.762 kHz MAS. The ¹H chemical shifts of the discernable aromatic protons (a-c) are highlighted in red and the dashed lines are guides to the eye. # indicate residual solvent and 'Glycol/M' denotes the position of the oligoglycol and methoxy protons. ¹H-¹H DQ-SQ correlation spectrum of complex 4 at 29.762 kHz MAS using one (b) and four (c) rotor periods of DQ recoupling. The proposed packing arrangement for 4 is shown in (d).

to 6.8 ppm) corresponds to the aromatic protons Hb (H_β-pyridyl) and Hc. The exact position of the two peaks varies between complexes **1** to **4**, going from $\delta_{iso}({}^{1}H_{a}) = 9.1$ ppm and $\delta_{iso}({}^{1}H_{b,c}) = 7.8$ ppm in complex **1**, to $\delta_{iso}({}^{1}H_{a}) = 8.1$ ppm and $\delta_{iso}({}^{1}H_{b,c}) = 6.8$ ppm in complexes **2** and **3**. Since the moieties are structurally identical, the difference can be solely attributed to packing effects, in this case to aromatic ring current effects caused by the neighboring aromatic backbone in **2** and **3**, or the lack thereof in **1**. The shift to lower ppm values is often indicative of π - π interactions as observed for example in π -conjugated polymers and other conjugated systems.^[14]

Replacing the EG moieties with methoxy groups as in complex 4 leads to a markedly different ¹H MAS NMR spectrum, cf. Fig. 2a. The signal at $\delta_{iso}(^{1}H) = 3.5$ ppm is now significantly reduced in intensity and width, and strong shifts of the ¹H signals in the aromatic region are observed. The upfield shift of proton **c** suggests an even stronger participation of the outer ring in π - π interactions compared to complexes **2** and **3**. In contrast, the ¹H signal **a** is situated at a higher ppm value than that of **2** and **3**, which might lead to the wrong conclusion that the pyridyl ring of **4** undergoes weaker aromatic interactions than that of **2** and **3**. However, this effect is typical for bispyridyldichlorido Pt(II) and Pd(II) complexes exhibiting a pseudo-parallel packing, and can be attributed to C-H_a...Cl interactions between the α -pyridyl protons of one molecule and the electron withdrawing Cl ligands of an adjacent molecule.^[4]

To further probe the molecular packing of complex **4**, twodimensional (2D) ¹H-¹H double-quantum single-quantum correlation (DQ-SQ) MAS NMR experiments were performed (Fig. 2b,c and S9). This kind of experiment allows to identify ¹H-¹H spin pairs in close spatial proximity to each other (up to ~3.5 Å in rigid organic solids and longer distances if the systems are flexible or proton diluted).^[15] The 2D spectra of complexes **1** to **3** (Fig. S8-9) are characterized by a broad auto-correlation signal situated at δ_{SQ} = 3.5 ppm and δ_{DQ} = 7.0 ppm (attributed to the EG units) with some smaller auto-correlation peaks visible at lower ppm values most likely originating from the residual trapped solvent. However, no auto-correlation signals in the aromatic region (around δ_{SQ} = 7 ppm) are observed.

In analogy to the ¹H MAS NMR spectrum, replacing the EG units with methoxy groups leads to the appearance of three aromatic ¹H signals in the DQ-SQ correlation spectra (Fig. 2b,c). While the cross-correlation signals of protons Ha and Hc are readily discernible at δ_{SQ} = 8.6 ppm and δ_{SQ} =5.9 ppm (δ_{DQ} = 14.6 ppm, dark blue, marked ac and ca), the broad Gaussian peak associated with protons Hb at around δ_{SQ} = 7 ppm is mostly obscured. In addition to the cross-correlation between the methoxy protons and aromatic proton **Hc** at δ_{DQ} = 9.4 ppm –which is expected due to the close spatial proximity of the methoxy groups on the same ring- a cross-correlation between the methoxy protons and proton **Ha** is observed at δ_{DQ} = 12.2 ppm. Interestingly, no cross-correlation between the aromatic proton Hb and the methoxy protons is observable, though this could be related to the broad nature and comparably low amplitude of the peak at δ_{SQ} = 7.0 ppm. These results suggest that the methoxy groups are placed in relatively close proximity to the complex center, though whether this is from above/below the aromatic backbone or from other neighboring complex is unclear at this point. The most significant difference between the spectra of 4 and the other three samples is the appearance of several autocorrelation peaks in the aromatic chemical shift range (marked orange aa, blue-green bb, and yellow-green cc). While these are barely discernible after one rotor period of DQ-excitation, Fig. 2b, their amplitude increases when going to longer (four rotor periods) DQ-excitation times, see Fig. 2c. This indicates a ¹H-¹H distance of around 3.5 Å-4.0 Å, pointing to π - π stacking of the monomers with a parallel arrangement of the molecular units (Fig. 2d).

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To summarize the results from ¹H MAS and ¹H-¹H DQ-SQ NMR correlation data, ¹H MAS NMR revealed changes in chemical shift of the aromatic protons associated with differences in aromatic ring current effects, with **1** showing weaker and **2** and **3** showing stronger ring current effects. Protons **Ha** and **Hb** in **4** show a moderate effect of ~0.5 ppm, which would indicate a packing motif where the protons are further away from the neighboring aromatic ring center pointing towards the edges of the said ring, though proximity of **Ha** to the electron-withdrawing Cl (H_a···Cl) could lead to the shift to higher ppm. These observations fit well with a packing model similar to the pseudo-parallel molecular arrangement observed by Allampally *et al.* for a longer, methoxy-functionalized OPE-based Pt(II) complex.^[4]

To confirm the results from ¹H MAS and ¹H-¹H DQ-SQ NMR correlation spectroscopy, ¹³C{¹H} cross polarization (CP/MAS) and 2D ¹³C{¹H} heteronuclear correlation (HETCOR) NMR experiments were performed (details are given in the Supporting Information, Figs. S12-S17). Figure 3 summarizes the ¹³C{¹H} CP/MAS NMR spectra of complexes **1-4** along with the peak assignment. Note that the assignment uses the numbering given in Fig. 3, which is different from the numbering of the carbons in the crystal structures. The assignment is based on a combination of variable contact time CP measurements for complex **1** as well as the corresponding 2D ¹³C{¹H} HETCOR NMR data (Fig. S14). To better visualize the changes in isotropic ¹³C chemical shift for the different complexes, the ¹³C signals associated with the OPE backbone are plotted in the lower part of Fig. 3. The most striking difference between the spectrum of complex **4** and those of

complexes 1-3 is the splitting of the broad ¹³C signal at $\delta_{iso}(^{13}C) = 129 - 122$ ppm, assigned to the *beta*-carbon of the pyridine moiety (C_{β} ; position **C2**). This carbon is directly bonded to proton Hb, which was previously attributed to a broad Gaussian-shaped peak in the ¹H MAS NMR spectra (vide supra). Thus, the doublet character of this ¹³C signal indicates a more complex ¹H line shape, with the Gaussian distribution being merely an approximation, which further explains the complex cross-correlation peaks observed in the ¹H-¹H DQ-SQ NMR spectrum of Fig. 2b,c. As the substitution of the EG groups occurs on the outer phenyl ring, these changes observed for C2 and Hb must be related to intermolecular packing effects. Another interesting feature of Fig. 3 is the low-field shift of the alkyne carbons C4 and C5 for complexes 2 and 3 compared to complex 1. This low-field shift is not observed for complex 4. Since the packing mode switches from the handshake motif with a longshifted arrangement in complex 1 to a less shifted, staircase pattern in complexes 2 and 3 with the Pt(II)Cl₂ center being close to the alkyne triple bond, we can attribute the low-field shift to a change in packing.

Several of the ¹³C signals across all four complexes in Fig. 3 are split into doublets, most notably the ¹³C signals assigned to carbon **C7** at $\delta_{iso}(^{13}C) = \sim 109$ ppm, as well as those for **C3**, **C4**, and **C8** in the case of complex **1**. The splitting of carbons **C7** and **C8** can be explained by two inequivalent carbon sites in the asymmetric unit of the crystal structure. However, according to the single-crystal XRD data, carbons **C3** and **C4** only occur once in the asymmetric unit of complex **1**. Therefore, it is likely that the



Figure 3. ¹³C{¹H} CP/MAS spectra of 1 to 4 acquired using a CP contact time of 2.0 ms at 9.4 T (2-4) and 7.05 T (1). The ¹³C assignment scheme (numbers) of the OPE backbone is shown at the top. Note that signal 1 is severely broadened under these CP conditions and overlaps with position 8. The plot at the bottom shows the variation of the ¹³C chemical shift between the complexes 1 to 4 highlighting changes in ¹³C chemical shift.

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sample used for MAS NMR has a slightly different packing and additional disorder compared to the single crystal used for XRD (cf. Figure S18-20). Figure 4 summarizes the 2D ¹³C{¹H} HETCOR spectra for 1, 2, and 4 acquired with 0.5 ms (green contour lines) and 3.0 ms CP contact time (black contour lines) to differentiate between directly bonded ¹H-¹³C and *inter*molecular ¹H-¹³C contacts, respectively. A comparison of these 2D HETCOR NMR datasets (green and black) allows us to identify the packing structure for each complex as illustrated by the structural fragments and corresponding assignments of ¹H-¹³C correlations below these spectra (see caption of Fig. 4 for details on the assignment). The spectrum of complex 1 shows two ¹³C signals for carbon C8 due to the existence of two inequivalent positions in the crystallographic asymmetric unit. As for complex 5 (data shown in Fig. S12-13), this also results in different intermolecular ¹H-¹³C distances for the two positions, manifested in the 2D HETCOR NMR spectra as correlations HbC8 and HbC8' labelled as b8 and b8', respectively, in Fig. 4a (complex 1). The large longitudinal shift between two molecules in 1 is also evident from the correlation HbC9, which links proton Hb (located at the complex center) to the outer most OPE carbon C9, a correlation that is only possible via intermolecular contacts. A further indicator for the magnitude of the longitudinal shift is the absence of potential *inter*molecular correlations HbC6 and HaC5. which would be expected for an intermediate shift (these are present in the case of complexes 2 and 3, see Fig. 4b).

Since the solid-state 2D HETCOR NMR spectra of 2 and 3 are very similar, only those for 2 will be discussed in the following (Fig. 4b). As mentioned before, the crystal structures of 2 and 3 lack the characteristic TEG handshake motif and feature a moderately shifted aromatic π - π stacking arrangement. This packing can be confirmed from the 2D HETCOR datasets in Figure 4b for 2 (see Fig. S16 for 3), which shows numerous intermolecular correlations, most notably HbC6, HaC5, HaC4, HbC9, HcC2, and HcC1. While HbC9 and HbC8 were also observed for complex 1, correlations HcC1, and HcC2 place the pyridine moiety close to the second phenyl ring of the OPE backbone. Interestingly, the correlations between C7 (bonded to proton Hc) and protons Ha or Hb (attached to carbons C1 and C2) are not observed. In addition, correlations HaC5 and HaC4 -which were not observed for complex 1- are indicators for the Pt(II)Cl₂ complex center being in the proximity to the alkyne triple bond of the neighboring molecule.

The 2D HETCOR spectra of 4 together with the proposed molecular arrangement are shown in Fig. 4c. In contrast to the 2D HETCOR spectra for 1 and 2, none of the intermolecular correlations such as HbC9, HaC9, HaC6, HaC5, and HaC4 are observed. This can only be achieved for a structural arrangement with a parallel or nearly parallel π - π stacked arrangement of the OPE backbones, similar to the one described by Allampally et al. complex the larger OPE-based with for methoxy functionalization.^[4] Such a structural arrangement is also supported by the ¹H-¹H DQ-SQ NMR correlation data, see Fig. 2. Thus, through a rigorous comparison and careful assignment of observed and non-observed ¹H-¹³C correlations for complexes 1-3 and 5 with known crystal structures, it can be concluded that the aromatic interactions for the OPE backbone of complex 4 occur

in a nearly parallel fashion as illustrated by the molecular fragments in Fig. 4c.

Conclusions

In summary, we have reported the synthesis and molecular packing of four new amphiphilic Pt(II) based complexes 1-4 with short aromatic OPE backbones and hydrophilic oligoethylene glycol termini of different length. A systematic length variation was achieved by gradually removing one (2), two (3) or three (4) OCH₂-CH₂ units from the TEG-substituted derivative 1. Data from single-crystal X-ray diffraction showed that complex 1 retained the characteristic handshake motif previously described for complex 5, which features the same TEG side chains, but has a larger aromatic surface than 1. The strong similarity between the packing motifs of 1 and 5 indicate that the TEG groups with their associated hydrophilic interactions are the primary forces dictating the solid-state structure. However, in contrast to 5, complex 1 shows no significant aromatic interactions due to the reduced aromatic surface. Shortening the hydrophilic side chains in complexes 2 and 3 resulted in structures with longitudinally shifted molecules involving more pronounced π - π interactions, though the bulky Pt(II)Cl₂ moiety in the complex center prevents efficient π - π stacking between neighboring complexes. Twodimensional solid-state ¹H MAS and ¹³C MAS NMR experiments for complexes 1, 2, 3, and 5 allowed us to identify ¹H-¹³C throughspace correlations characteristic for each packing motif. These, in turn, led us to propose a packing motif for the only complex (4) for which single crystals could not be grown, emphasizing the potential of solid-state NMR spectroscopy as a key tool for structural determination in the solid state. Complex 4 was found to exhibit a more parallel arrangement of the molecules stabilized by π - π interactions, most likely with a short longitudinal and lateral offset to accommodate the sterically demanding Pt(II)Cl₂ moiety at the complex center. On this basis, we conclude that the steric demand of the central Pt(II)Cl₂ moiety limits the effectiveness of π - π interactions, which is supported by the fact that even short monoethylene glycol termini appear to prevent an efficient π overlap of the ligands aromatic surface. A more pronounced π overlap is only possible after eliminating hydrophilic interactions by replacing the ethylene glycol termini with methoxy groups. Therefore, if π - π interactions are frustrated by steric demands, hydrophilic interactions will become the dominant factor in the self-assembly process leading to structural aggregation. Thus, our investigations illustrate that even minor changes in the glycol chain length can be used to modulate and control aromatic interaction strengths and packing arrangements, which in turn might be useful for the engineering of electronic devices based on Pt(II) and aromatic molecules. Finally, in our view, the combination of X-ray diffraction and solid-state NMR spectroscopy represents a general approach for detailed structural elucidation that is potentially applicable to virtually all types of molecular and macromolecular platforms.

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Experimental Section

See the supporting information for details on single-crystal diffraction and solid-state NMR experiments. CCDC-2004413 (1), -2004414 (2) and -2004415 (3) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <u>www.ccdc.cam.ac.uk/data_request/cif</u>.

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Keywords: Self-assembly • π -conjugated systems • weak noncovalent interactions • Pt(II) complexes • amphiphilic molecules

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Entry for the Table of Contents



Combined X-ray diffraction and advanced solid-state NMR studies have been introduced as a new, general tool for detailed structural and supramolecular elucidation, using a series of amphiphilic Pt(II) complexes as model compounds. Our approach provides an alternative for supramolecular systems where single-crystal growth is not possible, which can be potentially applied to multiple other molecular and macromolecular platforms.