ARTICLE

DOI: 10.1038/s42004-018-0021-3

OPEN

Oligoacetylacetones as shapable carbon chains and their transformation to oligoimines for construction of metal-organic architectures

Mitsuharu Uesaka¹, Yuki Saito¹, Shota Yoshioka¹, Yuya Domoto², Makoto Fujita² & Yasuhide Inokuma ^{1,3}

Flexible chain-like molecules can adopt various conformations, but fabrication of complex and higher-order architectures by chain networking or coiling is still a difficult task in organic chemistry. As the degree of freedom increases, the large entropy loss impedes conformation and orientation fixing. Here we report oligo (3,3-dimethylpentane-2,4-dione)s as flexible and shapable carbon chains with many carbonyl groups for chemical modification. Polycarbonylated chains of various lengths are synthesized by terminal-selective silylation and oxidative coupling reactions using silver(I) oxide. We use reactions of 1,3-diketones and 1,4-diketones to reduce the chain length and to induce favourable conformations. When the chains are treated with hydrazine, all the carbonyl groups are converted to imine groups, resulting in the formation of multidentate ligands. Finally, a two-dimensional sheet-like structure and a cylindrical assembly are generated by respectively networking and coiling the carbon chains, with the aid of metal coordination.

¹Division of Applied Chemistry, Faculty of Engineering, Hokkaido University, Kita 13 Nishi 8 Kita-ku, Sapporo 060-8628, Japan. ²Department of Applied Chemistry, School of Engineering, The University of Tokyo, Bunkyo-ku, Tokyo 113-8656, Japan. ³Japan Science and Technology Agency PRESTO, Kawaguchi, Japan. Correspondence and requests for materials should be addressed to Y.I. (email: inokuma@eng.hokudai.ac.jp)

Ancient pottery vessels were made by coiling ropes of clay¹, and a similar method can be used for constructing large three-dimensional structures from flexible strings. Flexible carbon chains can similarly play a crucial role in the synthesis of various organic architectures in molecular science because they can adopt various conformations without giving rise to large strain energies.² Structurally flexible frameworks generated from flexible components have attracted attentions because they can change structures and properties in response to guest accommodation and other stimuli^{3–5}. In the construction of high-order structures with flexible chain components, the main difficulties come from the large entropy losses caused by fixation of conformations and orientations. Flexible carbon chains such as alkyl groups have therefore been embedded in large organic nanostructures and assemblies often merely as hinges, linkers, aggregation agents and solubilizing groups^{6–8}. Given recent developments in synthetic reactions using transition-metal-catalyzed functionalization of aliphatic compounds⁹, the inducement of various conformations, and the construction of two- and three-dimensional assemblies with flexible carbon chains (Fig. 1a) become more important for synthesis of a new class of structurally flexible organic architectures with various size and shape. This prompted us to design and synthesize flexible, yet shapable, carbon chains.

We focused on aliphatic polyketones as flexible scaffolds. Carbonyl group is one of the most well-studied functional groups in organic chemistry, and various conversions and interactions derived from the lone pair of oxygen atom and electrophilic carbon atom are known. Biological systems also use polyketone chains as a common precursor for the production of a wide range of secondary metabolites known as polyketides¹⁰. Natural polyketones, which consist of repeated 1,3-diketones, readily undergo intramolecular cyclization reactions through enolization to form stable six-membered rings, which often aromatize after dehydration (Fig. 1c)^{11, 12}. These characteristics have prevented the synthesis and isolation of long polyketone chains without the aid

of enzymes, except oligomers and polymers with repeating 1,4-diketone units^{13, 14}.

Here, we design a new polyketone sequence consisting of alternating 1,3-diketones and 1,4-diketones. These polyketones can be synthesized by oligomerization of an acetylacetone derivative, 3,3-dimethylpentane-2,4-dione (**1**) (Fig. 1b). Despite the dense arrangement of carbonyl groups on the chain, none of them are located at the sixth position from any of the α -carbons that become nucleophilic on enolization. The arrangement of carbonyl groups enables synthesis and isolation of polyketone chains of various lengths, up to tetracontane (C40) with 16 carbonyl groups, as stable all-*keto* forms. The 1,3-diketone and 1,4-diketone subunits can undergo various types of reaction, enabling modulation of the chain lengths and conformations. We also achieve construction of sheet-like and cylindrical assemblies of flexible and shapable carbon chains with the aid of metal ion coordination after the conversion of the carbonyl groups to imine groups.

Results

Synthesis of polyketone chains. Polyketone chains composed of alternating 1,3-diketone and 1,4-diketone subunits were prepared by enol silyl ether formation at the terminal carbonyl group and subsequent stepwise oxidative homo-coupling (Fig. 2). When acetylacetone **1** was treated with chlorotrimethylsilane (1.2 equiv) in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)¹⁵, enol trimethylsilyl ether **2** was obtained in 93% yield. Excellent selectivity for the mono-silylated product was only observed for DBU, and bis-silylation concomitantly occurred when other amines such as triethylamine were used as a base. Pure enol trimethylsilyl ether **2** can be prepared on a 150 g scale by vacuum distillation. We, therefore, optimized the oxidative coupling conditions using compound **2**.

For the oxidative coupling of silyl enol ether **2**, we examined suitable oxidants to prevent side reactions of unprotected

Fig. 1 Construction of large organic architectures using flexible polyketone chains. **a** Strategy for construction of various higher-order organic assemblies. After the conformations of the carbon chains are induced by ketone-related reactions and interactions, the chains are assembled with the aid of metal coordination and other intermolecular interactions. **b** Design of a flexible and isolable polyketone chain composed of a sequence of alternating 1,3-diketones and 1,4-diketones. **c** Natural-type sequence of polyketone chains. These readily undergo intramolecular cyclization through enolization

Fig. 2 Synthetic scheme for acetylacetone **1**-based polyketone chains. Enol trimethylsilyl ethers are formed at the terminal ketone of acetylacetone monomer and oligomers. The enol silyl ethers are then homo-coupled using silver(I) oxide

carbonyl groups in the substrate and the products. Among the oxidants reported for 1,4-diketone synthesis with enolate synthons, silver(I) oxide¹⁶ was found to mediate the homo-coupling reaction to give dimer **3** without forming major side products other than the desilylated product **1**. Reactions with other oxidants^{17–19} such as copper(II) triflate, ammonium cerium (IV) nitrate, and hypervalent iodine gave complicated mixtures including a small amount of dimer **3** (<10% yield), presumably because of reactions at the carbonyl groups. Aprotic polar reaction media were suitable for the silver(I) oxide-mediated coupling reaction, and dimer **3** was obtained in 70% yield in a mixture of dimethylsulphoxide/dimethyl sulphone. It is worth noting that desilylation of substrate **2** was the major reaction in nonpolar and protic solvents because of deceleration of the coupling reaction and acceleration of desilylation, respectively.

Silylation of acetylacetone dimer **3** occurred selectively at the terminal carbonyl groups under mild conditions. When dimer **3** was treated with chlorotrimethylsilane, triethylamine, and sodium iodide in acetonitrile at 0 °C²⁰, the terminal enol silyl ethers **4** and **5** were obtained in 42 and 26% yields, respectively, along with the recovery of unreacted **3** (16%). For silylation of acetylacetone oligomers, conditions using DBU were not suitable because complicated mixtures were obtained presumably due to intramolecular aldol reactions. Enol silyl ether **4** also underwent a silver(I) oxide-mediated homo-coupling reaction to give tetramer **6** in 47% yield. Similar terminal-selective silylation of tetramer **6** took place, furnishing the mono-silylated product **7** in 26% yield along with 41% of bis-silylated product. Although the ratio of terminal/internal carbonyl groups was 1:3, formation of enol silyl ethers of the internal carbonyl groups was not detected using ¹H nuclear magnetic resonance (NMR) spectroscopy. The coupling reaction using silver(I) oxide and compound **7** gave acetylacetone octamer **8**, bearing 16 carbonyl groups on the tetracontane (C40)

main chain, as a colourless solid in 17% yield after high-performance liquid chromatography (HPLC) separation.

Oligoacetylacetone chains **3–8** were obtained as single tautomers, which enabled full characterization of their pure forms. The high-resolution electrospray-ionization time-of-flight (ESI-TOF) mass spectrum showed the ion peak at $m/z = 1033.5496$, which is assignable to $[8 + \text{Na}]^+$ (calculated for $\text{C}_{56}\text{H}_{82}\text{O}_{16}\text{Na}$ m/z 1033.5495). The ¹H NMR spectrum of octamer **8** in CDCl₃, showed the terminal acetyl proton signal at 2.15 p.p.m. as a singlet, but no signal was observed in the olefinic region at 4.0–7.0 p.p.m. This clearly shows that enolization is effectively suppressed by two methyl substituents in the 1,3-diketone subunits, even for octamer **8**, which still has 16 carbonyl groups and 34 α -CH protons. Other polyketone chains **3** and **6** were also detected as all-*keto* forms, on the basis of their NMR spectra. These polyketone chains are thermally stable at least up to 120 °C and did not undergo intramolecular aldol cyclization in solution under neutral conditions. On heating in the solid state, compounds **3**, **6**, and **8** melted at 78, 94, and 119 °C, respectively, without any decomposition. It should be emphasized that the two main problems in handling long polyketone chains, namely enolization and intramolecular cyclization, can be avoided by using an oligoacetylacetone sequence.

Length and conformation changes of chains. Single-crystal X-ray diffraction analysis revealed that the acetylacetone-based chains adopt unique conformations caused by interactions at carbonyl groups in the solid state. In particular, the main carbon chain conformations vary widely according to the torsion angles of the 1,4-diketone subunits. The central ethylene unit of dimer **3** adopts a *gauche* conformation with a torsion angle of 68.8°, making the decane (C10) main chain twisted (Fig. 3b). A similar

Fig. 3 Modulation of chain length and favourable conformations of flexible carbon chains. **a** Synthetic schemes for the chemoselective conversion of 1,3- and 1,4-diketone subunits. **b** X-ray crystal structure of dimer **3**. **c** X-ray crystal structure of tetramer **6**. **d** X-ray crystal structure of 2,5-furylene-bridged chain **9**. **e** X-ray crystal structure of compound **10**. **f** X-ray crystal structure of isopyrazole dimer **11**. **g** X-ray crystal structure of octamine chain **12**. All the thermal ellipsoids are drawn at the 50% probability level

tendency is observed in the crystal structure of tetramer **6**, in which two terminal 1,4-diketone subunits adopt *gauche* conformations (Fig. 3c). Only the central ethylene unit adopts a sterically favoured anti-periplanar conformation, therefore the icosane (C_{20}) main chain of compound **6** is folded into an S-shape. In addition to hydrogen bonding interactions in the crystal packing, dipole-dipole and $n-\pi^*$ interactions^{21, 22} are known to govern the conformation of the 1,4-diketone structure. These weak but favourable interactions in the diketone units are useful for inducing complex conformations of flexible chains.

The alternating 1,3-diketone and 1,4-diketone sequence is convenient for adjusting the lengths and conformations of the flexible polyketone chains through chemoselective reactions (Fig. 3a). When a toluene solution of tetraketone **3** was refluxed in the presence of p -toluenesulfonic acid (p -TsOH), the ethylene proton signals of **3** disappeared and a new aromatic peak appeared at 6.14 p.p.m. in the 1H NMR spectrum. Single-crystal X-ray analysis confirmed the formation of a planar 2,5-furylene bridge, which connects two dimethylmethylenes subunits with a distance of 4.87 Å (Fig. 3d). The distance is ~ 1 Å shorter than that in 1,4-diketone **3** (5.81 Å), resulting in a decrease in the chain length. The two terminal acetyl groups are located in parallel, and the decane (C_{10}) carbon chain takes a U-shape.

The acid-catalyzed Paal-Knorr type furan synthesis²³ is also applicable to tetramer **6**. Under the same conditions, all the 1,4-diketone units were converted to furan rings to give compound **10** in 76% yield. Single-crystal X-ray analysis showed that compound **10** had an S-shaped conformation, as in the corresponding octaketone **6**, but **10** was clearly smaller than **6** (Fig. 3e). The chain length was shortened by *ca.* 20% by formation of three furan rings in the chain (Supplementary Table 1). It is also worth noting that similar Paal-Knorr type reactions with poly(1,4-diketone)s often leave isolated ketones between two generated aromatic rings²⁴. The alternating 1,3- and 1,4-diketone system favours full conversion of 1,4-diketone subunits to aromatic rings via Paal-Knorr synthesis²⁵ in high yields, keeping only the terminal acetyl groups intact.

On treatment with hydrazine²⁶, the 1,3-diketone units of polyketone chains **3** and **6** were converted to isopyrazole rings to furnish polyimine chains **11** and **12** in 89 and 80% yields, respectively. Considering that eight imine bonds formed during the reaction with tetramer **6**, each reaction at the carbonyl group proceeded in more than 97% yield. The X-ray crystal structures of **11** and **12** show that the steric conformations of the ethylene bridges are all anti-periplanar, making the carbon chains straight, as is often observed in the most stable conformations of unsubstituted alkanes (Fig. 3f, g). All the isopyrazole rings in

11 and **12** are located roughly on the same plane. The distance between the two terminal carbon atoms in **12** was increased to 2.3 nm, as compared with that of 1.0 nm in S-shaped octaketone **6**. Octamine **12** was hygroscopic and crystallized with seven water molecules per chain molecule. The water molecules form clusters that are hydrogen bonded to the nitrogen atoms on compound **12** (Supplementary Fig. 5). As a result, carbon chains **12** are networked each other in the crystal by multiple hydrogen bonds. These multiple interactions on the nitrogen atoms are promising of not only for inducing conformations, but also producing assemblies of flexible carbon chains using hydrogen bonds and coordination bonds.

Assemblies of flexible carbon chains. Once we had achieved the length adjustment and the induction of various conformations of flexible carbon chains, we investigated methods for assembling large organic architectures using metal complexation²⁷. When tetraimine chain **11** was combined with zinc(II) tetrafluoroborate hexahydrate in methanol, colourless crystals were formed. Elemental analysis indicated a ligand **11** to metal ratio of 2:1. The crystals were almost insoluble in common organic solvents such as chloroform and diethyl ether. Single-crystal X-ray diffraction analysis showed a two-dimensional coordination polymer in which each zinc(II) ion has tetrahedral geometry and binds to four ligands **11** at the terminal imine nitrogen atoms. Because the internal imine nitrogen atoms remain uncoordinated, ligand **11** adopts almost the same linear conformation as that of its pure crystal (Figs. 4a and 3f).

In the crystal packing structure, the two-dimensional grids are stacked along the *b* axis to form infinite one-dimensional

channels, in which counter anions and solvent molecules were observed (Fig. 4c and Supplementary Fig. 8). On removal of solvent molecules under vacuum, the crystallinity was lost, reflecting the flexibility of the framework components. Two of the four ligand molecules **11** around a zinc centre are located close to each other with a terminal C...C distance of 3.98 and 4.01 Å. If we focus on the closest chains, the decane (C10) main chains of ligand **11** are one-dimensionally aligned to take wave-like orientations (Fig. 4d). This pre-organization could enable formation of a two-dimensional sheet covalent carbon network by generating terminal C–C bonds between the nearest terminal carbon atoms. These results clearly show the possibility of construction of elaborate carbon frameworks by assembling flexible, conformation-induced carbon chains.

To assemble a large, discrete architecture by coiling poly (acetylacetonate)-based chains, we examined coordination assembly of octamine chain **12** with a metal oxide cluster²⁸. Treatment with nickel(II) nitrate hexahydrate in chloroform/ethanol caused broadening of peaks in the ¹H NMR spectrum of compound **12** because of coordination of paramagnetic nickel(II) ions. After the solution had been allowed to stand at room temperature for 1 d, purple crystals, formulated as [Ni₄(**12**)₂(OH)₂(NO₃)₆•4H₂O•(solvents)], were formed in 55% yield. The ESI-TOF mass spectrum indicated cation peaks attributable to a nickel tetranuclear complex [Ni₄(**12**)₂(OH)₂(NO₃)₄]²⁺ at *m/z* = 748.1988 (calculated for [C₅₆H₈₆N₁₆Ni₄O₂]²⁺ *m/z* 748.1995) as a result of dissociation of hydrated water molecules and nitrate ions. The crystal structure shows that a pair of crystallographically equivalent ligands **12** twined around a hydroxo-bridged tetranuclear nickel cluster (Fig. 5 and Supplementary Fig. 10).

Fig. 4 Two-dimensional assembly of tetraimine chain **11**. **a** ORTEP diagram of coordination polymer [Zn(**11**)₂(BF₄)₂]_n around the zinc(II) centre with thermal ellipsoids at the 50% probability level. Zn, N, and C atoms are coloured in magenta, light blue, and grey, respectively. **b** Structural formula of coordination polymer [Zn(**11**)₂(BF₄)₂]_n. **c** two-dimensional sheet-like coordination network structure viewed along the *b* axis. The sequence of the closest carbon chains to **11** is highlighted in green. **d** Orientation of the closest carbon chains **11** highlighted in **c** viewed along the (1 0 -1) direction. Counter ions and solvent molecules are omitted for clarity

Fig. 5 Cylindrical assembly of coiled octamine chain **12**. **a** Structural formula of nickel complex $[\text{Ni}_4(\mathbf{12})_2(\text{OH})_2(\text{NO}_3)_6 \cdot 4(\text{H}_2\text{O})]$. **b** The conformation of the twined carbon chain ligand **12** in the nickel complex. The icosane (C_{20}) main carbon chain of the upper ligand is highlighted in orange. Solvent molecules and counter ions are omitted for clarity

Four nickel(II) ions are coordinated by two bridging hydroxo ligands, four aqua ligands and two imine ligands **12** to form a hexacationic complex. Each ligand **12** serves as a bidentate ligand for three of four nickel ions in an octahedral coordination geometry. The terminal imine nitrogen atoms of ligand **12** do not coordinate to a nickel ion, but they act as hydrogen-bond acceptors for hydrated water molecules on a nickel ion. The torsion angles of ethylene bridges in the icosane (C_{20}) main chain of ligand **12** vary from 54.9 to 90.0° . The carbon chain of ligand **12** is therefore considerably curved, and adopts a horseshoe-like conformation. Two horseshoe-shaped ligands are closely twined around the nickel cluster, and the icosane (C_{20}) main chains were arranged in a cylindrical assembly (Fig. 5b). It should be emphasized that the flexibility of, and multiple interaction sites on, the carbon chain enabled the cylindrical assembly of coiled carbon chains, as in the case of pottery made from clay ropes.

Discussion

We have achieved the synthesis, chain length modulation, conformation induction, and formation of assemblies of flexible carbon chains based on oligo(acetylacetonate)s. The alternate repetition of 1,3-diketone and 1,4-diketone subunits is the key to the suppression of intramolecular cyclization and to efficient functionalization of chains to induce various conformations. The terminal-selective silylation and subsequent homo-coupling reaction using silver(I) oxide provided a reliable method for obtaining long polyketone chains up to a tetracontane (C_{40}) bearing 16 ketones. Although many carbonyl groups neighbour each other, the 1,3-diketone and 1,4-diketone positions are independently converted to furan and isopyrazole rings in high yields, leading to the formation of shorter chains and multi-dentate polyimine ligands, respectively. Polyketone and polyimine chains combine structural flexibility and multiple interaction sites, therefore they can be suitable framework components for various types of complex carbon architectures. While generation of further huge and elaborate structures and investigation of their properties are next challenges, our approach using shapable carbon chains provided a new route to construct structurally flexible assemblies. Furthermore, given that many carbonyl or imine groups and α -carbons are embedded in the main carbon chains, our results promise fixation of the induced conformations by forming C–C covalent bonds.

Methods

Experimental data and procedures. For the experimental procedure, HPLC chromatogram, ^1H and ^{13}C NMR, high-resolution ESI-TOF mass spectra, infrared

spectroscopy and elemental analysis data, detailed crystallographic data, and chain lengths data, see [Supplementary Methods](#), Supplementary Figs. 1–10 and Supplementary Table 1.

Data availability. The X-ray crystallographic coordinates for the structures of compounds **3**, **6**, **9**, **10**, **11**, **12**, $[\text{Zn}(\mathbf{11})_2(\text{BF}_4)_2(\text{MeOH})_2\text{H}_2\text{O}]_n$ and $[\text{Ni}_4(\mathbf{12})_2(\text{OH})_2(\text{NO}_3)_6(\text{H}_2\text{O})_4]$ are available as Supplementary Data 1–8, respectively. These data have also been deposited at Cambridge Crystallographic Data Centre (CCDC), under deposition numbers CCDC1587959, CCDC1587960, CCDC1587961, CCDC1587962, CCDC1587963, CCDC1587964, CCDC1587965, and CCDC1587966, respectively. These data can be obtained free of charge from the CCDC via http://www.ccdc.cam.ac.uk/data_request/cif. All other data are available from the authors upon reasonable request.

Received: 11 December 2017 Accepted: 9 March 2018

Published online: 19 April 2018

References

- Blandino, B. Coiled Pottery: Traditional and Contemporary Ways (Krause Publications, Iowa, Wis; USA, 2004).
- Dobson, C. M. Protein folding and misfolding. *Nature* **426**, 884–890 (2003).
- Schneemann, A. et al. Flexible metal-organic frameworks. *Chem. Soc. Rev.* **43**, 6062–6096 (2014).
- Lin, Z.-J., Lü, J., Hong, M. & Cao, R. Metal-organic frameworks based on flexible ligands (FL-MOFs): structures and applications. *Chem. Soc. Rev.* **43**, 5867–5895 (2014).
- Beves, J. E. et al. Strategies and tactics for the metal-directed synthesis of rotaxanes, knots, catenanes, and higher order links. *Angew. Chem. Int. Ed.* **50**, 9260–9327 (2011).
- Lu, F. & Nakanishi, T. Alkyl- π engineering in state control toward versatile optoelectronic soft materials. *Sci. Technol. Adv. Mater.* **16**, 1–20 (2015).
- Lei, T., Wang, J.-Y. & Pei, J. Roles of flexible chains in organic semiconducting materials. *Chem. Mater.* **26**, 594–603 (2014).
- Babu, S. S., Praveen, V. K. & Ajayaghosh, A. Functional π -gelatros and their applications. *Chem. Rev.* **114**, 1973–2129 (2014).
- Girard, S. A., Knauber, T. & Li, C.-J. The cross-dehydrogenative coupling of C_{sp^3} –H bonds: a versatile strategy for C–C bond formations. *Angew. Chem. Int. Ed.* **53**, 74–100 (2014).
- Hertweck, C. The biosynthetic logic of polyketide diversity. *Angew. Chem. Int. Ed.* **48**, 4688–4716 (2009).
- Witte, P. J. & Harris, T. M. Synthesis of β -hexa, β -hepta, and β -octaketones. *J. Am. Chem. Soc.* **95**, 6865–6867 (1973).
- Gilbreath, S. G., Harris, C. M. & Harris, T. M. Biomimetic synthesis of preteramides. 1. Synthesis of preteramide by tandem extension of a polyketide chain. *J. Am. Chem. Soc.* **110**, 6172–6179 (1988).
- Alder, R. W., Hyland, N. P., Jeffery, J. C., Riis-Johannessen, T. & Riley, D. J. Poly(1,1-bis(dialkylamino)propan-1,3-diyl)s; conformationally-controlled oligomers bearing electroactive groups. *Org. Biomol. Chem.* **7**, 2704–2715 (2009).
- Drent, E. & Budzelaar, P. H. M. Palladium-catalyzed alternating copolymerization of alkenes and carbon monoxide. *Chem. Rev.* **96**, 663–681 (1996).

15. Taniguchi, Y., Inanaga, J. & Yamaguchi, M. Use of 1,8-diazabicyclo[5.4.0]undec-7-ene in preparation of trimethylsilyl enol ethers and trimethylsilylacetylenes. *Bull. Chem. Soc. Jpn* **54**, 3229–3230 (1981).
16. Ito, Y., Konoike, T. & Saegusa, T. Synthesis of 1,4-diketones by the reaction of silyl enol ether with silver oxide. Regiospecific formation of silver(I) enolate intermediates. *J. Am. Chem. Soc.* **97**, 649–651 (1975).
17. Kobayashi, Y., Taguchi, T., Morikawa, T., Tokuno, E. & Sekiguchi, S. Studies on organic fluorine compounds. XXXI. Oxidative coupling of ketone enolates and trimethylsilyl enol ethers by means of $\text{Cu}(\text{OTf})_2$. *Chem. Pharm. Bull.* **28**, 262–267 (1980).
18. Clift, M. D., Taylor, C. N. & Thomson, R. J. Oxidative carbon-carbon bond formation via silyl bis-enol ethers: controlled cross-coupling for the synthesis of quaternary centers. *Org. Lett.* **9**, 4667–4669 (2007).
19. Zhdankin, V. V. et al. Carbon-carbon bond formation in reactions of $\text{PhIO}\cdot\text{HBF}_4$ /silyl enol ether adduct with alkenes or silyl enol ethers. *J. Org. Chem.* **54**, 2605–2608 (1989).
20. Cazeau, P., Duboudin, F., Moulines, F., Babot, O. & Dunogues, J. A new practical synthesis of silyl enol ethers. Part. I. From simple aldehydes and ketones. *Tetrahedron* **43**, 2075–2088 (1987).
21. Kamer, K. J., Choudhary, A. & Raines, R. T. Intimate interactions with carbonyl groups: dipole–dipole or $n\rightarrow\pi^*$? *J. Org. Chem.* **78**, 2099–2103 (2012).
22. Newberry, R. W. & Raines, R. T. The $n\rightarrow\pi^*$ interaction. *Acc. Chem. Res.* **50**, 1838–1846 (2017).
23. Amarnath, V. & Amarnath, K. Intermediates in the Paal–Knorr synthesis of furans. *J. Org. Chem.* **60**, 301–307 (1995).
24. Zhang, Y., Broekhuis, A. A. & Picchioni, F. Thermally self-healing polymeric materials: the next step to recycling thermoset polymers? *Macromolecules* **42**, 1906–1912 (2009).
25. Cafeo, G., Kohnke, F. H., La Torre, G. L., White, A. J. P. & Williams, D. J. From large furan-based calixarenes to calixpyrroles and calix[n]furan[m] pyrroles: synthesis and structures. *Angew. Chem. Int. Ed.* **39**, 1496–1498 (2000).
26. Cafeo, G. et al. From calixfurans to heterocyclophanes containing isopyrazole units. *Tetrahedron* **60**, 1895–1902 (2004).
27. Furukawa, H., Cordova, K. E., O’Keeffe, M. & Yaghi, O. M. The chemistry and applications of metal-organic frameworks. *Science* **341**, 1230444–1230456 (2013).
28. King, P., Clérac, R., Wernsdorfer, W., Anson, C. E. & Powell, A. K. Synthesis and magnetism of oxygen-bridged tetranuclear defect dicubane $\text{Co}(\text{II})$ and $\text{Ni}(\text{II})$ clusters. *Dalton Trans.* **33**, 2670–2676 (2004).

Acknowledgements

This work was supported by Grant-in-Aid for Young Scientists (A) (No. 17H04872), Grant-in-Aid for Research Activity Start-Up (No. 16H06592), for Scientific Research on Innovative Areas (Coordination Asymmetry) (No. 17H05347) from MEXT, by JST-PRESTO, and by the Asahi Glass Foundation. We thank Mr. Ryota Kotani, Dr. Takayuki Tanaka, and Prof. Atsuhiko Osuka for providing X-ray diffraction data for compound **10**.

Author contributions

Y.I. designed the project, analyzed the experimental data and wrote the paper. M.U., Y.S., and S.Y. performed the experiments and analyzed the data. Y.D. and M.F. supported the synthesis and X-ray crystallographic analysis of compounds **3** and **6**.

Additional information

Supplementary information accompanies this paper at <https://doi.org/10.1038/s42004-018-0021-3>.

Competing interests: The authors declare no competing interests.

Reprints and permission information is available online at <http://npg.nature.com/reprintsandpermissions/>

Publisher’s note: Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made. The images or other third party material in this article are included in the article’s Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this license, visit <http://creativecommons.org/licenses/by/4.0/>.

© The Author(s) 2018