

Communication

Molecular Vises for Precisely Positioning Ligands near Catalytic Metal Centers in Metal-Organic Framework

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Molecular Vises for Precisely Positioning Ligands near Catalytic Metal Centers in Metal-Organic Framework

Wei Yan, Shenhui Li,^{*} Tao Yang, Yucong Xia, Xinrui Zhang, Chao Wang, Zier Yan, Feng Deng,^{*} Qianghui Zhou, Hexiang Deng^{*}

ABSTRACT: We report the construction of molecular vise by pairing a tritopic phenylphosphrous (III) linker and a monotopic linker in opposite position within metal-organic framework. The angle between these linkers at metal sites is fixed upon change of functionality in the monotopic linker, while the distance between them is precisely tuned. Such distance within molecular vise is accurately measured by ¹H-³¹P solid-state nuclear magnetic resonance (SSNMR). This unveils the impact of the distance on catalytic performance without interference from electrostatic effect or angle change of the ligand, unprecedented in classic organometallic complexes.

The use of phenylphosphorus compounds for the construction of organometallic complexes, exemplified by "Wilkinson catalyst", was a big leap for catalytic reaction towards molecular accuracy.1 It also intrigued the study of electrostatic and steric effects in ligand design.^{2,3} These two effects, however, are usually entangled upon ligand change. Typically, the distances between ligands and metal center are sensitive to their sizes as well as their geometric angles (Scheme 1A and 1B). Recently, we showed that these two effects could be isolated by creating molecular vise (MV) in metal-organic framework (MOF),⁴ where a pair of tritopic and monotopic linkers were anchored in an opposite position at the metal center (Scheme 1C and 1D). This avoided direct contact between the functional group in the monotopic linker and the metal coordinated to the tritopic linker, thus, their distance was precisely tuned without altering the geometric angle of the linkers. In this work, we constructed MVs using a tritopic phosphine linker, 4', 4"', 4""-phosphane-triyltris (1, 1'-biphenyl-4-carboxylic acid) (PBCA) to provide high polarizability hence strong coordination to late-transition metals. This P (III) linker made it possible to accurately measure the distances within MVs by 1H-31P rotational echo double resonance (REDOR) SSNMR. It also allowed for unveiling the role of distance on catalytic performance.

MOFs with rigid backbone provide fixed distance and geometry between functional groups,⁵⁻¹⁰ are favorable for the construction of molecular vises. Metal-binding sites have been successfully introduced into MOFs, where their isolation,¹¹⁻¹³ coupling¹⁴⁻¹⁵ and cooperation¹⁶⁻¹⁹ led to unique catalytic properties.²⁰ Here, the precise control on the coordination geometry and distances between ligand and metal center are rarely accessible in classic organometallic complex introduced into MOF structure. The distances at metal-binding site within MVs range from 3.9 to 10.2 Å by varying the functional groups of monotopic linker (formic acid, FA; benzoic acid, BA; and 4-nitrobenzoic acid, NBA). The accurate measurement of these distances further confirmed the geometry of the linker pairs, and led to the discovery of distance impact on catalytic performance beyond the primary coordination sphere of metal center.²¹⁻²² In the test reaction, halogenation of aromatics, using Au(III) as the metal center, too close position of functional group (NBA) resulted in the blockage of substrates, while sufficient distance (FA) brought in excellent conversion efficiency for all kinds of substrates with reasonable recyclability. It is worth noting that, when the functional group (BA) was arranged around the secondary coordination sphere of the metal, selectively towards different substrates was observed, demonstrating the uniqueness of MV approach.

The synthesis of tritopic phosphine linker was not trivial. Different from reported steps,^{11, 23-24} a new synthetic route, invoving *p*-toluenesulfonyl phosphine precursor, was developed to obtain PBCA with high reproducebility and purity (Section S2, Figures S18-S42). The parent MOF for the construction of phosphine MV is PCN-521, based 4',4''',4''''',4''''''tetratopic linker, on а methanetetrayltetrakis (1,1'-biphenyl)-4-carboxylic acid (MTBC).²⁵ The single crystals of the corresponding MVs, P-MV-PCN-521 were synthesized by mixing ZrCl₄, MTBC, PBCA and monotopic linkers with specific functional groups (Section S₃). These MVs exhibited identical space group to the parent PCN-521, I_4/m , as reveiled by single crystal X-ray diffraction. A slightly longer c axis, 42.1254(4) Å, and shorter a axis, 18.8155(4) Å was observed for P-MV-PCN-521-BA comparing to PCN-521. This likely originated from the steric tension induced by forcing the tritopic phosphine linker into original tetratopic geometry. Sharp peaks were observed in powder X-ray diffraction (PXRD) patterns of P-MV samples, demonstrating their high crystallinity. These patterns also matched well with those simulated from single crystal data (Figure S49). Nanocrystals of P-MVs were also prepared with different ratios of PBCA without affecting the phase purity.



Scheme 1. Distance control in molecular vise. A) and B) Alteration of both bond length and angles at metal center upon ligand change in freestanding organometallic molecule, in 3D and 2D illustration, respectively. C) and D) Fixed angle at metal sites upon functional group change, while the distance between the linkers is precisely tuned, in 3D and 2D illustration, respectively.

The exact percentage of tritopic PBCA linker in the corresponding P-MVs, P-MV-PCN-521-BA, -NBA and -FA were determined by ¹H NMR spectroscopy of the digested samples, 22%, 20% and 41%, respectively (Figure S99-S101). Its homogenous distribution in P-MV single crystals was revealed by laser scanning confocal microscopy with an excitation light of 405 nm wavelength, where characteristic fluorecence of PBCA was observed across the entire single crystals (Figure S108). This is further confirmed by energy dispersive spectra (EDS) mapping of P using scanning electron microscope (Figure S110). The reasonable percentage and homogenous distribution of PBCA, combained with the high natural abundance of ³¹P, made it ideally suited for NMR study to unveil the distance within molecular vises.

The measurement of distance between monotopic linker and PBCA in MV was carried out by ¹H-³P REDOR SSNMR. Others and we have successfully applied SSNMR for the measurement of distance between functional groups within MOFs using the recoupling between ¹⁵N and ¹³C.²⁶⁻²⁷ This usually required isotopically enriched samples, and took several days to obtain reasonable data. In comparison, ¹H-³P REDOR experment here allowed for the direct use of P containing samples without further preperation. The data collection time was also reduced into hours. Two monotopic linkers, dichloroacetic acid (DCA) and *p*-toluic acid (PTA), with different characteristic ¹H, were used to construct MVs, P-MV-PCN-521-DCA and -PTA, respectively. Prior to REDOR experiment, 2D ¹H-¹H spin diffusion homonuclear correlation (HOMCOR) NMR was performed to identify the characteristic [']H chemical shifts for these two P-MVs (Figure 1C and 1D). The auto-correlation peak at (5.3, 5.3) ppm and cross-correlation peak at (1.8, 6.4) ppm were unambiguously assigned to the coordinated DCA and PTA in the corresponding MVs, respectively. These isolated peaks were used for the REDOR experiment (Figure 1E and 1F). The peaks at 2.4~3.2 ppm correlated with 7.1~8.1 ppm in both 2D spectra indicate the spatial proximity between $Zr_3(\mu$ -OH) and aromatic protons of MTBC or PBCA linkers, confirming their robust anchoring in the framework. The characteristic chemical shifts of ¹³C and ³¹P signals were identified by 1D [']H-¹³C/³¹P CP/MAS and 2D heteronuclear correlation (HETCOR) NMR experiments (Figures S64-S69).

In 1H-13P REDOR experiments, frequency switched Lee-Goldburg (FSLG) homonuclear decoupling was applied during dipolar recoupling. The spectra obtained with (S) and without (S_0) ¹H-³¹P REDOR dipolar dephasing were displayed in red and blue, respectively (Figures 1E-1F). Direct comparison between the spectra readily revealed the existence of interaction between ¹H from monotopic linkers (DCA and PTA) and ³¹P of PBCA within MVs, indicating their proximity in space (Figures 1A-1B). Specifically, the dipolar dephasing for the characteristic peaks at 5.3 and 6.4 ppm were used for the distance assessment for MVs with DCA and PTA, respectively (Figures 1G-1H). Dipolar dephasing is also observed on ¹H signals at 8.1, 7.1 and 2.4~3.2 ppm, assigning to aromatic protons of PBCA,

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Figure 1. Accurate measurement of distances within MVs. A) and B) simulated structure models of P-MV-PCN-521-DCA and -PTA, respectively. C) and D) 2D 'H-'H spin diffusion homo-nuclear correlation NMR spectra of P-MV-PCN-521-DCA and -PTA, respectively. E) and F) The spectra obtained with (S) in red and without (So) in blue 'H-3'P REDOR dipolar dephasing of P-MV-PCN-521-DCA and -PTA, respectively. G) and H) 'H-3'P REDOR dephasing curves of the protons from dichloromethyl group of DCA and aromatic ring of PTA.

MTBC and $Zr_3(\mu$ -OH), respectively. These peaks are far apart from the main characteristic peaks, hence their interaction with ³¹P are treated independently. ¹H-¹³P REDOR dephasing ratio was proportional to the reciprocal of internuclear distance in cubic power, which allows for the accurate determination of distance between specific ¹H-³¹P spin pairs. The experimental data are fitted to give ¹H-³¹P dipolar coupling constants (D_{H-P}) between P in PBCA and H in each monotopic linker, 34 Hz for dichloromethyl proton in DCA (Figure 1G), 46 Hz for aromatic protons in PTA (Figure 1H). The detailed analysis of REDOR dephasing curves for the other ¹H-³¹P pairs were also summarized (Figures S74-S80).

The distances within molecular vises, reflected in those of the corresponding ${}^{1}\text{H}{}^{-31}\text{P}$ spin pairs, are derived from ${}^{1}\text{H}{}^{-31}\text{P}$ dipolar coupling constant ($D_{\text{H-P}}$) by considering dynamic amplitude of the nuclei. The local dynamic motion of ${}^{1}\text{H}$ in DCA, PTA, MTBC and PBCA linkers was quantified by ${}^{13}\text{C}{}^{-1}\text{H}$ 2D dipolar chemical shift correlation (DIPSHIFT)

experiments (Figures S70-S71). The phenyl ring flip in MTBC or PBCA linkers was reflected from the determined order parameter of 0.44 for their aromatic carbon sites. The order parameters for dichloromethyl group in DCA and unsubstituted aromatic carbons in PTA were 0.80 and 0.40, respectively, consistent with their dynamic structure features. The dynamic of ³¹P (S_P) was set to 0.44~1 as referring to the adjacent C-H in PBCA. 1H-31P distance between DCA dichloromethyl proton and PBCA phosphorus site was quantitatively determined, in the range from 8.0 to 10.4 Å after considering the dynamic motion (Figure 1G). Similarly, the ¹H-³¹P distances between PTA aromatic protons and P atom in PBCA was measured to be 5.7~7.5 Å (Figure 1H), with ${}^{1}\text{H}{}^{-31}\text{P}$ dipolar coupling constant (D_{H-P}) being scaled to 0.18~0.40. These experimental values can readily differentiate the length of these two monotopic linkers as well as their distances within MVs. The distances estimated from simulated P-MV-PCN-521-DCA and -PTA models were 8.5 and 6.6 Å, respectively (Figure 1A-1B, Figure S62). The consistency to the experimental data further validated the models of P-MV structures, which allowed for the use of estimated values in the study of distance impact on catalytic performance.

The porosity and chemical stability of these P-MVs were assessed before the catalytic tests. The surface areas of P-MV samples were 3150, 2590, 3410 m² g⁻¹ for P-MV-PCN-521-BA, -NBA and -FA, respectively, similar to that of the parent MOF, 3460 m² g⁻¹ (Figures S82-95). The pore size remained nearly unaltered upon functional group change (Figures S82-95), due to the restriction of translational and rotational freedom of functional group. This favored the diffusion of substrates and products in catalytic reaction, standing as a unique feature for the design of MOFs. PXRD patterns of MVs obtained after immersion in water, 1M HCl aqueous solution, dichloroethane (DCE) for 24h, exhibited excellent match with pristine MVs, revealing their high chemical stability (Figure S81). Thermalgravimetric analysis of these MVs also showed their high thermal stability in air (Figures S111-S117).

The metal-binding sites in these MVs were coordinated with Au(III) to construct catalysts (Figure S3) for a classic reaction, halogenation of aromatics.²⁸⁻²⁹ Here, this reaction was tested under ambient temperature without additional Lewis acids (Figure 2B). All the Au-P-MVs were capable of converting mesitylene to 2, 4, 6-trimethybromombenzene within 5 hrs, while non-metalated MVs as control showed negligible activity (Figure 2B, entries 1-6). We also synthesized Au-N-MVs using N-based linker, 4',4"',4""-nitrilotris ((1,1'biphenyl)-4-carboxylic acid),^{3, 30} as control. X-ray photoelectron spectroscopy analysis confirmed that all Au(III) species were coordinated (Figures S118-S119), while elemental analysis revealed a higher loading of Au(III) in Au-P-MVs than that in Au-N-MVs (Tables S12). This could be attributed to the higher affinity and polarizability of P to latetransition metals,4 thus PBCA was better suited linker for catalysis. Indeed, Au-P-MVs exhibited much better performance than the Au-N-MVs counterparts with identical monotopic linker (Figure 2B, entries 7-12).

The impact of distance was investigated by changing the monotopic linkers. In Au-P-MV-PCN-521-NBA, nitro group was directly bonded to Au (III) at the primary coordinate



Figure 2. Catalytic tests of MVs A) N-MVs and P-MVs vary functional groups. B) Bromination of mesitylene with N-Bromosuccinimide (NBS) with various MV and solvent combinations. C) Assessment of Au-P-MV catalysts with different aromatic substrates.

sphere based on the estimated distance, which blocked its access to the substrates, resulted in only 5% conversion. In contrast, the one with FA linker gave the largest distance, 10.2 Å, leading to a high yield of 97% for mesitylene, while more than 90% conversion was also observed for other substrates (Figure 2B). In a consecutive 5 cycle test, negligible decrease in activity was observed, with only 3% leaching of Au (III) (Figure S57, Figure S120 and Tables S13). Although the activity of Au-P-MV-PCN-521-FA was high, it was not selective to different substrates, because the functional group was too far from the metal center. Such selectivity was observed in Au-P-MV-PCN-521-BA, with identical -H functional group, but a smaller H-P distance, 4.0 Å. This rendered the position of -H around the secondary coordination sphere of Au (III), close enough to influence the metal center but not too close blocking its access to substrates. Reasonable vield of 56% and 67% were observed in the conversion of oxylene and anisole, while a lower conversion of 14% for bulkier substrate, mesitylene (Figure 2C). Such difference was also observed among other substrates. This unveiled the critical role of distance with MVs and demonstrated the power of MVs constructed in MOF.

ASSOCIATED CONTENT

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Supporting Information. The Supporting Information is available free of charge on the ACS Publications website at https://pubs.acs.org/doi/10.1021/jacs.xxxxxx.

Details of the synthesis procedures of MV-MOFs, structure determination and simulations, spectroscopic characterizations of MV-MOFs using solid state NMR, LSCM, SEM, ICP, TGA, XPS, and catalytic performance. (PDF)

Crystal data for PCN-521 (cif) Crystal data for N-MV-PCN-521-BA (cif) Crystal data for P-MV-PCN-521-BA (cif)

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Notes

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