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Double Helix-to-Double Helix Transformation, Using Platinum(II) Acetylide Complexes as Surrogate Linkers

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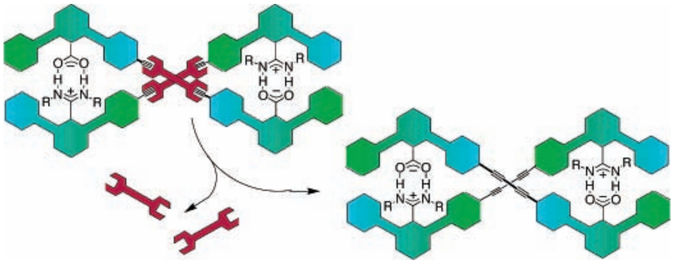
ABSTRACT



We describe novel optically active double helices consisting of complementary strands stabilized by amidinium–carboxylate salt bridges. The *m*-terphenyl groups of each strand are joined by *trans*-Pt(II) acetylide complexes with pendant PPh_3 ligands as the surrogate linker, which converts to cis counterparts by a ligand exchange reaction with *cis*-1,2-bis(diphenylphosphino)ethylene, resulting in the formation of double helices with different structures. Subsequent iodine-promoted reductive elimination on the Pt(II) atoms generates the fully organic, enantiomerically pure double helices.

The helix, a central structural motif for biological macromolecules, has inspired synthetic chemists to synthesize artificial helices.[1] In particular, the double helix has attracted significant attention, since the discovery of the double-stranded structure of DNA.[2] The metal-directed self-assembly is the most widely used approach to build double-stranded helices.[3] On the other hand, only a few synthetic double helices have been synthesized by utilizing hydrogen bonds,[4] although the hydrogen-bond-driven self-assembly is a common approach to various kinds of supramolecules.[5] We have recently reported a novel strategy to build artificial double

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[1] For reviews on artificial helical polymers and oligomers, see: (a) Gellman, S. H. *Acc. Chem. Res*. **1998**, *31*, 173−180. (b) Rowan, A. E.; Nolte, R. J. M. *Angew. Chem., Int. Ed.* **1998**, *37*, 63−68. (c) Nielsen, P. E. *Acc. Chem. Res.* **1999**, *32*, 624−630. (d) Green, M. M.; Park, J.-W.; Sato, T.; Teramoto, A.; Lifson, S.; Selinger, R. L. B.; Selinger, J. V. *Angew. Chem., Int. Ed.* **1999**, *38*, 3138−3154. (e) Hill, D. J.; Mio, M. J.; Prince, R. B.; Hughes, T. S.; Moore, J. S. *Chem. Rev.* **2001**, *101*, 3893−4011. (f) Nakano, T.; Okamoto, Y. *Chem. Rev*. **2001**, *101*, 4013−4038. (g) Schmuck, C. *Angew. Chem., Int. Ed*. **2003**, *42*, 2448−2452. (h) Yashima, E.; Maeda, K.; Nishimura, T. *Chem. Eur. J.* **2004**, *10*, 42−51. (i) Huc, I. *Eur. J. Org. Chem.* **2004**, 17−29. (j) Albrecht, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 6448−6451.

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[3] For reviews on helicates, see: (a) Piguet, C.; Bernardinelli, G.; Hopfgartner, G. *Chem. Rev.* **1997**, *97*, 2005−2062. (b) Albrecht, M. *Chem. Rev.* **2001**, *101*, 3457−3497.

[4] (a) Sánchez-Quesada, J.; Steel, C.; Prados, P.; de Mendoza, J. *J. Am. Chem.* Soc. **1996**, *118*, 277−278. (b) Berl, V.; Huc, I.; Khoury, R. G.; Krische, M. J.; Lehn, J.-M. *Nature* **2000**, *407*, 720−723. (c) Berl, V.; Huc, I.; Khoury, R. G.; Lehn, J.-M. *Chem. Eur. J.* **2001**, *7*, 2810−2820.

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helices **1·2** using complementary amidinium−carboxylate salt bridges to intertwine the two crescent-shaped strands (Figure 1).[6] In this system, the double helical structure and its helical sense are determined by the crescent-shaped *m*-terphenyl ligands and the chiral amidine groups, respectively, so that the diacetylene linkers can be utilized as the site for introducing new functional groups. In this paper, we describe the synthesis and in situ structural transformations of new artificial double helices using Pt(II) acetylide complexes as surrogate linkers.

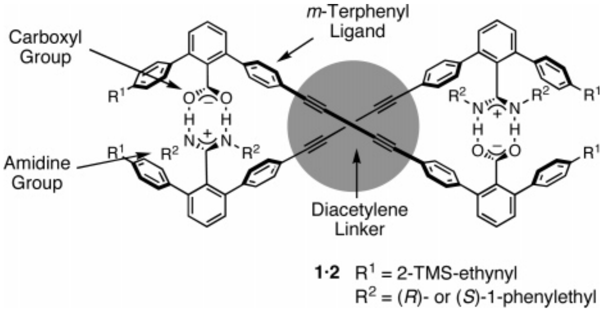
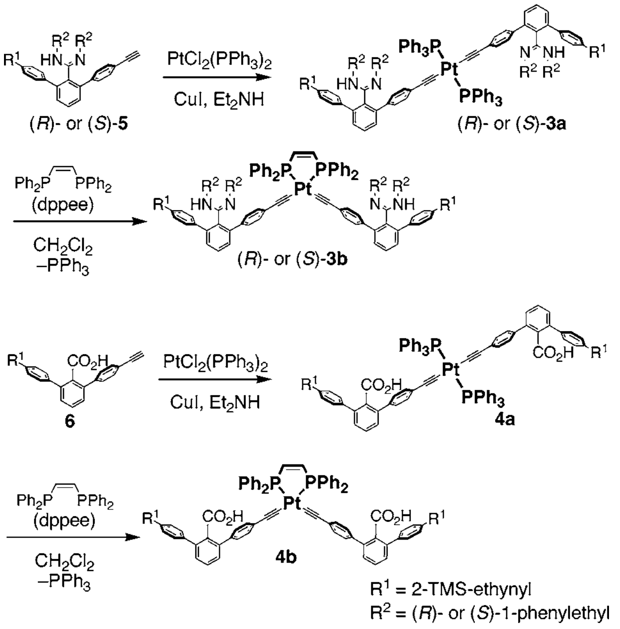


Figure 1. Artificial double helices **1·2**.

Platinum has long been one of the favorite metals in the field of metal-directed self-assembly.[7] In particular, the Pt(II) acetylide complexes have been increasingly utilized as building blocks for metal-containing materials because of their well-defined geometry and photoproperties together with their synthetic accessibility.[8] Recently, Tykwinski and co-workers reported the trans-to-cis isomerization of Pt(II) acetylide complexes by ligand exchange reactions.[9] In addition, the *cis*-Pt(II) acetylide complexes undergo a 1,1-reductive elimination to form diacetylenes.[10] Hence, by substituting Pt(II) acetylide complexes for the diacetylene linkers, one can expect that new double helices with an optical activity containing the organometallic linkers are constructed and undergo transformations into other double helices through ligand exchange reactions or reductive eliminations on the Pt(II) atoms.

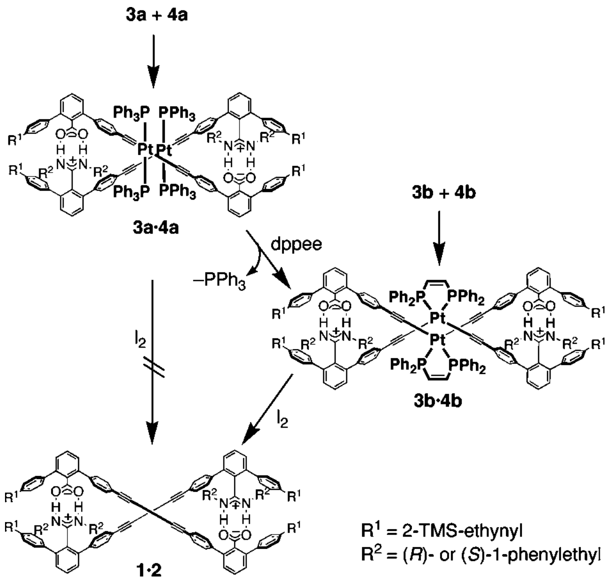
The chiral amidine dimers linked by the Pt(II) complexes (*R*)- and (*S*)-**3a** and **3b** were prepared according to Scheme 1.[11] The monosilylated amidine (*R*)-**5**[6] and its antipode (*S*)-**5**[6] were allowed to react with $PtCl_2(PPh_3)_2$ to afford the *trans*-Pt(II)-PPh_3 amidines (*R*)-**3a** and (*S*)-**3a**, respectively. The ligand exchange of (*R*)-**3a** and (*S*)-**3a** with *cis*-bis(diphenylphosphino)ethylene (dppee)[9] gave the *cis*-Pt(II)-dppee diamidine (*R*)-**3b** and (*S*)-**3b**, respectively. Similarly, the achiral carboxylic acid dimers linked by Pt(II) complexes **4a** and **4b** were synthesized in high yields starting from the monosilylated carboxylic acid **6**.[6]

Scheme 1. Synthesis of the Strands **3** and **4**



Duplex formation of the *trans*-Pt(II)-PPh_3 diamidine (*R*)- or (*S*)-**3a** and the *trans*-Pt(II)-PPh_3 dicarboxylic acid **4a** was easily carried out by mixing them in $CHCl_3$ to give the corresponding duplex (*R*)- or (*S*)-**3a·4a** (Scheme 2).[11] The formation of the duplex (*R*)-**3a·4a** was confirmed by ESI-

Scheme 2. Synthesis and In Situ Transformations of the Double Helices **3a·4a**, **3b·4b**, and **1·2**



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[6] Tanaka, Y.; Katagiri, H.; Furusho, Y.; Yashima, E. *Angew. Chem., Int. Ed.* **2005**, *44*, 3867−3870.

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MS measurements; the ESI-MS spectrum of a $CHCl_3$ solution of (*R*)-**3a·4a** showed signals at *m*/*z* 3426.51 and 1713.77 corresponding to [**3a·4a**+H]$^+$ and [**3a·4a**+2H]$^{2+}$, respectively. The ^{1}H NMR (500 MHz, $CDCl_3$) spectra of (*R*)- and (*S*)-**3a·4a** showed that most of the signals were highly broadened, suggesting that the molecular motion of the duplexes is highly restricted probably due to the steric repulsion of the triphenylphosphine ligands.[12] The resonances of the NH protons were observed as two broad singlets at the low magnetic field of δ 12.9 and 12.2 ppm, indicating the formation of salt bridges.[6] The CD spectra of the duplexes (*R*)- and (*S*)-**3a·4a** show intense mirror image CD signals below 400 nm, whereas (*R*)- and (*S*)-**3a** exhibit weak Cotton effects in this region (Figure 2B). The significant enhancement of the Cotton effects for the complexes (*R*)- and (*S*)-**3a·4a**, especially in the *trans*-Pt(II) acetylide complex region (ca. 300−390 nm), indicates that (*R*)- and (*S*)-**3a·4a** likely adopt an excess single-handed double helical structure as in the case of the diacetylene analogues (*R*)- and (*S*)-**1·2**.[6,13]

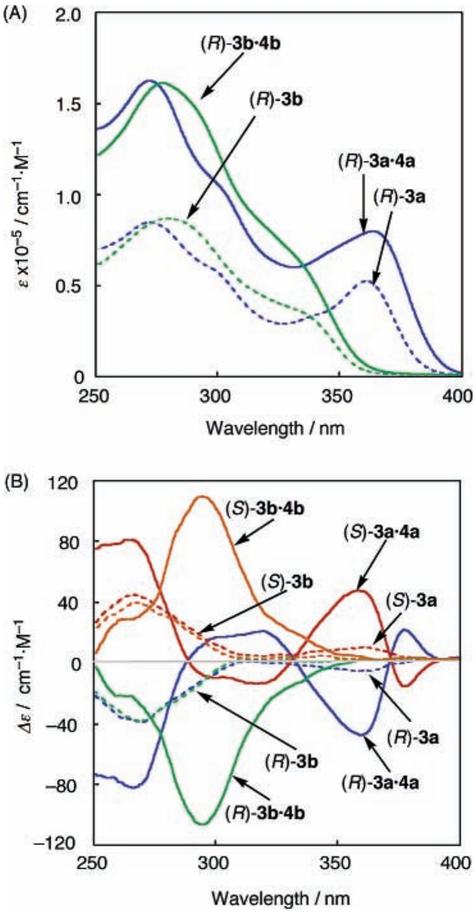

Figure 2. (A) UV/vis spectra (0.1 mM, 25 °C) of (*R*)-**3a**, **3a·4a**, **3b**, and **3b·4b** in $CDCl_3$. (B) CD spectra (0.1 mM, 25 °C) of (*R*)- and (*S*)-**3a**, **3a·4a**, **3b**, and **3b·4b** in $CDCl_3$.

The *cis*-Pt(II)-dppee duplexes (*R*)- and (*S*)-**3b·4b** were similarly prepared from (*R*)- or (*S*)-**3b** and **4b** in $CHCl_3$ (Scheme 2).[11] The ESI-MS spectrum of (*R*)-**3b·4b** showed signals at *m*/*z* 3170.39 ([**3b·4b**+H]$^+$) and 1585.66 ([**3b·4b**+2H]$^{2+}$), indicating the formation of the duplex (*R*)-**3b·4b**. In the ^{1}H NMR spectra (500 MHz, $CDCl_3$) of (*R*)- or (*S*)-**3b·4b**, most signals are much less broadened than those of (*R*)- or (*S*)-**3a·4a**. The low-field signals of the N−H groups observed at δ 13.2 and 12.9 ppm indicate the formation of the salt bridges. The absorption spectrum of the cis-duplex (*R*)-**3b·4b** shows a blue shift of the absorption in the longer wavelengths compared to that of the trans-duplex (*R*)-**3a·4a** (Figure 2A), as observed in the case of the *trans*- and *cis*-Pt(C≡CPh)$_2$(PPh$_3$)$_2$ complexes.[14] The CD signals of (*R*)- and (*S*)-**3b·4b** in the *cis*-Pt(II) acetylide complex region (ca. 300−360 nm) were significantly enhanced, when compared to the diamidines (*R*)- and (*S*)-**3b**, suggesting that (*R*)- and (*S*)-**3b·4b** also take an excess single-handed double helical structure.[13,15]

Finally, the in situ structural transformations of the double helices were investigated (Scheme 2). The (*R*)-*trans*-Pt(II)-PPh$_3$ duplex **3a·4a** was treated with an equimolar amount of dppee in $CDCl_3$ at ambient temperature, and the reaction progress was monitored by ^{1}H NMR and CD. About 1 h after the addition of dppee, the ligand exchange was completed that nearly quantitatively formed the (*R*)-*cis*-Pt(II)-dppee duplex **3b·4b**.[16] Furthermore, the reductive elimination of the Pt(dppee) linkers was achieved by treatment with I_2.[10] Upon the addition of 2 equiv of iodine to a $CDCl_3$ solution of (*R*)-**3b·4b** at ambient temperature, the reaction was almost simultaneously completed and the formation of the C−C coupled product (*R*)-**1·2** was confirmed by ^{1}H NMR and CD measurements.[17] For comparison, (*R*)-**3a·4a** was treated with iodine in $CDCl_3$ at ambient temperature. However, the reductive elimination did not proceed at all.[18]

In summary, we have constructed new artificial double helices using the Pt(II) acetylide complexes as the surrogate linkers of the strands. They underwent a nearly quantitative in situ structural transformation through ligand exchange reactions on the Pt(II) atoms. Furthermore, the Pt(II) linkers

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[11] See the Supporting Information for details of the synthesis, characterization, and structural transformations of the compounds **3a**, **3b**, **4a**, **4b**, **3a·4a**, and **3b·4b**.

[12] The ^{1}H NMR spectra of (*R*)-**3a·4a** recorded in $CDCl_3$ showed no concentration dependence from 1.0 down to 0.01 mM. Therefore, it seems unlikely that the broadening of the spectra comes from the monomeric strand−duplex equilibrium of the system.

[13] The Cotton effect intensities of **3a·4a** and **3b·4b** in $CHCl_3$ showed almost no temperature dependency between +55 and −10 °C. In the ^{1}H NMR spectra of **3a·4a** and **3b·4b**, all the signals did not show splits attributable to the diastereomeric pairs within the temperature range of +55 to −40 °C and thereby it is not possible to quantify the diastereomeric excesses of the chiral helices. For the double-stranded helical structures of **3a·4a** and **3b·4b** optimized by MM calculations, see the Supporting Information.

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[15] However, the CD spectra could not rule out the possibility of a side-on complexation of **3b·4b**, i.e., a mesocate-like duplex formation.[3b]

[16] The second-order rate constants for the ligand exchange reactions of **3a**, **4a**, and **3a·4a** were determined to be 140 ± 1, 180 ± 2, and 3.27 ± 0.01 s^{-1}·M^{-1}, respectively. Considering the large decrease in the reaction rate for **3a·4a** together with the observation that both **3a·4a** and **3b·4b** quantitatively form the duplexes in $CHCl_3$, it seems probable that the ligand exchange reaction occurs without decomplexation.

were removed by treatment with iodine to form the "original" fully organic enantiomerically pure double helices. To the best of our knowledge, this is the first example of double helix-to-double helix transformations for artificial double helices. Further studies to improve the reductive elimination efficiency of the *cis*-Pt(II) linkers directed toward polymeric systems are now in progress.

Supporting Information Available: The experimental procedures and the MM calculations of the duplexes **3a·4a** and **3b·4b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) The yield of (*R*)-**1·2** was estimated to be 34% by ^{1}H NMR and 37% by CD.[11] These values correspond to ca. 60% yield of the reductive elimination for each strand.

(18) It is reported that the cis isomers of some Pt(II) acetylide complexes undergo oxidatively induced reductive elimination, whereas the trans isomers do not. Sato, M.; Mogi, E.; Kumakura, S. *Organometallics* **1995**, *14*, 3157−3159.