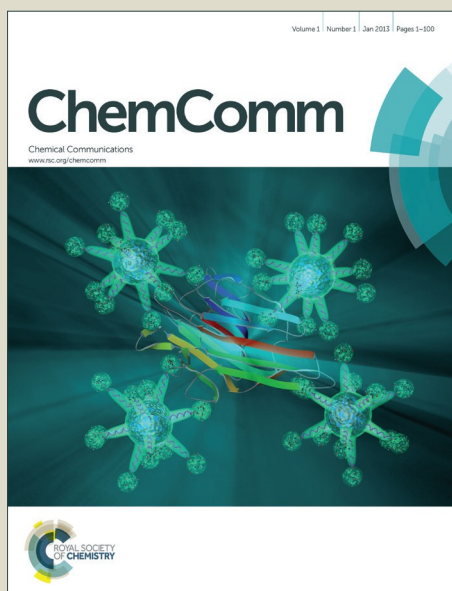


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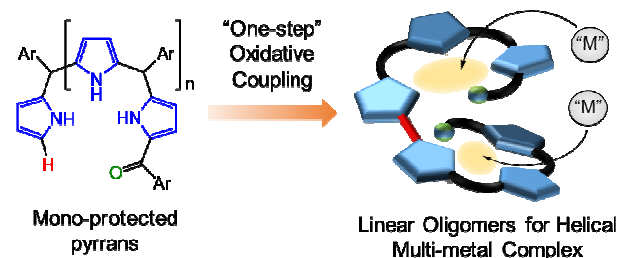
Rational Syntheses of Helical π -Conjugated Oligopyrrins with a Bipyrrrole Linkage: Geometry Control of Bis-Copper(II) CoordinationKai Zhang,^a Mathew Savage,^b Xin Li,^a Yu Jiang,^c Masatoshi Ishida,^d Koki Mitsuno,^d Satoru Karasawa,^e Tatsuhisa Kato,^f Weihua Zhu,^c Sihai Yang,^b Hiroyuki Furuta,^d and Yongshu Xie*^a⁵ Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
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A rational and effective approach for synthesizing linear π -conjugated hexa-, hepta- and octapyrrins through regioselectively oxidative coupling of monoacylated tripyrrane and bilane is described. Dependent upon the numbers of pyrrolic units, the geometry and properties of bis-copper(II) complexes could be systematically modulated.

Oligopyrrins have been widely used as building blocks toward syntheses of various porphyrins and their analogues.¹⁻⁴ However, the syntheses of long-chain oligopyrroles with more than five pyrrolic units still remain challenging owing to the limited methodologies.⁵ To date, the preparation of long-chain oligopyrranes have been taken into account either in stepwise or one-pot synthetic manners. The former stepwise approach is based on regioselective pyrrolic condensation through successive pyrrolic CH acylation, reduction, and subsequent condensation in the presence of excess pyrrole.⁶ Repeating these tedious reactions for longer derivatives is however not efficient, since the control in the reaction site becomes harder and the reactivity becomes lower with increasing number of pyrrolic units. On the other hand, one-pot condensation reaction of pyrrole and the corresponding aldehyde in a controlled stoichiometry usually affords a complicated reaction mixture containing different lengths and types of oligopyrranes (e.g., N-confused derivatives), which impedes the isolation of the desired linear products in a practical scale.⁷ Hence, it is desirable to develop a concise and practical approach for preparation of long-chain oligopyrroles.

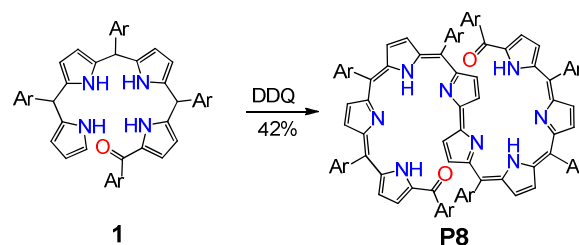
In fact, Osuka *et al.* have reported an indirect but nice way to obtain helical bis-copper(II) complexes supported by π -conjugated heptapyrrin and octapyrrin ligands approached by

oxidative cleavage of the corresponding expanded porphyrin copper(II) complexes.⁸ Toward further practical applications, a rational and efficient synthetic method suitable for long-chain oligopyrrins in a gram scale is however likely needed without employing the macrocyclic precursors. Furthermore, in-depth investigation of multi-metal coordination ability of the freebase oligopyrrins, and properties of the corresponding metal complexes supported by the smoothly π -conjugated backbones are sought.



⁴⁵ Fig. 1 Modular Approach toward Linear Oligopyrrins.

In this study, we have prepared longer oligopyrrin derivatives, **P6-P8** (the number of pyrrole subunits in the molecules are six, seven and eight, respectively) by simple oxidative homo/hetero-coupling reactions of monoacylated bilane (**1**) and/or tripyrrane (**2**) using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (Fig. 1). Furthermore, the oligopyrrin derivatives are capable of formation of bis-copper(II) complexes (**Pn-Cu2**; n = 6–8) in a self-assembled reaction manner, which demonstrated chain length-dependent spiral geometries and intramolecular antiferro-



⁵⁵ Scheme 1 Syntheses of oligopyrrin derivatives, **P8**. Ar = pentafluorophenyl

magnetic interactions. This iterative approach has an advantage: the mono-acylated pyrrole precursor can be systematically

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prepared in a gram-scale with the desired number of pyrrole units. The linking bipyrrrole unit can adopt two possible conformations as *syn*- and *anti*-structures, which modulates the magnetic interactions of the coordinated metals.

Regarding the synthetic strategy for longer oligopyrrins, simple oxidation of a bilane tends to form the corresponding "corrole" through C_α-C_α linkage.⁹ Hence, we envision that one of the terminal α-pyrrolic CHs of the tripyrrane and bilane should be protected to avoid the undesired cyclization. Therefore, we used a mono-acylated oligopyrranes as coupling substrates. The oxidation of the monoacylated bilane (**1**) with DDQ indeed afforded a stable linear octapyrrin (**P8**) in a 42% yield (Scheme 1), and the reaction could be performed in a gram scale.¹⁰ High resolution ESI-TOF mass spectroscopy of **P8** showed a parent ion

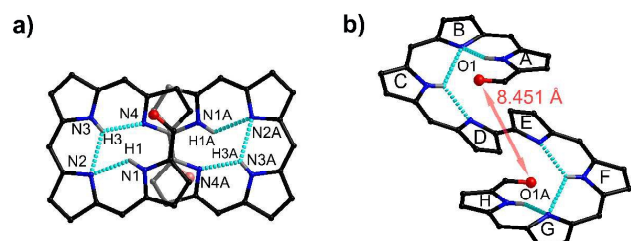


Fig. 2 Views of molecular structures of the octapyrrins in the crystals, **P8**. C₆F₅ groups and the hydrogens attached to carbon atoms are omitted for clarity.

peak at $m/z = 1980.1185$ (Fig. S9, ESI), which approximately equals to the double of the monoacyl bilane, indicative of the formation of a dimeric structure of bilane **1**. Due to the flexibility of the core skeleton, the ¹H NMR spectrum of the CDCl₃ solution of **P8** revealed the presence of a C₂-like symmetric conformer along with minor conformational isomers at room temperature. The broad pyrrolic NHs at 13.14 and 12.08 ppm could be assigned to the major conformer, which is downfield shifted due to the effective intramolecular hydrogen bonding interactions. The small peaks near the NH resonances could be assigned to the different conformers, since the spectrum is sensitive to the solvent media (Fig. S4, ESI). With theoretical support, the energy difference between the present conformation of **P8** and the potential isomer **P8'** is found to be 10 kJ mol⁻¹. The relatively smaller difference resulted in the mixture under the experimental conditions (Fig. S14 and Table S1, ESI).¹¹

Conclusively, X-ray crystallographic analysis of **P8** revealed an open-chain spiral octapyrrrolic core winding through multiple intramolecular hydrogen bonds, with the two tripyrrrolic units bridged by a C_α-C_α linkage of a coplanar 2,2'-bipyrrrolic unit in a *anti* conformation (Fig. 2a, 2b).¹² The presence of four amino and four imino N atoms can be clearly assigned by considering distribution of the C-C single bonds judging from the bond lengths and the C_α-N-C_α bond angles (Fig. S15, ESI).^{5,13} Thus, the molecule adopts an "S-shape" spiral conformation, with all the amino and imino moieties pointed inward and involved in intramolecular hydrogen bonds (Fig. 2b).

The UV-vis-NIR absorption spectra of **P8** in CH₂Cl₂ (Fig. 3) revealed broad low-energy bands centered at 1073 nm, suggesting full π-conjugation over both of the oligopyrrrolic backbones. DFT calculations likewise support this conclusion by that the whole electron delocalization nature of **P8** is observed in

their HOMOs and LUMOs (Fig. S16, ESI).¹¹ Notably, the narrower HOMO-LUMO energy gap of **P8** obtained by cyclic voltammetry was estimated to be 0.83 V (Fig. S25, Table S2, ESI), which is also consistent with the absorption spectra.

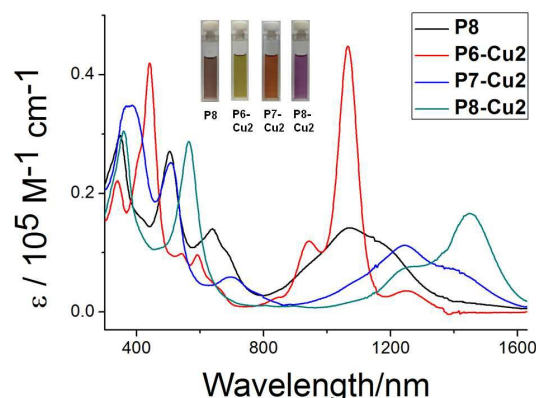
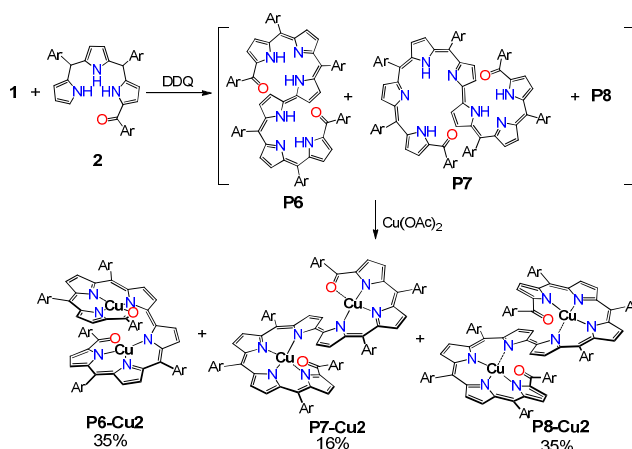


Fig. 3 UV-vis-NIR absorption spectra of oligopyrrins **P8** and bis-copper complexes, **Pn-Cu2** ($n = 6-8$) in CH₂Cl₂. Photographs of the corresponding solutions are shown in the insets.

In an effort to gain further insight into the reaction scopes for preparation of a series of oligopyrrins, a mixed coupling reaction of equimolar bilane **1** and tripyrrane **2** under a similar condition was conducted (Scheme 2). As the result, a mixture of oligopyrrins **P6-P8** was observed by TLC analysis and the mass spectroscopy. Although, the complete isolation of the oligopyrrins was unsuccessful due to their similar chromatographic polarities, direct metallation of the mixed linear oligopyrrins with excess copper(II) acetate allowed us to isolate each of the corresponding copper(II) complexes (**Pn-Cu2**; $n = 6-8$) in the yields of 35%, 16%, and 35%, respectively. Along with the consistent HRMS results, the crystal structures of the copper(II) complexes exhibited that all the complexes possess two copper centers surrounded by pyrrolic nitrogens and carbonyl oxygen donor sites in the oligopyrrins (Fig. 4 and Figs. S32-S34, ESI).¹²



Scheme 2 Syntheses of bis-copper complexes of the oligopyrrins, **Pn-Cu2** ($n = 6-8$). Ar = pentafluorophenyl

In complex **P6-Cu2**, a helical coil type conformation was observed with a short Cu...Cu distance of 3.278(3) Å (Fig. 4a,

4b). This helical conformation was realized by that a bipyrrrole unit adopts a *syn*-configuration accompanied with the copper coordination. In contrast, complexes **P7-Cu2** and **P8-Cu2** involve *anti*-oriented bipyrrrole units, thus giving rise to “S-shape” open-spiral conformers (Fig. 4c-f).¹⁴ The structure of the supposed open-form of **P6-Cu2** is unfavorable by 20.1 kJ mol⁻¹ than the observed helical one as estimated by DFT calculations (Fig. S17, ESI).¹¹ It is noteworthy that the winding structures of hepta- and octapyrrolic systems (i.e., **P7-Cu2** and **P8-Cu2**) are different from those of all methine-bridged helical hepta- and octapyrrolic bis-Cu(II) complexes presumably due to the steric factors constrained by the bipyrrrole units.⁸

The coordination ability of **P8** in solution was also examined. The finding that an instant absorption spectral change of **P8** upon addition of Cu(OAc)₂ as well as the Job's plot analysis suggested the formation of a stable bis-copper(II) complex, **P8-Cu2** in solution as observed in the X-ray crystal structures (Figs. S21–23, ESI).

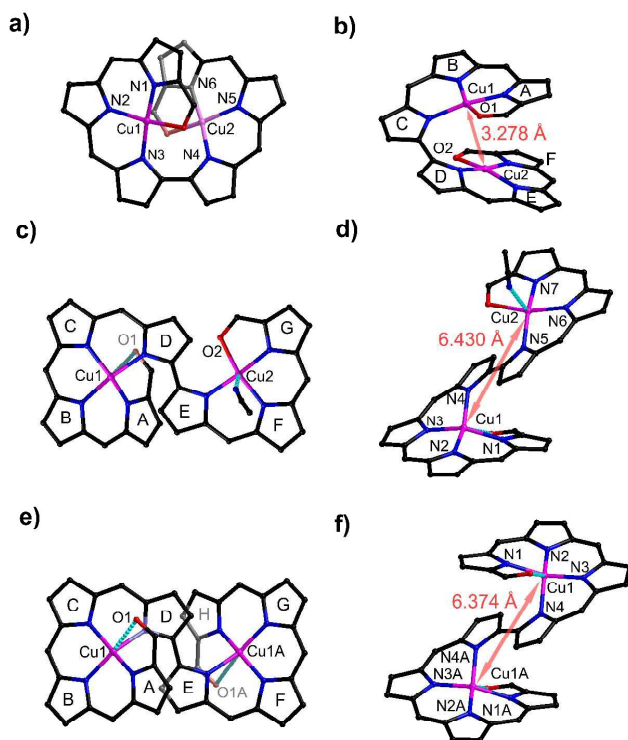


Fig. 4 Perspective and side views of the molecules of **P6-Cu2** (a, b), **P7-Cu2** (c, d), and **P8-Cu2** (e, f). Pentafluorophenyl groups, hydrogens attached to carbon atoms and co-crystallized solvent molecules are omitted for clarity.

The remarkably different geometry of **Pn-Cu2** can manifest to tune the magnetic coupling interactions between the d⁹-electron copper(II) centers. The electron paramagnetic resonance (EPR) spectra of the solid samples of **Pn-Cu2** recorded at 4 K showed broadened signals at $g_{\text{average}} \approx 2.06$ – 2.07 with faint Cu(II) hyperfine features (Fig. S29, ESI). The hyperfine lines may be weak and/or even concealed by the broad lines due to the delocalization of spin density from the Cu(II) centers to the π -conjugated scaffolds. Characteristic signal corresponding to the $\Delta M_S = \pm 2$ forbidden transition could be observed in the half-field

region, which indicates the presence of a magnetically isolated triplet state ($S = 1$). These features were also observed in the frozen CH₂Cl₂ solutions of **Pn-Cu2** (Fig. S30, ESI).

In order to further rationalize the magnetic behaviors of **Pn-Cu2**, the thermal profiles of χ_{mol} values were determined under 10 kOe using a SQUID susceptometer (Fig. 5). The $\chi_{\text{mol}}T$ value of the helical complex, **P6-Cu2** at 300 K was observed to be 0.72 cm³ K mol⁻¹, consistent with the theoretical value of 0.75 cm³ K mol⁻¹ estimated from two magnetically isolated $S = 1/2$ spin with $g = 2$. Upon cooling, the $\chi_{\text{mol}}T$ values were almost constant until 50 K and then steeply decreased to reach 0.01 cm³ K mol⁻¹ at 2 K. Fitting by the Bleaney-Bower equation,¹⁵ the intramolecular antiferromagnetic interaction constant between the two copper ions was estimated to be $J/k_B = -11.4$ K, which is indeed stronger than those of **P7-Cu2** and **P8-Cu2** ($J/k_B = -6.5$ and -4.3 K, respectively) (Table S3, ESI). Compared to the structures of bis-copper complexes reported by Osuka *et al.*,⁸ the antiferromagnetic coupling interactions are stronger in **P6-Cu2** surrounded by a shorter oligopyrrolics containing a bipyrrrole unit. In the intermolecular magnetic profiles, a cusp of χ_{mol} was only observed in the χ_{mol} vs T plot of **P6-Cu2** at 14 K, indicating the stronger intra- (*vide supra*) and/or intermolecular antiferromagnetic interaction with $\theta = -0.4$ K operated rather than **P7-Cu2** and **P8-Cu2** ($\theta \approx 0$). This might be interpreted by the spin density map of **P6-Cu2** (triplet; UB3LYP); more spin delocalized nature over the associated π -ligand could allow interacting intermolecularly respect to those of **P7-Cu2** and **P8-Cu2** (Fig. S31, ESI). On this basis, the shortest helical oligopyrrolic complex of **P6-Cu2** revealed the strongest intra- and intermolecular magnetic interactions through bond and/or space.

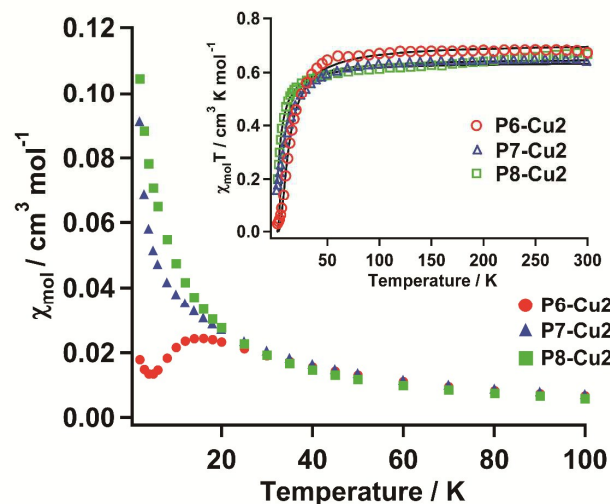


Fig. 5 The plots of $\chi_{\text{mol}}T$ for **Pn-Cu2** ($n = 6$ – 8) in the range of 2–100K; inset shows the $\chi_{\text{mol}}T$ - T plots for **Pn-Cu2** ($n = 6$ – 8) along with the fitting curves (black line).

In the UV-vis-NIR absorption spectra of **Pn-Cu2**, the characteristics for spiral π conjugative frameworks are evident (Fig. 3). The spectral features of **P7-Cu2** and **P8-Cu2** resemble to those of ligand **P8** (Fig. 3) due to the similar electronic structures. In contrast, the helical orientation of the conjugated π -backbone in **P6-Cu2** may intensify the transition of low energy NIR band. Consistent with the electrochemical analysis of the complexes,

Pn-Cu2 (Figs. S26–S28, ESI), the calculated HOMO-LUMO energy gaps become narrower upon increasing the number of pyrrolic units (Fig. S36, ESI). Therefore, smooth π -conjugations present in the copper complexes, **Pn-Cu2** demonstrate that further red-shift of NIR absorptions would be realized upon increasing the number of the π components.

In summary, we have developed a rational synthetic methodology for gram-scale preparation of long-chain oligopyrins (**P6–P8**) by simple oxidative homo- and hetero-coupling of monoacylated bilane (**1**) and/or tripyrrane (**2**). These oligopyrins can easily form bis-copper(II) complexes, adopting different conformations dependent upon the lengths of the chains, e.g., helix coil for **P6-Cu2** and S-shaped open-spiral for **P7-Cu2** and **P8-Cu2**, respectively. The helical complex **P6-Cu2** revealed the stronger intra- and intermolecular antiferromagnetic interactions than the rest of complexes. With this approach, further investigations on the structures and properties of other metal complexes supported by the linear π -conjugated oligopyrins synthesized are in progress in our laboratory.¹⁶

Acknowledgements

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† Electronic Supplementary Information (ESI) available: ¹H NMR, ¹³C NMR and HRMS spectra of intermediates and target products. See DOI: 10.1039/b000000x/

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- The oxidative coupling reaction of acylated tripyrrane, **2** resulted in the observation of the corresponding ESI-TOF mass signal at m/z 1495.0936 for the proposed hexapyrrane, **P6**. Unfortunately, the isolation of product **P6** was unsuccessful owing to the inherent instability on silica gel.
- All the calculations were achieved with Gaussian09 program package at the (U)B3LYP/6-31G* level.
- CCDC 1060306 (**P8**), 1060309 (**P6-Cu2**), 1060310 (**P7-Cu2**), 1060311 (**P8-Cu2**) and 1455046 (**P8-Zn2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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- Our repeated attempt on chiral separation of the complex was not successful under the given conditions in ESI. In this regard, we have carried out the stability test for the open spiral conformation of **P8** and **P8-Cu2** in solution (See; Figs. S19, 20 and 24, ESI).
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- A preliminary example of zinc(II) complex of **P8** (**P8-Zn2**) is given in ESI. See the supporting figures; Figs S5, S13, S18 and S35. These results indicate the oligopyrrin can form the similar open-spiral bis-metal complex, acting as a versatile cation receptor.