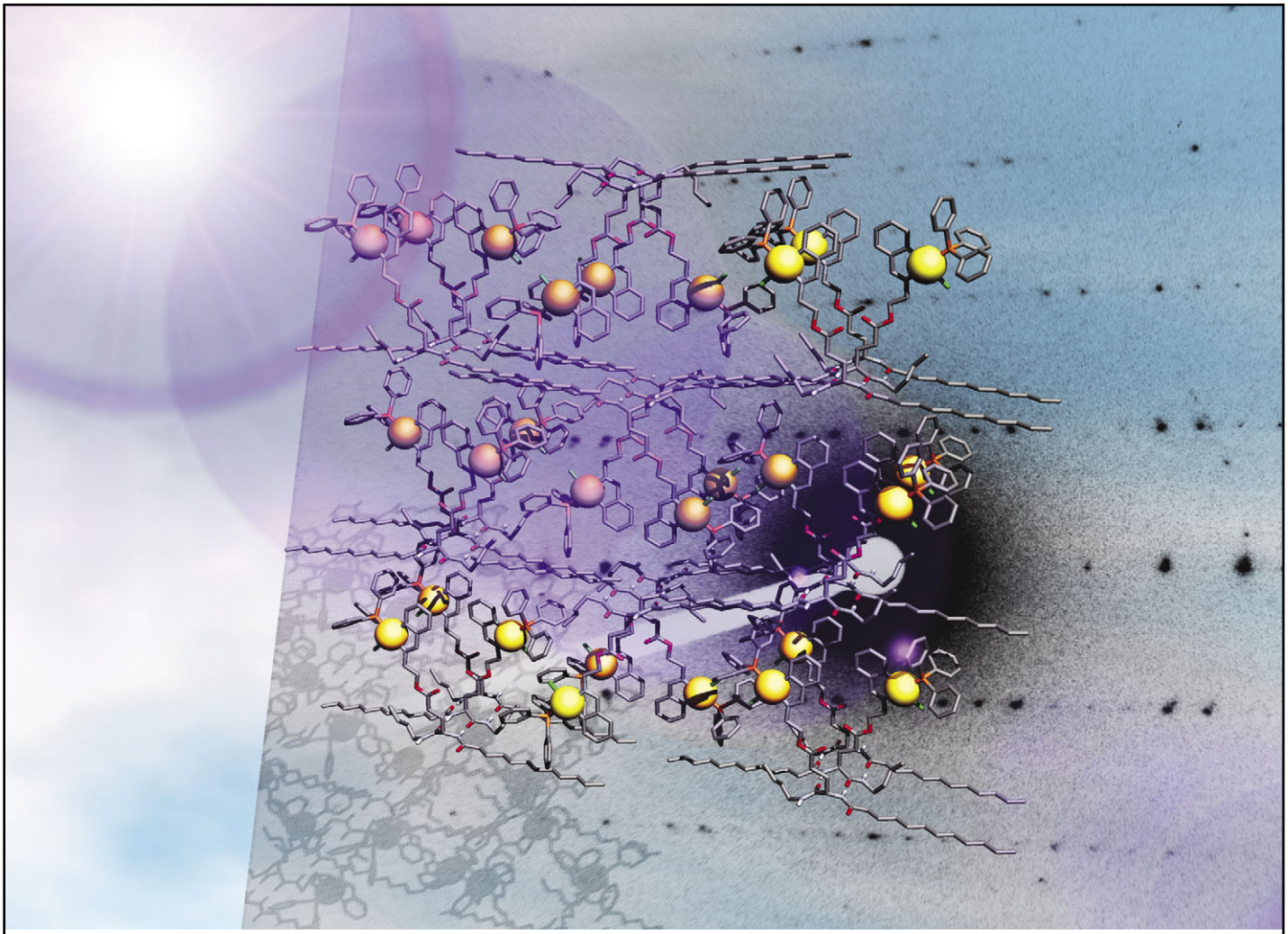

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Metal array fabrication through self-assembly of Pt-complex-bound amino acids

A self-assembled Pt-bound amino acid in a supramolecular fibril gives an extremely beautiful and sharp electron diffraction pattern under cryo-TEM conditions, that enables us to find a highly oriented Pt-array supported by a supramolecular β-sheet scaffold.

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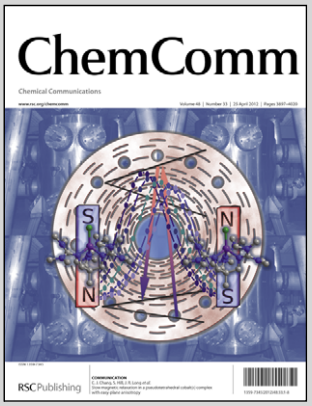

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Metal array fabrication through self-assembly of Pt-complex-bound amino acids†

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A new type of Pt-complex-bound amino acid was synthesized by condensation of a cyclometalated Pt complex with the side-chain residue of *N*- and *C*-alkylated glutamic acid. Self-assembly of the Pt-bound lipophilic amino acid afforded a supramolecular gel in organic solvents, which comprised fibrous lamellar aggregates that supported a highly oriented Pt array.

Supramolecular self-assembly of amino acids and peptides constitutes a rational approach to fabricating nanostructures comprising highly ordered arrays of functional groups with tailored chemical and physical properties.[1] Indeed, this approach has been widely exploited using various artificial amino acids and peptides which conjugate to photoactive[2] as well as electrically[3] and catalytically[4] active functional groups. Thus, a supramolecular architecture with a well-oriented and highly periodic array of functionalities can be obtained, even with enhanced inherent functions. In addition, the chemistry of amino acid–[5,6] and peptide–metal[7,8] conjugates has been widely explored. However, metal array fabrication using such conjugates still remains a largely untouched field, barring a few studies on peptides.[9] For example, we reported that palladium complex-bound peptides efficiently self-assemble into fibrous aggregates that constitute a supramolecular gel supporting a highly oriented palladium array.[10] Such findings show the potential of this route in constructing ordered metal arrays. Herein we report a newly synthesized Pt complex-bound glutamic acid **1** which acts as a building block for a supramolecular β-sheet structure that supports a highly oriented Pt array.

The Pt-complex-bound glutamic acid **1** (Fig. 1a) was synthesized by the condensation of *N*- and *C*-alkylated glutamic acid *n*-$C_{11}H_{23}$CO-Glu-NH-*n*-C_4H_9 with the cyclometalated Pt complex chloro{2-[[2-hydroxy-ethylimino-κ*N*]methyl]-phenyl-κ*C*}-(triphenylphosphine)Pt(II) (**2**). The cyclometalated structure and molecular geometry of parent complex **2** were unequivocally confirmed by single-crystal X-ray crystallographic analysis (Fig. 1b). The geometry around the Pt centre is almost square planar, where the sum of four angles at Pt(1), involving Cl(1), P(1), N(1), and C(1), is 360.24°.

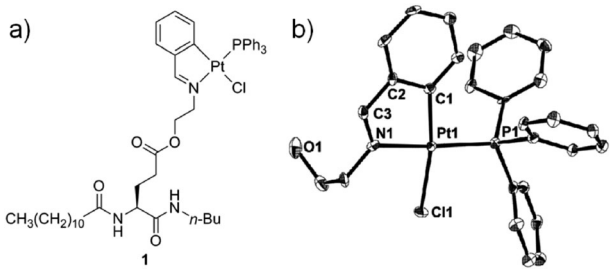

Fig. 1 (a) Pt-bound glutamic acid **1**. (b) ORTEP drawing for **2**.

The self-assembly of Pt-complex-bound glutamic acid **1** efficiently proceeded in organic solvents such as toluene (MGC, 1.89×10^{-2} M), diethyl ether (1.42×10^{-2} M), and *tert*-butyl methyl ether (2.00×10^{-2} M) to afford a supramolecular gel.[11] Typically, a mixture of **1** and toluene was heated until the solid was completely dissolved (Fig. 2a). After cooling to room temperature, the solution gradually lost its fluidity and transformed into an opaque gel when left standing for a few minutes (Fig. 2b). Further, the gel of **1** melted upon heating to afford a clear solution again; this sol–gel transition was completely reversible in further heating–cooling cycles. Such a thermoreversible phase transition strongly supports that the gelation is induced by self-assembly through non-covalent interactions such as hydrogen bonding. Notably, the same gelation behaviour was also observed under ultrasonication

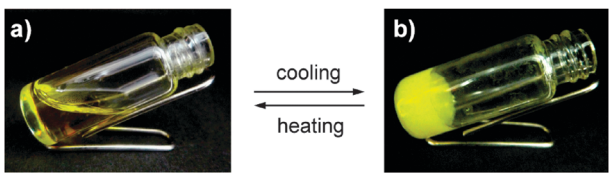

Fig. 2 Thermoreversible gelation of a 2.0×10^{-2} M toluene solution of **1** at 25 °C: (a) solution state, (b) gel state.

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† Electronic supplementary information (ESI) available: CCDC 656104. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2cc17530d

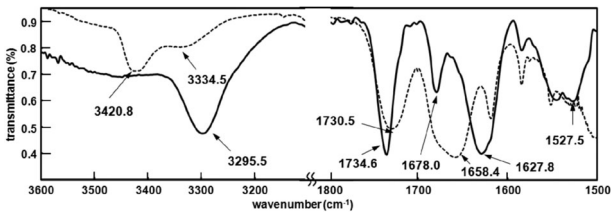

Fig. 3 IR spectra of toluene gel (2.0×10^{-2} M, bold line) and solution in $CHCl_3$ (2.0×10^{-2} M, dotted line) of **1**.

(0.45 W cm^{-2} at 40.0 kHz), despite the fact that ultrasound usually destroys non-covalently bonded aggregates of peptides.[12] In fact, we found that ultrasonication triggers cleavage of intramolecular hydrogen bonds[10,13] of peptide along with molecular conformation change, followed by self-assembly *via* intermolecular association to afford the supramolecular aggregates. Recently, some amides,[14] including peptides, were also reported to be ultrasound-responsive gelators by switching intra- to intermolecular amide–amide hydrogen bonding.

As shown in Fig. 3, the IR spectrum of the toluene gel of **1** (2.0×10^{-2} M) exhibited C=O and N–H stretching frequencies at 1627.8 (amide I band) and 3295.5 cm^{-1}, which are lower than those (1658.4 and 3420.8 cm^{-1}, respectively) in the solution state (2.0×10^{-2} M in $CHCl_3$). This can be ascribed to the formation of intermolecular hydrogen bonds between amides, which is typical for β-sheet peptide aggregates.[15] Importantly, antiparallel β-sheet association is strongly supported by the absorption at 1678.0 and 1527.5 cm^{-1} (amide II band).[16] WAX analysis showed a broad diffraction peak centred at $2\theta = 20.6°$, corresponding to a 4.7 Å *d*-spacing,[17] which is the typical interstrand distance for a β-sheet structure held together by intermolecular hydrogen bonds. The structure of the supramolecular fibrous aggregates was directly investigated at the micro- and nanoscale by SEM, cryo-TEM and AFM.[18] The toluene gel of **1** (2.0×10^{-2} M) dispersed into hexane was dropped on carbon tape with Pt deposition for SEM analysis. Bundled tape-like fibrils were observed with sub-micrometre widths and lengths on the order of tens of micrometres as shown in the inset to Fig. 4. Cryo-TEM observation of a gel fibril showed a fine, periodic striped structure with a spacing of approximately 2.1 nm (= *b*) (Fig. 4).

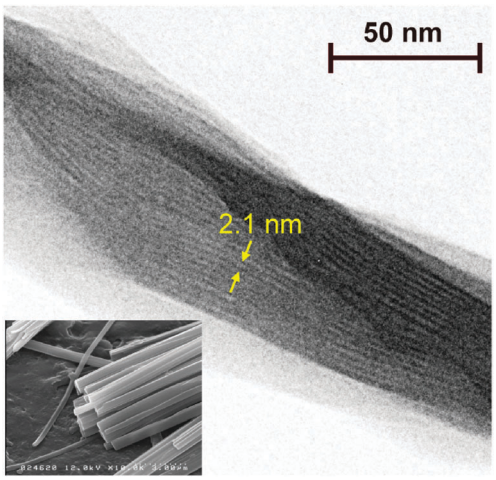

Fig. 4 Cryo-TEM images of fibrils of **1** in its toluene gel. The inset is an SEM image of bundled fibrils in the same sample.

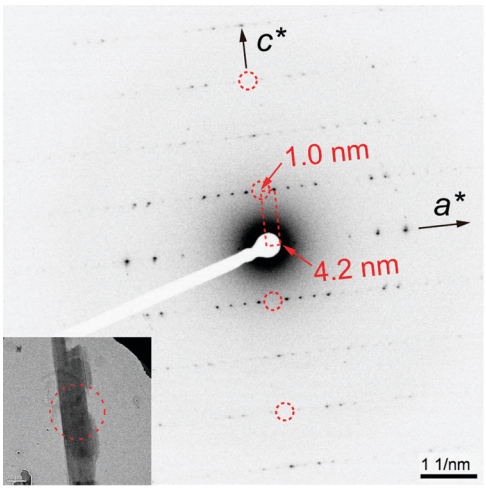

Fig. 5 Selected area electron diffraction pattern with a real space image (inset) of the gel fibril **1**.

Selected area electron diffraction analysis was carried out to elucidate the self-assembled structure of **1** in the gel fibrils (Fig. 5). The rectangular lattice (dashed red box) arising from orthogonally oriented *a* and *c* axes allowed the unit cell to be indexed to *p2gg* two-dimensional symmetry with $a = 4.2$ and $c = 1.0$ nm. The absence of diffraction spots at (00*l*) with odd *l* (dashed circles) indicates the existence of a two-fold screw axis perpendicular to the sheet structure (paper plane) in the fibril. The presence of this feature is strongly consistent with the antiparallel β-sheet self-assembly deduced from the IR analysis. Molecular modelling study based on these crystallographic parameters and the geometrical data obtained from WAX and SAXS spectrum afforded an assembly structure of **1** as depicted in Fig. 6. The 2.18 nm-interspaced lamellar structure formed by the alternating arrangement of Pt-containing layers and alkyl chain layers matches the periodic band structure of the gel fibril in the cryo-TEM image in Fig. 4. Antiparallel hydrogen-bonding association in a direction orthogonal to the *ab* plane was found, as depicted in Fig. 7. The 0.47 nm spacing of the staggered arrangement of **1** affords a 1.0 nm pitch built-up along the *ab* plane, as indicated by the diffraction spot in Fig. 5.

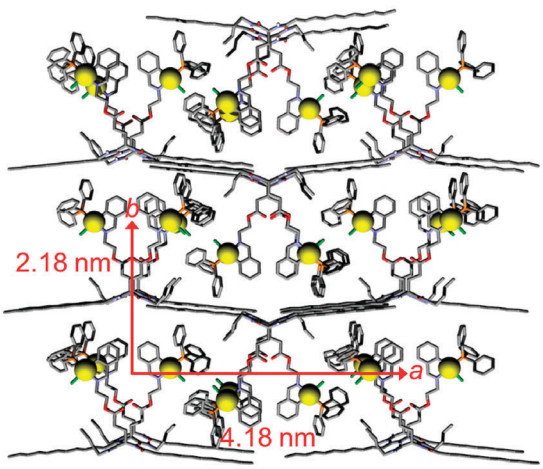

Fig. 6 Structure of self-assembled gel fibrils. The yellow spheres are Pt centres.

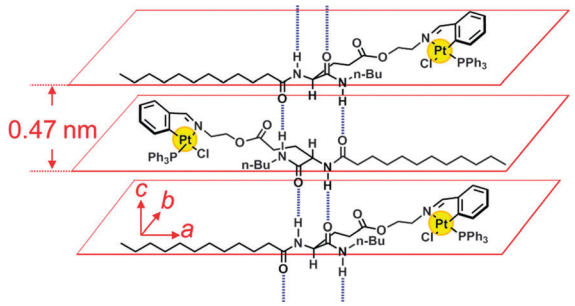

Fig. 7 Antiparallel β-sheet type association of **1**.

The observed layering of Pt complexes demonstrates that this supramolecular gel formation through the self-assembly approach of metalated amino acids has strong potential in the fabrication of precisely controlled metal arrays.

In conclusion, we designed and synthesized a new type of Pt-complex-bound amino acid which showed excellent self-assembly properties *via* intermolecular hydrogen bonding, affording β-sheet aggregates that support well-regulated Pt arrays. This supramolecular gel-templated metal aggregation approach will constitute an efficient methodology to control metal accumulation in the production of functional organometallic materials.

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17 For WAX and SAXS spectra of toluene gel of **1**, see ESI†, Fig. S1.

18 For AFM topographic images of a gel fibril, see ESI†, Fig. S2.

