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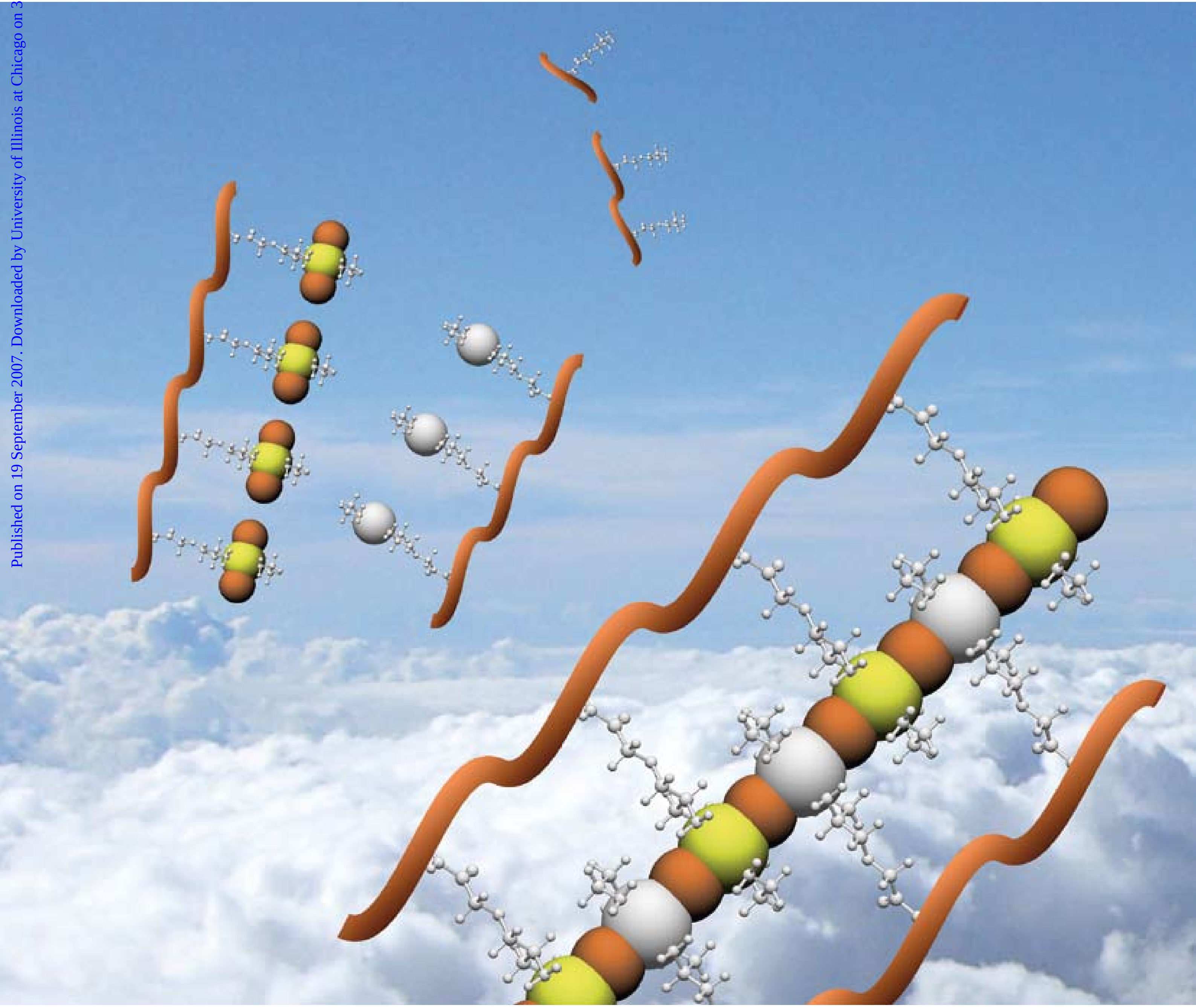

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**PERSPECTIVE**
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# A template-directed synthetic approach to halogen-bridged mixed-valence platinum complexes on artificial peptides in solution†

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**A template-directed synthetic approach to halogen-bridged mixed-valence platinum complexes has been performed in organic media using, for instance, a synthetic peptide bearing two bis(ethylenediamine)-based Pt(IV) complexes with two axial bromide anionic ligands, [1a(Pt(IV)Br$_2$(en))$_2$](RSO$_3$)$_4$, and a [Pt(II)(en)$_2$](RSO$_3$)$_2$ complex (R = (C$_{12}$H$_{25}$OCH$_2$)$_2$CHO(CH$_2$)$_3$–).**

Recently, a number of excellent examples of synthetic approaches to molecular wires consisting of a discrete number of metals in the solid state[1] and in solution[2] have been reported. In particular, a template-directed strategy is a key to the alignment of functional subunits in a way that their number, composition, sequence and direction are programmable.[2,3] Biomacromolecules such as nucleic acids and peptides have a structural basis as a molecular template for aligning functional building blocks in a way that their number and sequence are predetermined. For instance, artificial DNAs are known to act as templates for homogeneous and heterogeneous metal arrays.[2,4]

In this study, we used synthetic peptide templates for an approach to quasi-1D halogen-bridged mixed-valence metal complexes with a discrete number of alternating transition metal (M) and halide (X) ions.[5,6] A series of polymeric quasi-1D halogen-bridged mixed-valence metal complexes reported so far have attractive physicochemical properties such as intense intervalence charge-transfer absorption,[7,8] semiconductivity[9] and large third-order nonlinear optical susceptibilities[10] arising from strong electron-lattice interactions and tunable electronic states.[11] Most of them are generated in the solid state and only a few examples in solution or in liquid crystal,[12,13] and thus, to the best of our knowledge, there is no report on discrete halogen-bridged mixed-valence metal complexes that exist in solution. Herein, we report a template-directed synthetic approach in solution to halogen-bridged mixed-valence metal complexes using synthetic peptides bearing a discrete number of Pt(II or IV)(en)$_2$ units (en = ethylenediamine) on the side chains and Pt(IV or II)(en)$_2$ counterparts (Fig. 1). The interactions between these Pt(II) and Pt(IV) complexes were examined by photometric titration, $^1$H NMR spectroscopy and mass spectrometry.

The basic design concept for the synthetic peptides is as follows. Each building block of peptide templates has a side-chain ethylenediamine unit as an optically-active metal binding site on an oligo-ether-containing main chain. The number of building blocks on one peptide template can be predetermined in the synthetic procedure. The length of the main chain was determined by molecular modelling so as to adjust the distance around 11–12 Å between the adjacent two metal centers on the template. This distance was expected to be equivalent to that between two metal centers M in a linearly arranged -(M-X-M′-X-)$_n$- unit where X and M′ denote a halogen bridging ligand and a counterpart of M in the mixed-valence complex, respectively.

Synthetic procedures for the peptide templates and their Pt(II) and Pt(IV) complexes are briefly summarized in Scheme 1. For instance, a dipeptide (**1a**(CF$_3$COOH)$_4$) was prepared according

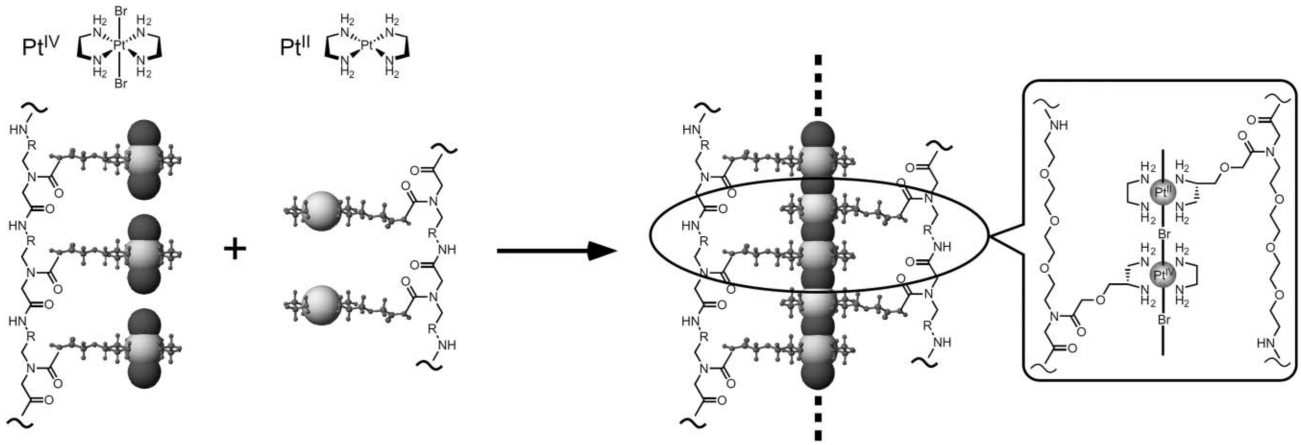

**Fig. 1** Schematic representation of a discrete association of Pt(II) and Pt(IV)Br$_2$ species with the aid of synthetic peptide templates used in this study.

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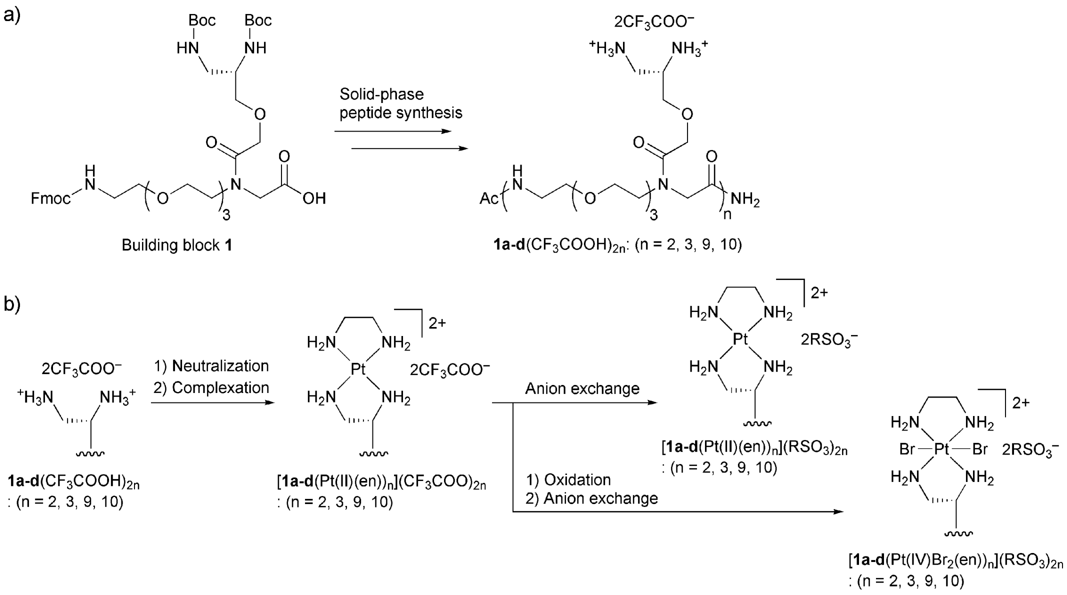

**Scheme 1** Synthetic routes to (a) peptide templates and (b) their platinum complexes.

to a solid-phase synthetic procedure in Fmoc chemistry using building block **1** (Scheme 1a) prepared from *N*α-*t*-Boc-β-amino-L-alanine as the starting material (see ESI†). The resulting peptides were purified by reversed-phase HPLC with CF$_3$COOH-containing eluents and isolated as CF$_3$COOH salts. The Pt(II) complex-pendant water-soluble dipeptide, [**1a**(Pt(II)(en))$_2$](CF$_3$COO)$_4$, was synthesized by the reaction of acid-free **1a** with [Pt(II)Br$_2$(en)] in 75% yield (2 steps). The dinuclear Pt(II) complex was then oxidized by bromination, followed by anion exchange with RSO$_3^-$ (R = (C$_{12}$H$_{25}$OCH$_2$)$_2$CHO(CH$_2$)$_3$–) to afford lipophilic [**1a**(Pt(IV)Br$_2$(en))$_2$](RSO$_3$)$_4$ in 49% yield (2 steps) (Scheme 1b). We thereby expected that a halogen-bridged trinuclear platinum complex would be formed as a thermodynamically stable clip-shaped structure in a self-assembled manner from [**1a**(Pt(IV)Br$_2$(en))$_2$](RSO$_3$)$_4$ and [Pt(II)(en)$_2$](RSO$_3$)$_2$ in organic solvents. Other peptides, [**1b–d**(Pt(IV)Br$_2$(en))$_n$](RSO$_3$)$_{2n}$: ($n$ = 3, 9, 10) and [**1a–d**(Pt(II)(en))$_n$](RSO$_3$)$_{2n}$: ($n$ = 2, 3, 9, 10), were also prepared according to the same synthetic procedure (see ESI†).

Photometric titration experiments were firstly performed to see interactions between [**1a**(Pt(IV)Br$_2$(en))$_2$](RSO$_3$)$_4$ and [Pt(II)(en)$_2$](RSO$_3$)$_2$. When [**1a**(Pt(IV)Br$_2$(en))$_2$](RSO$_3$)$_4$ (25 μM) was titrated with [Pt(II)(en)$_2$](RSO$_3$)$_2$ in CH$_2$Cl$_2$ at 293 K, new peaks gradually appeared at 360 and 390 nm (Fig. 2). This result indicates a significant interaction between [**1a**(Pt(IV)Br$_2$(en))$_2$](RSO$_3$)$_4$ and [Pt(II)(en)$_2$](RSO$_3$)$_2$ even under dilute conditions.[14] The molar extinction coefficient at 360 nm as a 1 : 1 complex was estimated to be more than 8 × 10$^3$ M$^{-1}$ cm$^{-1}$.

Photometric titration experiments of [**1b**(Pt(IV)Br$_2$(en))$_3$](RSO$_3$)$_6$ with [**1a**(Pt(II)(en))$_2$](RSO$_3$)$_4$ and [**1d**(Pt(IV)Br$_2$(en))$_{10}$](RSO$_3$)$_{20}$ with [**1c**(Pt(II)(en))$_9$](RSO$_3$)$_{18}$ showed a new absorption peak at 360 and 357 nm, respectively, similar to the above-mentioned result (Fig. S1 and S2, ESI†), suggesting a quite similar interaction between the Pt(II) and Pt(IV) species.

The interactions of [**1a**(Pt(IV)Br$_2$(en))$_2$](RSO$_3$)$_4$ with [Pt(II)(en)$_2$](RSO$_3$)$_2$ were then examined by $^1$H NMR titration experiment. Upon addition of [Pt(II)(en)$_2$](RSO$_3$)$_2$ to a solution of [**1a**(Pt(IV)Br$_2$(en))$_2$](RSO$_3$)$_4$ in CD$_2$Cl$_2$ ([[**1a**(Pt(IV)Br$_2$(en))$_2$](RSO$_3$)$_4$] = 5 mM, [[Pt(II)(en)$_2$](RSO$_3$)$_2$] = 2.5 mM) at 293 K, the signals assigned to the methylene protons of ethylenediamine moieties in [**1a**(Pt(IV)Br$_2$(en))$_2$](RSO$_3$)$_4$ shifted to upfield with broadening (Fig. S3†). The spectra continuously changed even when the ratio of Pt(II) to Pt(IV) reached higher than 1 : 1, indicating that these Pt(II) and Pt(IV) complexes significantly interact with each other in a faster equilibrium than the NMR timescale but not quantitatively under this condition. It is a noteworthy observation that the CH$_2$ proton signals of ethylenediamine moieties for [Pt(II)(en)$_2$](RSO$_3$)$_2$ showed downfield shift in contrast with [**1a**(Pt(IV)Br$_2$(en))$_2$](RSO$_3$)$_4$, suggesting a significant interaction between Pt(IV) and Pt(II)species.

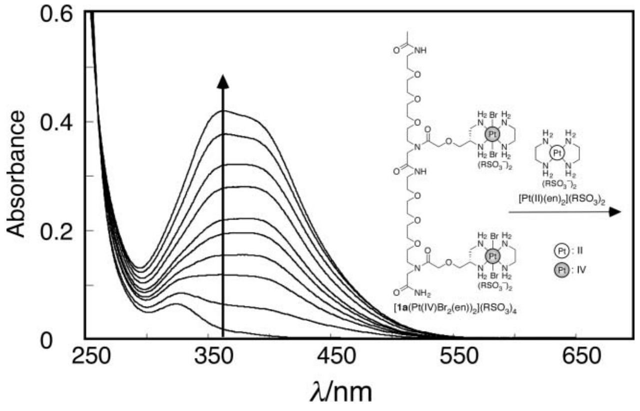

**Fig. 2** Photometric titration spectra of dinuclear [**1a**(Pt(IV)Br$_2$(en))$_2$](RSO$_3$)$_4$ with [Pt(II)(en)$_2$](RSO$_3$)$_2$ in CH$_2$Cl$_2$ at 293 K ($l$ = 1). [[**1a**(Pt(IV)Br$_2$(en))$_2$](RSO$_3$)$_4$] = 25 μM. [[Pt(II)(en)$_2$](RSO$_3$)$_2$] = 0, 5, 10, 15, 20, 25, 38, 50, 75 and 100 μM. Inset; The reaction scheme of [**1a**(Pt(IV)Br$_2$(en))$_2$](RSO$_3$)$_4$ and [Pt(II)(en)$_2$](RSO$_3$)$_2$.

The magnitude of association seemed to vary with the constituent concentrations, as compared with the NMR and photometric titration studies. This is probably because the concentration-dependent self-association of counter anions with long-alkyl-chains affects the stability of complexes formed between the Pt(II) and Pt(IV) species in a rather complicated manner.

The electrospray ionization-time-of-flight (ESI-TOF) mass spectrum of a mixture of [**1a**(Pt(IV)Br$_2$(en))$_2$](RSO$_3$)$_4$ and [Pt(II)(en)$_2$](RSO$_3$)$_2$ in a 1 : 1 ratio showed a series of peaks around 2064.48 corresponding to a doubly-charged cationic species, [**1a**(Pt(IV)Br$_2$(en))$_2$·Pt(II)(en)$_2$·(RSO$_3$)$_4$]$^{2+}$, as shown in Fig. 3. This result indicates the formation of a mixed-valence trinuclear complex in solution containing a 1 : 1 mixture of [**1a**(Pt(IV)Br$_2$(en))$_2$]$^{4+}$ and [Pt(II)(en)$_2$]$^{2+}$ species.

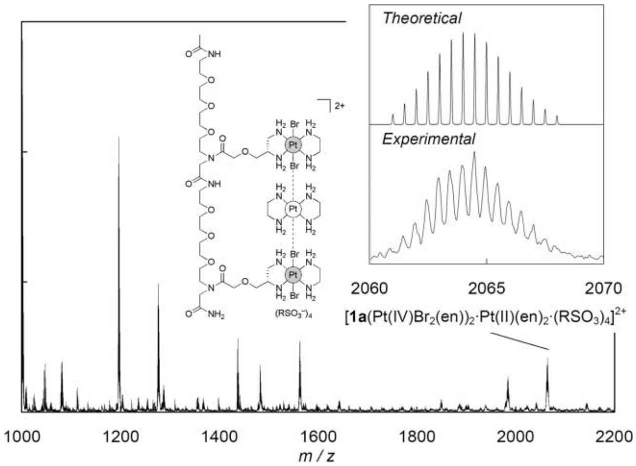

**Fig. 3** ESI-TOF mass spectrum of a 1 : 1 mixture of [**1a**(Pt(IV)Br$_2$(en))$_2$]-(RSO$_3$)$_4$ and [Pt(II)(en)$_2$](RSO$_3$)$_2$ in 1,2-dichloroethane.

In summary, we have designed and synthesized novel synthetic peptides and their complexes bearing a discrete number of Pt(II) or Pt(IV) ions for a template-directed synthetic approach to discrete halogen-bridged mixed-valence platinum complexes in solution. In the $^1$H NMR, UV-vis absorption and ESI-TOF mass spectral studies using [**1a**(Pt(IV)Br$_2$(en))$_2$](RSO$_3$)$_4$ and [Pt(II)(en)$_2$](RSO$_3$)$_2$, a significant interaction was observed between [**1a**(Pt(IV)Br$_2$(en))$_2$]$^{4+}$ and [Pt(II)(en)$_2$]$^{2+}$ and the formation of a mixed-valence trinuclear complex in solution containing a 1 : 1 mixture of the Pt(IV) and Pt(II) species was confirmed by mass spectrometry. The present study would provide a new clue to a template-directed synthesis of discrete halogen-bridged mixed-valence platinum complexes with novel functions depending on their number and sequence in relation to nanomagnetism, conductivity or catalysis.

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