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Engineering Functionalization in a Supramolecular Polymer: Hierarchical Self-Organization of Triply Orthogonal Non-covalent Interactions on a Supramolecular Coordination Complex Platform

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Supporting Information

ABSTRACT: Here we present a method for the construction of functionalizable supramolecular polymers by controlling three orthogonal interactions within a single system: (i) coordination-driven self-assembly; (ii) H-bonding; and (iii) host−guest interactions between crown ether and dialkylammonium substrates. Three unique molecules constitute the supramolecular construct, including a 2-ureido-4-pyrimidinone (UPy)-functionalized rigid dipyridyl donor and a complementary organoplatinum(II) acceptor decorated with a crown ether moiety that provide the basis for self-assembly and polymerization. The final host−guest interaction is demonstrated by using one of two dialkylammonium molecules containing fluorophores that bind to the benzo-21-crown-7 (B21C7) groups of the acceptors, providing a spectroscopic handle to evaluate the functionalization. An initial coordination-driven self-assembly yields hexagonal metallacycles with alternating UPy and B21C7 groups at their vertices. The assembly does not interfere with H-bonding between the UPy groups, which link the discrete metallacycles into a supramolecular network, leaving the B21C7 groups free for functionalization via host−guest chemistry. The resultant network results in a cavity-cored metallogel at high concentrations or upon solvent swelling. The light-emitting properties of the dialkylammonium substrates were transferred to the network upon host−guest binding. This method is compatible with any dialkylammonium substrate that does not disrupt coordination nor H-bonding, and thus, the unification of these three orthogonal interactions represents a simple yet highly efficient strategy to obtain supramolecular polymeric materials with desirable functionality.

Self-assembly is a simple and efficient strategy for building large, complex molecular architectures. It is a key process in all living organisms, wherein biomolecules such as nucleic acids, polypeptides, and phospholipids interact and self-organize to form well-defined structures with emergent functions.[1] Inspired by nature's elegant self-assembly processes, chemists exploit a range of non-covalent interactions to construct supramolecular assemblies. When non-covalent interactions are used as the basis for polymerization, so-called supramolecular polymers are obtained. These materials often share characteristics of conventional covalent polymers yet may also exhibit properties originating from their non-covalent interactions, including dynamic behaviors and high degrees of internal order.[2] As a result of these unique features, supramolecular polymers are applicable as self-healing materials, as optoelectronic materials, and in biomedical science.[2,3] The functions of supramolecular polymers are generally dependent on the nature of the non-covalent interactions and the building blocks that are employed in their preparations. The construction of supramolecular polymers with well-defined functionalities is challenging because of the difficulties associated with the synthesis of functionalized precursors and potential interference with the self-assembly process by these moieties.

In the past two decades, coordination-driven self-assembly, i.e., the spontaneous formation of metal−ligand bonds between Lewis acidic acceptors (metals) and Lewis basic donors (organic ligands) to form metallacycles and metallacages, has proven to be a powerful methodology for constructing discrete supramolecular ensembles with predesigned, well-defined sizes and shapes.[4] Covalent attachment of functional moieties to the precursor building blocks allows the formation of assemblies in which their number and orientation can be readily tuned. As such, various functional moieties have been installed either on the periphery or at the vertices of a number of discrete supramolecular assemblies. The latter have already proven useful in a wide range of applications, including selective encapsulation,[5] chemosensing,[6] optical and electronic materials,[7] and so on.[8] Since the formation of metal−ligand bonds can occur in concert with other non-covalent interactions, supramolecular polymer systems that mimic the hierarchical ordering observed in natural systems can be designed using supramolecular coordination complex scaffolds.[9] For example, the unification of coordination-driven self-assembly with hydrogen bonding leads to the formation of robust and flexible metallacycle-cored supramolecular polymer gels.[9a]

The use of multiple orthogonal interactions to build supramolecular systems offers advantages over conventional strategies that utilize only one type of non-covalent interaction, as much more complex architectures may be obtained.[3d] Whereas many examples of dual orthogonal interactions have been developed, superstructures formed from three orthogonal interactions that do not interfere with one another are rare. In

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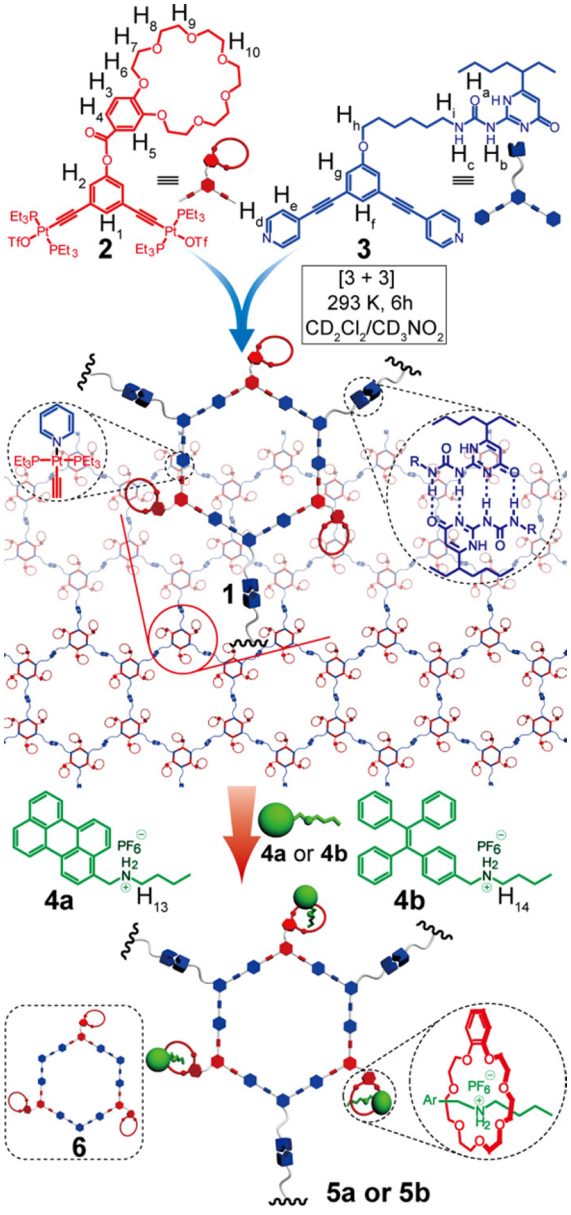
this work, we exploited the hierarchical unification of coordination-driven self-assembly, hydrogen bonding, and crown ether-based host–guest interactions to obtain the functionalizable supramolecular polymeric network **1** (Scheme 1). Specifically, a well-established Pt(II)–pyridine motif was used to assemble a metallahexagon bearing two different functional moieties: a 2-ureido-4-pyrimidinone (UPy) group and a benzo-21-crown-7 (B21C7) motif. The complementary hydrogen-bonding interactions of the UPy groups[10] result in the formation of a hexagon-cored supramolecular polymer network with free B21C7 moieties. Further functionalization can be efficiently achieved via crown ether–dialkylammonium salt-based host–guest interactions. The postfunctionalization process is not expected to disrupt the structure of the supramolecular network because of the orthogonality of the non-covalent interactions employed. In addition, the cross-linked supramolecular polymer was found to form gels at high concentrations or upon swelling in appropriate solvents, demonstrating that novel functional soft materials may be obtained by means of the strategy developed here.

Scheme 1. Cartoon Representation of the Formation and Functionalization of a Cross-Linked 3D Supramolecular Polymeric Network from Hierarchical Self-Assembly of 2, 3, and 4 via Triply Orthogonal Non-covalent Interactions



Supramolecular polymer network **1** was obtained by stirring a mixture of 120° B21C7-tethered acceptor **2** and UPy-decorated 120° donor **3** in 1:1 stoichiometry in CD_2Cl_2/CD_3NO_2 (1:1 v/v) for 6 h (Scheme 1). Multinuclear (^1H and ^{31}P) NMR spectroscopy (Figure 1) supported the formation of hexagonal metallacyclic cores within the network. In the ^1H NMR spectrum, signals corresponding to protons $H_{d,e}$ of the pyridyl rings in **1** (Figure 1b) displayed downfield shifts relative to those of free donor **3** (Figure 1c) due to the loss of electron density that occurs upon Pt(II)–N coordination. Likewise, the $^{31}P\{^1H\}$ NMR spectrum of the product revealed a sharp singlet at 14.28 ppm with concomitant ^{195}Pt satellites (Figure 1e), consistent with a single phosphorus environment. This peak was shifted upfield by 7.64 ppm relative to that of **2** (Figure 1d). Electrospray ionization time-of-flight mass spectrometry (ESI-TOF-MS) provided further evidence for the formation of hexagonal metallacycles as the repeating units of the polymer network. The mass spectrum of the product in dimethyl sulfoxide (DMSO), a solvent that disrupts hydrogen bonding between the UPy groups,[10] showed an isotopically resolved peak consistent with an intact and discrete [3 + 3] assembly with a +5 charge state that results from the loss of trifluoromethanesulfonate (OTf) counterions (Figure 1f).

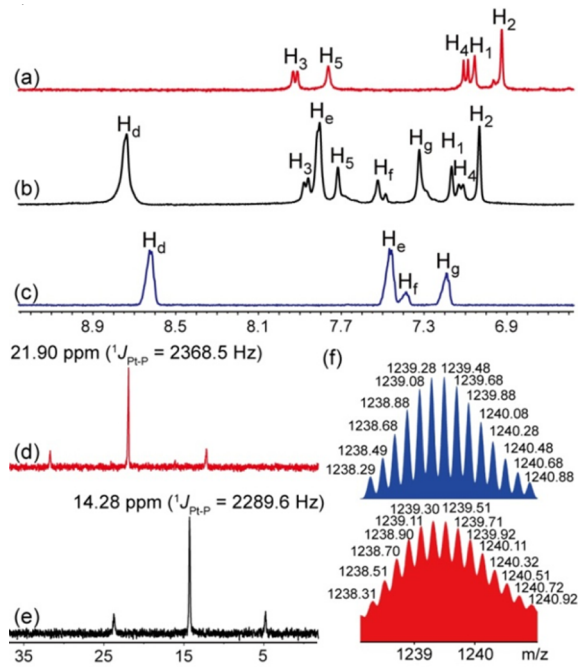


Figure 1. Partial (a–c) ^1H and (d, e) $^{31}P\{^1H\}$ NMR spectra [CD_2Cl_2/CD_3NO_2 (1:1 v/v), 298 K] of (a, d) acceptor **2**, (b, e) supramolecular network **1**, and (c) donor **3**. (f) Experimental (red) and calculated (blue) ESI-TOF-MS spectra of discrete metallacycles $[M - 5OTf]^{5+}$.

The formation of a supramolecular network upon dimerization of the UPy groups was supported by ^1H NMR spectroscopy: the N–H signals H_{a-c} from the UPy groups displayed large downfield shifts (observed between 10.0 and 13.5 ppm) and lower intensities in CD_2Cl_2/CD_3NO_2 (1:1 v/v) relative to those in DMSO-d_6 (Figure S17), providing evidence for the formation

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of hydrogen bonds.[10] Dynamic light scattering (DLS) experiments were used to determine the size distribution profile of the polymeric material. The average hydrodynamic diameter of **1** was found to be 82.3 nm at a concentration of 10.0 mM (based on the hexagonal units), whereas hexagon **6** without UPy groups (Schemes 1 and S6) showed an average hydrodynamic diameter of 7.7 nm under the same conditions (Figure 2a), suggesting that

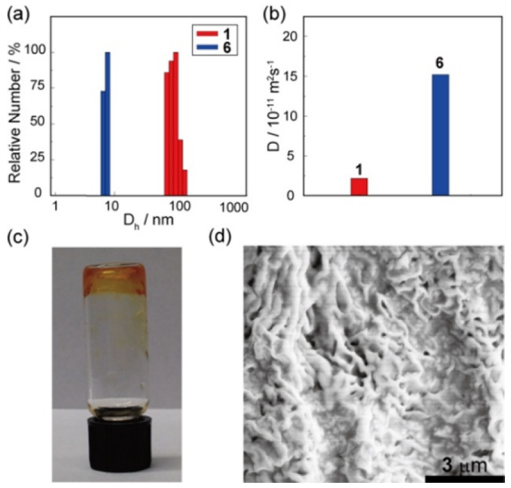

Figure 2. (a) Size distributions of network **1** (red) and crown ether-functionalized hexagon **6** (blue) in CH_3NO_2 at 10.0 mM by DLS. (b) Diffusion coefficient (D) values [500 MHz, CD_2Cl_2/CD_3NO_2 (1:1 v/v), 298 K] for **1** (red) and **6** (blue) at 10.0 mM. (c) Photograph of the metallogel formed by **1**. (d) SEM image of the xerogel of **1** prepared by a freeze-drying method.

UPy is responsible for aggregation. Furthermore, diffusion-ordered ^{1}H NMR spectroscopy (DOSY) was used to probe the dimensions of the supramolecular aggregates, as the diffusion coefficient obtained in a DOSY study is inversely proportional to the size of the supramolecular polymer.[11] DOSY of **1** was performed using a 10 mM solution (based on the hexagonal units) in CD_2Cl_2/CD_3NO_2 (1:1 v/v) and yielded an average diffusion coefficient of 0.21×10^{-10} m^2·s^{-1} (Figures 2b and S19). The average diffusion coefficient of discrete hexagon **6** under the same conditions was 1.57×10^{-10} m^2·s^{-1} (Figures 2b and S18). The decrease in diffusion coefficient due to the introduction of UPy groups supports the formation of a polymeric network. In addition, network **1** forms a gel-like soft material at high concentrations or upon solvent swelling (Figures 2c and S29). The gel self-heals in situ as a result of the synergistic effect of H-bonding and metal−ligand coordination (Figure S28). Scanning electron microscopy (SEM) was employed to examine the morphology of the xerogel, which was prepared by a freeze-drying method. An extended and interconnected fibrous network was observed (Figure 2d). The critical gel concentration was determined to be 25.0 mM UPy units at 4 °C. The observation of such a phenomenon further supports the formation of an extended hexagonal network.

The B21C7 units within the polymer network provide a further platform for introducing a third non-covalent interaction, in this case crown ether−dialkylammonium complexation, resulting in a functionalized network. Perylene-decorated dialkylammonium salt **4a** and tetraphenylethylene (TPE)-decorated dialkylammonium salt **4b** were introduced to network **1** to obtain light-emitting supramolecular polymers. The complexation behavior was studied using ^{1}H NMR spectroscopy. In both cases, the addition of the dialkylammonium salt to a solution of the network resulted in a complicated spectrum (Figure 3b,d). The slow-exchange nature of the host−guest

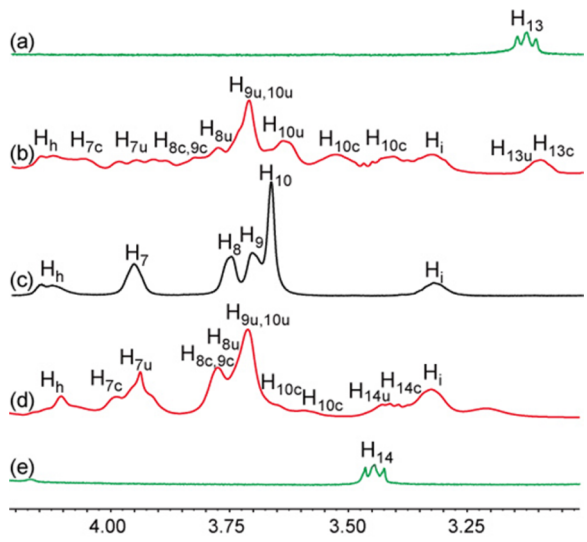

Figure 3. Partial ^{1}H NMR spectra [400 MHz, CD_2Cl_2/CD_3NO_2 (1:1 v/v), 298 K] of (a) dialkylammonium salt **4a**, (b) functionalized network **5a**, (c) network **1**, (d) functionalized network **5b**, and (e) dialkylammonium salt **4b**. The labels "c" and "u" denote complexed and uncomplexed moieties, respectively.

complexation on the ^{1}H NMR time scale resulted in a splitting of the proton resonances of the B21C7 groups and those of the dialkylammonium salts into two sets of signals, corresponding to the complexed and uncomplexed species.[12] Signals for the ethylenoxy protons H_{7-9} displayed downfield chemical shifts, whereas those for the methylene protons $H_{13,14}$ and the ethylenoxy protons H_{10} shifted upfield. These changes suggest that host−guest complexation between B21C7 and dialkylammonium salts exists in the network, allowing the construction of a functional network by postfunctionalization. In addition, as suggested by ^{1}H NMR studies, reversible functionalization of the network can be achieved by the addition and removal of K^+ (Figures S22−S27).

As both **4a** and **4b** are fluorophores, the light-emitting properties of the functionalized networks **5a** and **5b** were studied. The emission maximum and fluorescence intensity of **5a** exhibited a slight red shift and decrease, respectively, relative to those of free **4a** (Figure 4a), which is attributed to perturbations of the electronic structure by the host−guest interactions, as evidenced by the fluorescence spectra of acceptor **2** and hexagon **6** with **4a** (Figure S21). TPE-based dialkylammonium salt **4b** is a fluorophore that has aggregation-induced emission characteristics.[13] As such, it is not emissive in a dilute solution but is highly emissive in the solid state (Figure 4b, blue). Complexation of **4b** with **1** does not inhibit the free rotation of the phenyl groups in solution, and no obvious fluorescence enhancement was observed after complexation. In the solid state, **5b** displayed an emission maximum at 450 nm (Figure 4b, red), which was blue-shifted by 10 nm relative to that of free **4b** (Figure 4b, blue). In a gel of **5a**, the emission maximum was further blue-shifted to 438 nm (Figure 4b, black). This difference is attributed to a decrease in the planarization of the TPE moieties, wherein the phenyl moieties in the polymeric network become more twisted relative to those in the uncomplexed state.[14] These results indicate that

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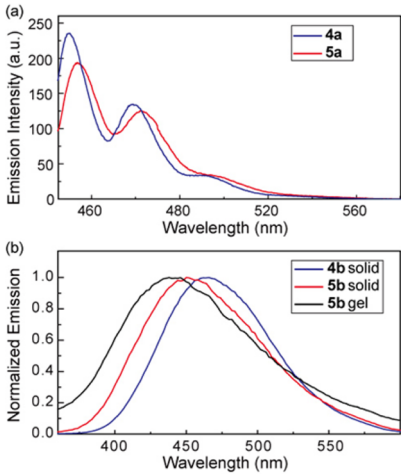

Figure 4. Fluorescence emission spectra: (a) **4a** (blue) and **5a** (red) in CH_2Cl_2 (λ_{ex} = 441 nm, c = 30.0 μM based on the perylene-decorated dialkylammonium salt unit); (b) **4b** in the solid state (blue), **5b** in the solid state (red), and **5b** in a gel (black) (λ_{ex} = 343 nm).

the photophysical properties of the dialkylammonium substrate are largely preserved after incorporation of the substrate into the supramolecular network via host–guest interactions.

In summary, by the combination of metal–ligand coordination, hydrogen bonding, and host–guest interactions in a hierarchical fashion, a method for building functionalizable supramolecular polymers has been established. The noncovalent functionalization strategy used here offers advantages over covalent methods for obtaining functionalized polymers in that the self-assembly reduces the number of steps, resulting in a fast and facile synthesis. Furthermore, the final functionalization step is highly modular, and as long as the substrate is competent for host–guest chemistry and does not interfere with the coordination or hydrogen bonding, the functionalization may occur. As demonstrated with emissive substrates, the properties of the functional groups are retained upon introduction of the substrate into the supramolecular network without interference from the underlying polymeric structure. In addition, conditions may be found such that these polymers form gels for applications in which soft materials are desirable. Thus, this work provides a simple yet highly efficient strategy to obtain modular functional materials. Further investigations aimed at expanding the functionality of such networks, with an emphasis on exploring the scope of substrates that may participate in the final host–guest interaction, are underway.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b12986.

Experimental details and additional data (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Whitty, A. *Nat. Chem. Biol.* **2008**, *4*, 435. (b) Branden, C.; Tooze, J. *Introduction to Protein Structure*; Garland: New York, 1999.

(2) (a) Aida, T.; Meijer, E. W.; Stupp, S. I. *Science* **2012**, *335*, 813. (b) Yang, L.; Tan, X.; Wang, Z.; Zhang, X. *Chem. Rev.* **2015**, *115*, 7196. (c) Wang, F.; Han, C.; He, C.; Zhou, Q.; Zhang, J.; Wang, C.; Li, N.; Huang, F. *J. Am. Chem. Soc.* **2008**, *130*, 11254. (d) Zhang, Z.; Luo, Y.; Chen, J.; Dong, S.; Yu, Y.; Ma, Z.; Huang, F. *Angew. Chem., Int. Ed.* **2011**, *50*, 1397. (e) Li, Q.; Zhang, W.; Miljanić, O. Š.; Sue, C.-H.; Zhao, Y.-L.; Liu, L.; Knobler, C. B.; Stoddart, J. F.; Yaghi, O. M. *Science* **2009**, *325*, 855.

(3) (a) Xu, J.-F.; Chen, Y.-Z.; Wu, D.; Wu, L.-Z.; Tung, C.-H.; Yang, Q.-Z. *Angew. Chem., Int. Ed.* **2013**, *52*, 9738. (b) De Greef, T. F. A.; Smulders, M. M. J.; Wolffs, M.; Schenning, A. P. H. J.; Sijbesma, R. P.; Meijer, E. W. *Chem. Rev.* **2009**, *109*, 5687. (c) Whittell, G. R.; Hager, M. D.; Schubert, U. S.; Manners, I. *Nat. Mater.* **2011**, *10*, 176. (d) Wei, P.; Yan, X.; Huang, F. *Chem. Soc. Rev.* **2015**, *44*, 815. (e) Niu, Z.; Huang, F.; Gibson, H. W. *J. Am. Chem. Soc.* **2011**, *133*, 2836.

(4) (a) Cook, T. R.; Stang, P. J. *Chem. Rev.* **2015**, *115*, 7001. (b) Harris, K.; Fujita, D.; Fujita, M. *Chem. Commun.* **2013**, *49*, 6703. (c) Brown, C. J.; Toste, F. D.; Bergman, R. G.; Raymond, K. N. *Chem. Rev.* **2015**, *115*, 3012. (d) Oliveri, C. G.; Ulmann, P. A.; Wiester, M. J.; Mirkin, C. A. *Acc. Chem. Res.* **2008**, *41*, 1618. (e) De, S.; Mahata, K.; Schmittel, M. *Chem. Soc. Rev.* **2010**, *39*, 1555. (f) Newkome, G. R.; Moorefield, C. N. *Chem. Soc. Rev.* **2015**, *44*, 3954. (g) Han, M.; Engelhard, D. M.; Clever, G. H. *Chem. Soc. Rev.* **2014**, *43*, 1848. (h) Stang, P. J.; Olenyuk, B. *Acc. Chem. Res.* **1997**, *30*, 502. (i) Chakrabarty, R.; Mukherjee, P. S.; Stang, P. J. *Chem. Rev.* **2011**, *111*, 6810. (j) Cook, T. R.; Zheng, Y.-R.; Stang, P. J. *Chem. Rev.* **2013**, *113*, 734. (k) Mukherjee, P. S.; Mukherjee, S. *Chem. Commun.* **2014**, *50*, 2239.

(5) (a) Inokuma, Y.; Kawano, M.; Fujita, M. *Nat. Chem.* **2011**, *3*, 349. (b) Roy, B.; Ghosh, A. K.; Srivastava, S.; D'Silva, P.; Mukherjee, P. S. *J. Am. Chem. Soc.* **2015**, *137*, 11916.

(6) (a) Shanmugaraju, S.; Mukherjee, P. S. *Chem. - Eur. J.* **2015**, *21*, 6656. (b) Yan, X.; Wang, H.; Hauke, C. E.; Cook, T. R.; Wang, M.; Saha, M. L.; Zhou, Z.; Zhang, M.; Li, X.; Huang, F.; Stang, P. J. *J. Am. Chem. Soc.* **2015**, *137*, 15276.

(7) (a) Yamashina, M.; Sartin, M. M.; Sei, Y.; Akita, M.; Takeuchi, S.; Tahara, T.; Yoshizawa, M. *J. Am. Chem. Soc.* **2015**, *137*, 9266. (b) Yan, X.; Cook, T. R.; Wang, P.; Huang, F.; Stang, P. J. *Nat. Chem.* **2015**, *7*, 342.

(8) (a) McConnell, A. J.; Wood, C. S.; Neelakandan, P. P.; Nitschke, J. R. *Chem. Rev.* **2015**, *115*, 7729. (b) Xu, L.; Wang, Y.-X.; Chen, L.-J.; Yang, H.-B. *Chem. Soc. Rev.* **2015**, *44*, 2148.

(9) (a) Yan, X.; Li, S.; Pollock, J. B.; Cook, T. R.; Chen, J.; Zhang, Y.; Ji, X.; Yu, Y.; Huang, F.; Stang, P. J. *Proc. Natl. Acad. Sci. U. S. A.* **2013**, *110*, 15585. (b) Li, Z.-Y.; Zhang, Y.; Zhang, C.-W.; Chen, L.-J.; Wang, C.; Tan, H.; Yu, Y.; Li, X.; Yang, H.-B. *J. Am. Chem. Soc.* **2014**, *136*, 8577. (c) Foster, J. A.; Parker, R. M.; Belenguer, A. M.; Kishi, N.; Sutton, S.; Abell, C.; Nitschke, J. R. *J. Am. Chem. Soc.* **2015**, *137*, 9722. (d) Yan, X.; Xu, J.-F.; Cook, T. R.; Huang, F.; Yang, Q.-Z.; Tung, C.-H.; Stang, P. J. *Proc. Natl. Acad. Sci. U. S. A.* **2014**, *111*, 8717. (e) Zhukhovitskiy, A. V.; Zhong, M.; Keeler, E. G.; Michaelis, V. K.; Sun, J. E. P.; Hore, M. J. A.; Pochan, D. J.; Griffin, R. G.; Willard, A. P.; Johnson, J. A. *Nat. Chem.* **2016**, *8*, 33.

(10) Beijer, F. H.; Sijbesma, R. P.; Kooijman, H.; Spek, A. L.; Meijer, E. W. *J. Am. Chem. Soc.* **1998**, *120*, 6761.

(11) Liu, Y.; Wang, Z.; Zhang, X. *Chem. Soc. Rev.* **2012**, *41*, 5922.

(12) (a) Zhang, C.; Li, S.; Zhang, J.; Zhu, K.; Li, N.; Huang, F. *Org. Lett.* **2007**, *9*, 5553. (b) Zhang, M.; Xu, D.; Yan, X.; Chen, J.; Dong, S.; Zheng, B.; Huang, F. *Angew. Chem., Int. Ed.* **2012**, *51*, 7011.

(13) Mei, J.; Leung, N. L. C.; Kwok, R. T. K.; Lam, J. W. Y.; Tang, B. Z. *Chem. Rev.* **2015**, *115*, 11718.

(14) Parrott, E. P. J.; Tan, N. Y.; Hu, R.; Zeitler, J. A.; Tang, B. Z.; Pickwell-MacPherson, E. *Mater. Horiz.* **2014**, *1*, 251.

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