Fabrication of Neutral Supramolecular Polymeric Films *via* Post-electropolymerization of Discrete Metallacycles

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Self-assembly post-modification has proven to be an efficient strategy to build higher-order supramolecular architectures and functional materials. In this study, we successfully realized the construction of a new family of neutral supramolecular polymeric films containing well-defined metallacycles as the main scaffolds through combination of coordination-driven self-assembly with post-electropolymerization. The obtained neutral polymeric materials were fully characterized by the cyclic voltammogram (CV), SEM, and TEM. The thickness of the films was able to be well regulated by the number of scanning cycles. Moreover, we found that the shape of the metallacycles and the number of triphenylamine moieties played important roles in the formation of the final polymer films. We believe that the introduction of the neutral metallacycles into the final polymer structures not only enriches the library of supramolecular polymeric films but also provides a new platform to study neutral molecule detection, separation, and capture.

Keywords coordination-driven self-assembly, post-electropolymerization, neutral metallacycle, triphenylamine, supramolecular polymeric films

Introduction

Coordination-driven self-assembly has evolved to be a powerful bottom-up approach to construct discrete supramolecular architectures with well-defined shapes and sizes including two-dimensional (2-D) polygons and three-dimensional (3-D) polyhedra.¹ These discrete metallosupramolecular architectures are of particular interest not only because of their aesthetically pleasing structures but also due to their wide applications in many areas such as host-guest chemistry, catalysis, bioengineering, etc.² Notably, inspired by the fact that biological systems in nature frequently employ self-assembly postmodification strategy to tune the structures and functionalities of biological scaffolds³, recent research effort has been devoted to construction of functionalized metallosupramolecular complexes by employing self-assembly post-modification strategy⁴. Generally, post-modification of discrete metallacycles or metallacages can be obtained through combining supramolecular self-assembly with facile covalent reaction or polymerization. For example, Nitschke et al. have successfully employed imine exchange reaction to realize multistep transformation of their metallacages guided by the Hammett equation.⁵ Moreover, we have also previously reported the construction of smart supramolecular polymeric hydrogels via self-assembly post-polymerization of discrete organoplatinum(II) metallacycles.⁶ However, it is still very challenging to realize the construction of well-controlled polymeric films though post-modification of discrete supramolecular architectures due to the lack of suitable organometallic scaffolds with proper covalent reaction sites.

Scheme 1 Dimerization of Triphenylamine (TPA) through

Electrochemical Oxidation.

$$2 \operatorname{Ph}_{3} \operatorname{N} \xrightarrow{-2 \operatorname{e}^{-}}_{-2 \operatorname{H}^{+}} \xrightarrow{\operatorname{Ph}}_{\operatorname{Ph}} \xrightarrow{\operatorname{Ph}}_{\operatorname{Ph}} \xrightarrow{\operatorname{Ph}}_{\operatorname{Ph}}$$

As an electrochemically active moiety, triphenylamine (TPA) has proven to be dimerized to form tetraphenylbenzidine (TPB) through electrochemical oxidation (scheme 1).⁷ Thus, TPA derivatives have been successfully employed as a handle for electropolymerization to form ordered films such as conjugated donor-acceptor polymer films.⁸ Previously, we reported the fabrication of a series of well structurally defined polymeric films from TPA functionalized metallacycles by means of post-electropolymerization.⁹ However, the obtained polymeric films contained multiple positive charges around the pore channel due to the formation of nitrogen-to-metal coordination bonds in metallacycles skeleton, thus limiting their further application in detection or capture of neutral molecules. The construction of new polymeric film with neutral metallacycles as main scaffold through postpolymerization has not been explored yet. It should be noted that there is another established way to construct metallacycles based on oxygen-to-platinum coordination-driven self-assembly that resulted in the formation of neutral supramolecular assemblies. Compared to the charged metallacycles, neutral metallacycles have proven to have higher solubility in organic solvents and exhibit better encapsulation ability for neutral organic guests.¹⁰ Thus, we envision that self-assembly post-electropolymerization of neutral metallacycles may lead to the generation of a new family of neutral polymeric film and pro-

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vide a better understanding of the influence to electropolymerization caused by the structural factors.

Herein, we designed and synthesized a new 120° TPA substituted dicarboxylate donor ligand and the complementary 120° TPA functionalized di-Pt(II) acceptor building blocks, from which two novel neutral multi-TPA functionalized 2-D metallacycles with different shape and size were successfully obtained *via* the formation of oxygen-to-platinum coordination bonds. Subsequent post-electropolymerization of those two neutral multi-TPA containing metallacycles allowed for fabrication of a new type of neutral polymeric film with well-controlled cavity sizes and thickness, which may have potential application in neutral molecule detection, separation, and capture.

Experimental Section

All reagents were analytical purity and used without further purification. L1 was synthesized according to the literature procedures.⁹ Metallacycles M1 and M2 were dissolved in CD_2Cl_2 for ¹H and ³¹P{¹H} NMR analysis.

Preparation of Hexagon M1.

To a mixture of L1 (29.26 mg, 0.021 mmol) and L2 (10.00 mg, 0.021 mmol) in a 10 dram vial, the mixture solvents (3.0 mL) of acetone and H₂O (v/v, 5/1) was added. Then the mixture was stirred at 50 °C for 8 h. After being cooled down to room temperature, acetone was removed by nitrogen gas flow. The suspension was then centrifuged. The precipitate was washed with distilled water for three times and then dried under vacuum at room temperature to afford hexagon M1 as a white solid (33.0 mg, 93%). ¹H NMR (400 MHz, CD₂Cl₂): δ 8.36 (s, 1H), 8.07 (s, 2H), 7.32 – 7.27 (m, 4H), 7.21 (t, *J* = 7.4 Hz, 8H), 7.01 (dd, *J* = 17.5, 8.8 Hz, 15H), 6.91 (d, *J* = 7.7 Hz, 4H), 1.87 (d, *J* = 3.1 Hz, 24H), 1.18 – 1.11 (m, 36H). ³¹P NMR (162 MHz, CD₂Cl₂): δ 18.75 (s, ¹*J*_{Pt-P} = 2522.34 Hz).

Preparation of Rhomboid M2.

To a mixture of L2 (10.00 mg, 0.021 mmol) and 12 (24.41 mg, 0.021 mmol) in a 10 dram vial, the mixture solvents (2.4 mL) of acetone and H₂O (v/v, 5/1) was added. Then the mixture was stirred at 50 °C for 8 h. After being cooled down to the room temperature, acetone was removed by nitrogen gas flow. The suspension was then

centrifuged. The precipitate was then washed with the distilled water for three times and dried under vacuum at room temperature to afford rhomboid **M2** as a white solid (29.3 mg, 95%). ¹H NMR (400 MHz, CD₂Cl₂): δ 8.72 (s, 2H), 8.60 (s, 1H), 8.26 (d, *J* = 1.4 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.46 (s, 2H), 7.42 (d, *J* = 8.5 Hz, 4H), 7.31 (t, *J* = 7.9 Hz, 4H), 7.13 (d, *J* = 7.6 Hz, 4H), 7.09 (t, *J* = 7.4 Hz, 2H), 7.02 (d, *J* = 8.6 Hz, 2H), 1.56 (dd, *J* = 7.2, 3.6 Hz, 24H), 1.22 – 1.16 (m, 36H). ³¹P NMR (162 MHz, CD₂Cl₂): δ 16.96 (s, ¹*J*_{Pt-P} = 2885.22 Hz).

General Procedure for Post-Electropolymerization

Post-electropolymerization of the neutral metallacycles **M1** or **M2** (0.2 mM) was carried out by taking cyclic voltammetric method ($+0.4 \sim +1.5$ V) in CH₂Cl₂ with *n*-Bu₄NPF₆ (0.1 M) as the supporting electrolyte. Cyclic voltammograms of the polymers were obtained on a Pt working electrode with a Pt wire as the counter electrode and an Ag/AgCl (saturated) electrode as the reference electrode.

Results and discussion

Scheme 2 Synthetic Route of 120° TPA Donor L2.



According to the "directional bonding" model and the "symmetry interaction" model¹¹, the ligands that incorporate a 120° angle between the active coordination sites can interact with the suitable complementary ditopic molecular modules to yield molecular rhomboids or hexagons. Thus, 120° TPA functionalized

Scheme 3 Graphical Representation of Self-assembly of Neutral Metallacycles M1 and M2.



di-Pt(II) acceptors building block L1 and 120° TPA substituted dicarboxylate donor ligand L2 were designed and synthesized. For instance, L2 was readily synthesized by several steps of a Pd-catalyzed Sonogashira coupling reaction in high yield as shown in Schemes 2. All the new compounds were characterized by multiple nuclear NMR spectroscopies (${}^{1}H$, ${}^{31}P$ { ${}^{1}H$ }, and ${}^{13}C$) (Figs. S1-S12). With these TPA decorated building blocks in hand, the construction of neutral TPA modified metallacycles were then carried out. The hexagonal metallacycle M1 was selected as a representative to illustrate the formation process. Stirring a mixture of L1 and L2 in an exact stoichiometric ratio (1:1) in acetone/H₂O (v/v, 5/1) mixed solvent at 50 °C for 8 h led to the formation of hexagon M1 without the need for further purification. Similarly, selfassembly of L2 assembled with an equimolar amount of 12 resulted in the formation of rhomboid M2 in almost quantitative yield.

The formation of the discrete, neutral macrocyclic structures with high symmetry was further evidenced by ¹H and ³¹P $\{^{1}H\}$ NMR spectroscopy (Figs. 1, 2, and S6-S12). For example, the ${}^{31}P{}^{1}H{}$ NMR spectrum of hexagon M1 (Fig. 1b) presented a sharp singlet (ca. 16.96 ppm) shifted towards upfield compared with the starting platinum acceptor L1 (Fig. 1a) by approximately 2.10 ppm due to the electron back-donation from the platinum atoms. Moreover, in the ¹H NMR spectrum of **M1** (Figs. 2b and S7), all signals of protons of L1 (Figs. 2c) exhibited nearly unchanged. While the protons that corresponded to L2 (Figs. 2a) showed significantly downfield shifts, which is consistent with the coordination of oxygen atoms to platinum centers. For instance, the signals of H₁ and H₂ protons of L2 shifted towards downfield by 0.23 and 0.18 ppm, respectively. Multinuclear NMR (¹H and ${}^{31}P{}^{1}H{}$ analysis of M2 (Figs. S9-S12) displayed very similar sharp and order characteristics to M1. For example, as shown in the Fig. S10, all signals of protons of L2 shifted towards downfield ($\Delta\delta[H_1] = 0.40$ ppm; $\Delta \delta[H_2] = 0.76$ ppm) due to the loss of electron density upon coordination of the oxygen atom with platinum metal centers. The peaks assigned to H_a and H_b protons of ligand 12 shifted considerably into the upfield region by 0.24 ppm and 0.18 ppm, respectively, associating with This article is protected by copyright. All rights reserved.

the increase of electron density. The sharp NMR (1 H and ${}^{31}P{{}^{1}H}$) signals along with the good solubility strongly demonstrated that a set of discrete, highly symmetric metallacycles were assembled rather than the random linear supramolecular polymers.



Fig. 1 The ³¹P NMR spectra (162 MHz, CD₂Cl₂, 298 K) of (a) ligand **L1** and (b) metallacycle **M1**.



Fig. 2 Partial ¹H NMR spectra (400 MHz, in CD₂Cl₂, 298 K) of (a) donor **L2**, and (b) metallacycle **M1**, (c) acceptor **L1**.

With the considerable efforts, the single crystal of rhomboid M2 was obtained by slow diffusion of ether into a solution of M2 (10.0 mM) in dichloromethane at ambient temperature for two weeks. The crystal structure of M2 (Fig. 3) clearly demonstrated the successful [2+2] self-assembly of L2 and 12 with a rhombic structure. In the crystal structure of M2, the coordinated angle of L2 is about 123°, which was extremely close to the ideal value 120°. The distance of TPA units is approximately 3.4 nm. Interestingly, as shown in Fig. 3b, the side view of the crystal displayed an "S" shape with four PEt₃ groups being perpendicular to the plane of the metallacy-cle.

All attempts to characterize the neutral metallacycles M1 and M2 by using ESI-MS or MALDI-TOF-MS have so far proven unsuccessful which might be caused by the labile interaction of platinum-oxygen coordination as well as the relatively large molecular weight of both metallacycles. Notably, the X-ray crystallographic analysis of rhomboid M2 clearly demonstrated the existence of neutral rhomboidal metallacycle. In addition, according to the "directional bonding" model and the "symmetry interaction" model^{6a,d,j,k,p}, the combination of two complementary ditopic building blocks A^2 and X^2 , each incorporating 120° angels between their coordination sites, allows for the formation of hexagonal structures of type $A^{2}_{3}X^{2}_{3}$. It should be noted that it is not possible to form polygons with an odd number of sides (i.e. triangle, pentagon, heptagon, etc.) by combining 120° donors with 120° acceptors since they would require the direct connection of either two acceptor or two donor moieties. The successful formation of neutral dendritic hexagons via oxygen-to-platinum coordination has been realized previously through the similar strategy^{10d}. Thus the sharp ¹H NMP signals as well as the singularity of each ³¹P NMR signal ensures that only [3+3] hexagon M1 was formed in this study.



Fig. 3 The X-ray crystal structures of macrocycle M2 (a) top view, (b) side view. A molecule of dichloromethane is encapsulated.

All above-mentioned data strongly indicated that the neutral metallacycles decorated with different numbered TPA moieties can be easily prepared through the formation of Pt-O bonds *via* coordination-driven self-assembly. This strategy avoided the time-consuming procedures and lower yields often encountered in covalent synthetic protocols. More importantly, the presence of the regular cavity core with different shape and size offered the possibility of the formation of well-controlled porous structures.

With the aim to obtain neutral polymeric film, the subsequent cyclic voltammetry (CV) electropolymerization of these two neutral multi-TPA metallacycles M1 and M2 was performed in a dichloromethane solution containing 0.1 M *n*-Bu₄NClO₄ as the supporting electrolyte at a \sim 7.0 mm² Pt disk electrode. As shown in Fig. 4a and Fig. 4c, the CV of M1 and M2 with the repeatedly scanning the potential from +0.4 to +1.5 V vs Ag/AgCl for 15 cycles was performed. The anodic/catholic peak current ratios of $i_a/i_c \approx 1$ was observed due to the one electron oxidation of the TPA groups. In addition, during CV experiment, the gradual increase of current indicated that the electropolymerization of M1 or M2 proceeded smoothly and successfully,^{8a} resulting in the deposition of macroscopic polymer films on the electrode surface. The mechanism of TPA polymerization is believed to possess a highly unstable monocation radical intermediate.^{8c,d} Both peak potential shifts along with the emergence of a new shoulder redox peak was attributed to the $N^{0/+}$ process of the newly generated tetraphenylbenzidine unit as a result of the oxidative coupling between the diphenylaminegroups of M1 or M2.



Fig. 4 Electropolymerization of M1 (a) and M2 (c) (0.2 mM in CH_2Cl_2) at a Pt disc electrode (d = 2 mm). Film thickness vs scan cycles for M1 (b) and M2 (d).

Furthermore, the thickness of films was estimated by scanning electronic microscopy (SEM) images. Intriguingly, the thickness of poly-**M1** (Figs. 4b, S13) or poly-**M2** (Figs. 4d, S14) were increased steadily as the number of scan increased. This finding indicated that the thickness of the obtained film could be readily regulated. For example, the poly-**M1** films with different thickness such as 15, 30, 50, 70 nm were achieved with 1, 2, 4, 6 scan cycles, respectively. By this means, a series of neutral polymeric films with certain thickness could be easily prepared.

With the aim to probe the film morphology, the electropolymerization of neutral metallacycles M1 and M2 was successfully performed on indium tin oxide (ITO) glass electrode to prepare poly-M1 and poly-M2 films in situ. Scanning electronic microscopy (SEM) and transmission electron microscopy (TEM) are highly reliable tools to provide evidence for the morphology of the films. The SEM analysis of poly-M1/ITO (Fig. 5a) as well as poly-M2/ITO (Fig. 5e) indicated that the poly-M1 and poly-M2 films were adhered tightly to the ITO substrate. Apparently, the morphology of poly-M1 films was much more smooth and compact than poly-M2 film. Notably, as shown in the TEM, poly-M1 film (Figs. 5c and 5d) displayed a sheet like morphology rather than linear fiber as poly-M2 film (Figs. 5g and 5h). Actually, the results of SEM and TEM of poly-M1 and poly-M2 films were consistent with structures of neutral metallacycles M1 and M2 as linear and 120° orientation of TPA moieties, respectively. This finding indicated that the structural effect of the metallacycle played an important role in the formation of the final polymeric film materials.

Conclusions

In summary, we designed and synthesized a new series of TPA substituted dicarboxylate donor and complementary 120° TPA functionalized di-Pt(II) acceptor building blocks. Through the formation of Pt–O bonds *via* coordination-driven self-assembly, the successful fabricatation of neutral multi-TPA functionalized metallacycles with different shape and size were obtained. The This article is protected by copyright. All rights reserved.

synthetic methodology is rather straightforward with high-yield as well as without further purification process. More importantly, the neutral polymeric films containing the uncharged metallacycles were successfully prepared *via* post-electropolymerization. The further investigation revealed that thickness of the obtained polymer films was readily controlled by the number of scan cycles. Moreover, the poly-M1 exhibited well-defined and compact polymeric sheet-like film instead of fiber-like morphology of the poly-M2. To the best of our knowledge, this study provides the first successful example of neutral polymeric films containing the well-defined metallacycles as the main scaffolds through post-electropolymerization. The investigation on the future application of these neutral polymeric films like the selective molecular transformation is undergoing in our lab.



Fig. 5 Side view (a) and top view (b) of representative SEM pictures of poly-**M1**/ITO film. TEM micrographs of thin film fragment at low magnification (c) and the enlarged area (d). Side view (e) and top view (f) of representative SEM pictures of poly-**M2**/ITO film. TEM micrographs of thin film fragment at low magnification (g) and the enlarged area (h).

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References

- (a) Cook, T. R.; Stang, P. J. Chem. Rev. 2015, 115, 7001; (b) Fujita, M.; Tominaga, M.; Hori, A.; Therrien, B. Acc. Chem. Res. 2005, 38, 369; (c) Fiedler, D.; Leung, D. H.; Bergman, R. G.; Raymond, K. N. Acc. Chem. Res. 2005, 38, 349; (d) Smulders, M. M. J.; Riddell, I. A.; Browne, C.; Nitschke, J. R. Chem. Soc. Rev. 2013, 42, 1728; (e) Spokoyny, A. M.; Kim, D.; Sumrein, A.; Mirkin, C. A. Chem. Soc. Rev. 2009, 38, 1218; (f) Han, M.; Engelhard, D. M.; Clever, G. H. Chem. Soc. Rev. 2014, 43, 1848; (g) Chen, L.-J.; Yang, H.-B.; Shionoya, M. Chem. Soc. Rev. 2017, 46, 2555; (h) Li, H.; Yao, Z.; Liu, D.; Jin, G. Coord. Chem. Rev. 2015, 293-294, 139; (i) Lescop, C. Acc. Chem. Res. 2017, 50, 885; (j) Xu, L.; Wang, Y.-X.; Chen, L.-J.; Yang, H.-B. Chem. Soc. Rev. 2015, 44, 2148; (k) Wang, W.; Wang, Y.-X.; Yang, H.-B. Chem. Soc. Rev. 2016, 45, 2656. (1) Lu, Y.; Deng, Y.-X.; Lin, Y.-J.; Han, Y.-F.; Weng, L.-H.; Li, Z.-H.; Jin, G.-X. Chem. 2017, 3, 110; (m) Zhang, L.; Lin, L.; Liu, D.; Lin, Y.-J.; Li, Z.-H.; Jin, G.-X. J. Am. Chem. Soc. 2017, 139, 1653; (n) Huang, S.-L.; Hor, T. S. A.; Jin, G.-X. Coord. Chem. Rev. 2017, 333, 1; (o) Han, Y.-F.; Jin, G.-X. Acc. Chem. Res. 2014, 47, 3571; (p) Chakrabarty, R.; Mukherjee, P. S.; Stang, P. J. Chem. Rev. 2011, 111, 6810.
- 2 (a) Cullen, W.; Misuraca, M. C.; Hunter, C. A.; Williams, N. H.; Ward, M. D. Nat. Chem. 2016, 8, 231; (b) Jiang, B.; Zhang, J.; Ma, J.; Zheng, W.; Chen, L.-J.; Sun, B.; Li, C.; Hu, B.; Tan, H.; Li, X.; Yang, H.-B. J. Am. Chem. Soc. 2016, 138, 738; (c) Chen, L.-J.; Ren, Y.-Y.; Wu, N.-W.; Sun, B.; Ma, J.-Q.; Zhang, L.; Tan, H.; Liu, M.; Li, X.; Yang, H.-B. J. Am. Chem. Soc. 2015, 137, 11725; (d) Chen, L.-J.; Jiang, B.; Yang, H.-B. Org. Chem. Front. 2016, 3, 579; (e) Zhang, C.-W.; Ou, B.; Yin, G.-Q.; Chen, L.-J.; Yang, H.-B. Acta. Polymerica. Sinica. 2017, 71; (f) Zhang, C.-W.; Chen, L.-J.; Yang, H.-B. Chin. J. Chem. 2015, 33, 319; (g) He, M.; Han, O.; He, J.; Li, O.; Abliz, Z.; Tan, H.; Xu, L.; Yang, H. Chin. J. Chem., 2013, 31, 663; (h) Oldacre, A. N.; Friedman, A. E.; Cook, T. R. J. Am. Chem. Soc. 2017, 139, 1424; (i) Yan, X.; Cook, T. R.; Wang, P.; Huang, F.; Stang, P. J. Nature Chem. 2015, 7, 342; (j) Yu, G.; Cook, T. R.; Li, Y.; Yan, X.; Wu, D.; Shao, L.; Shen, J.; Tang, G.; Huang, F.; Chen, X.; Stang, P. J. Proc. Nat. Acad. Sci. U.S.A 2016, 113, 13720; (k) Zhou, J.; Yu, G.; Huang, F. Chem. Soc. Rev. 2017, DOI: 10.1039/c6cs00898d; (1) Jiang, B.; Chen, L.-J.; Zhang, Y.; Tan, H.-W.; Xu, L.; Yang, H.-B. Chin. Chem. Lett. 2016, 27, 607; (m) Ou-Yang, J.-K.; Chen, L.-J.; Xu, L.; Wang, C.-H.; Yang, H.-B., Chin. Chem. Lett. 2013, 24, 471.
- 3 (a) Dawson, P. E.; Muir, T. W.; Clark-Lewis, I.; Kent, S. B. Science 1994, 266, 776; (b) Hang, H. C.; Bertozzi, C. R. Bioorg. Med. Chem. 2005, 13, 5021; (c) Blanco-Canosa, J. B.; Dawson, P. E. Angew. Chem., Int. Ed. 2008, 47, 6851; (d) Yang, X.-J.; Seto, E. Mol. Cell 2008, 31, 449; (e) Agard, N. J.; Bertozzi, C. R. Acc. Chem. Res. 2009, 42, 788; (f) Khan,

S.; Sur, S.; Dankers, P.; Stupp, S. I. *Bioconjugate. Chem.* **2014**, 25, 707.

- 4 (a) Sun, S.-S.; Anspach, J. A.; Lees, A. J. Inorg. Chem. 2002, 41, 1862; (b) Sun, S.-S.; Stern, C. L.; Nguyen, S.-B. T.; Hupp, J. T. J. Am. Chem. Soc. 2004, 126, 6314; (c) Heo, J.; Jeon, Y.-M.; Mirkin, C. A. J. Am. Chem. Soc. 2007, 129, 7712; (d) Zhao, L.; Northrop, B. H.; Stang, P. J. J. Am. Chem. Soc. 2008, 130, 11886; (e) Campbell, V. E.; de, H. X.; Delsuc, N.; Kauffmann, B.; Huc, I.; Nitschke, J. R. Nat. Chem. 2010, 2, 684; (f) Wang, M.; Lan, W.-J.; Zheng, Y.-R.; Cook, T. R.; White, H. S.; Stang, P. J. J. Am. Chem. Soc. 2011, 133, 10752; (g) Zheng, Y.-R.; Lan, W.-J.; Wang, M.; Cook, T. R.; Stang, P. J. J. Am. Chem. Soc. 2011, 133, 17045; (h) Chen, S.; Chen, L.-J.; Yang, H.-B.; Tian, H.; Zhu, W. J. Am. Chem. Soc. 2012, 134, 13596; (i) Chakrabary, R.; Stang, P. J. J. Am. Chem. Soc. 2012, 134, 14738; (j) Roberts, D. A.; Castilla, A. M.; Ronson, T. K.; Nitschke, J. R. J. Am. Chem. Soc. 2014, 136, 8201.
- 5 Roberts, D. A.; Pilgrim, B. S.; Cooper, J. D.; Ronson, T. K.; Zarra, S.; Nitschke, J. R. J. Am. Chem. Soc. 2015, 137, 10068.
- 6 (a) Zheng, W.; Chen, L.-J.; Yang, G.; Sun, B.; Wang, X.; Jiang, B.; Yin, G.-Q.; Zhang, L.; Li, X.; Liu, M.; Chen, G.; Yang, H.-B. J. Am. Chem. Soc. 2016, 138, 4927; (b) Zheng, W.; Yang, G.; Shao, N.; Chen, L.-J.; Ou, B.; Jiang, S.-T.; Chen, G.; Yang, H.-B. J. Am. Chem. Soc. 2017, DOI: 10.1021/jacs.7b07303.
- 7 (a) Mizoguchi, T.; Adams, R. N. J. Am. Chem. Soc. 1962, 84,2058; (b) Iwan, A.; Sek, D.; Prog. Polym. Sci. 2011, 36, 1277; (c) Liang, M.; Chen, J. Chem. Soc. Rev. 2013, 42, 3453.
- 8 (a) Leung, M.-K.; Chou, M.-Y.; Su, Y. O.; Chiang, C. L.; Chen, H.-L.; Yang, C. F.; Yang, C.-C.; Lin, C.-C.; Chen, H.-T. Org. Lett. 2003, 5, 839; (b) Beaupré, S.; Dumas, J.; Leclerc, M. Chem. Mater, 2006, 18, 4011; (c) Seo, E. T.; Nelson, R. F.; Fritsch, J. M.; Marcoux, L. S.; Leedy, D. W.; Adams, R. N.; J. Am. Chem. Soc. 1966, 88, 3498; (d) Oyama, M.; Nozaki, K.; Okazaki, S. Anal. Chem., 1991, 63, 1387.
- 9 Xu, X.-D.; Yao, C.-J.; Chen, L.-J.; Yin, G.-Q.; Zhong, Y.-W.; Yang, H.-B. *Chem.-Eur. J.* **2016**, *22*, 5211.
- (a) Das, N.; Arif, A. M.; Stang, P. J.; Sieger, M.; Sarkar, B.; Kaim, W.; Fiedler, J. *Inorg. Chem.* 2005, *44*, 57984; (b) Das, N.; Stang, P. J.; Arif, A. M.; Campana, C. F. *J. Org. Chem.* 2005, *70*, 10440; (c) Das, N.; Ghosh, A.; Singh, O. M.; Stang, P. J. *Org. Lett.* 2006, *8*, 1701; (d) Yang, H.-B.; Northrop, B. H.; Zheng, Y.-R.; Ghosh, K.; Stang, P. J. *Org. Chem.* 2009, *74*, 7067; (e) Zhao, G.-Z.; Li, Q.-J.; Chen, L.-J.; Tan, H.-W.; Wang, C.-H.; Wang, D.-X.; Yang, H.-B. *Organometallics* 2011, *30*, 5141; (f) Li, Q.-J.; Zhao, G.-Z.; Chen, L.-J.; Tan, H.-W.; Wang, C.-H.; Wang, D.-X.; Lehman, D. A.; Muddiman, D. C.; Yang, H.-B. *Organometallics* 2012, *31*, 7241.
- (a) Stang, P. J.; Olenyuk, B. Acc. Chem. Res. 1997, 30, 502;
 (b) Seidel, S. R.; Stang, P. J. Acc. Chem. Res. 2002, 35, 972;
 (c) Chakrabarty, R., Mukherjee, P. S., Stang, P. J., Chem. Rev. 2011, 111, 6810;
 (d) Xu, L.; Wang, Y.-X.; Yang, H.-B. Dalton Trans., 2015, 44, 867;
 (e) Xu, L.; Chen, L.-J.; Yang, H.-B. Chem. Commun. 2014, 50, 5156;
 (f) Yoshizawa, M.; Klosterman, J. K. Chem. Soc. Rev. 2014, 43, 1885.

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