BRIEF COMMUNICATION

Tunable Assembly and Magnetic Interactions in Two Cyano-bridged Fe(III)–Co(II) Bimetallic Complexes

Nian-Di Yao[2] · Xi-Lun Wang[3] · Xiao-Qin Wang[1] · Jun-Shen Liu[1] · Hui Zheng[1]

Abstract

Using a new semi-rigid tetradentate ligand and two cyanometalate building blocks with different steric hindrance, a Fe_2Co triangular unit $[(Tp)Fe^{III}(CN)_3]_2Co^{II}(bpmb)\cdot 2H_2O$ [**1**; Tp = hydrotris(pyrazolyl)borate; bpmb = 1,2-bis(3-(2-pyridyl)pyrazol-1-ylmethyl)benzenes] and a Fe_2Co_2 square unit $\{[(pzTp)Fe^{III}(CN)_3]_2[Co^{II}(bpmb)]_2\}\cdot[(pzTp)Fe^{III}(CN)_3]_2\cdot 4H_2O$ [**2**; pzTp = tetrakis(pyrazolyl)borate] were synthesized via tunable assembly. Both compounds adopt *cis* arrangement because of the structural distorted semi-rigid bpmb. Tetranuclear square of **2** was formed due to larger steric hindrance building block of $[(pzTp)Fe^{III}(CN)_3]^-$ compared with $[(Tp)Fe^{III}(CN)_3]^-$ in trinuclear **1**. Magnetic measurements show that antiferromagnetic interactions dominate in **1** and **2**. The fitting results of *J* values suggest a positive correlation between magnetic orbitals overlap of Fe(III) and Co(II) ions and Co–N≡C bond angles.

Graphical Abstract

Two *cis* arrangement cyanometalate [Fe-Co] clusters were synthesized via tunable assembly with a new semi-rigid tetradentate ligand. The tetranuclear cluster was formed because of larger steric hindrance of pzTp. Both compounds exhibit dominant antiferromagnetic couplings. The fitting results of *J* values suggest a positive correlation between magnetic orbitals overlap of Fe(III) and Co(II) ions and Co–N≡C bond angles.
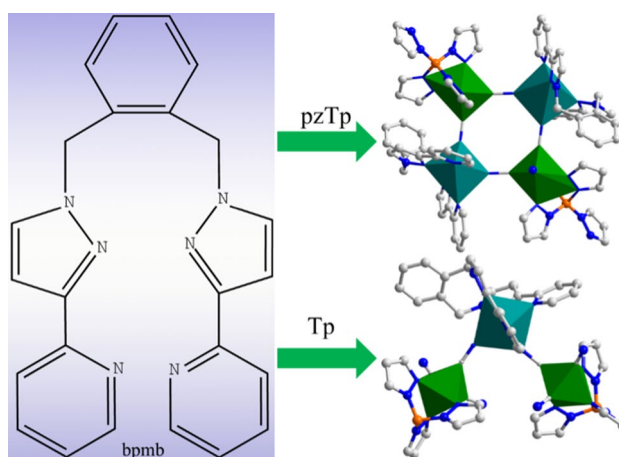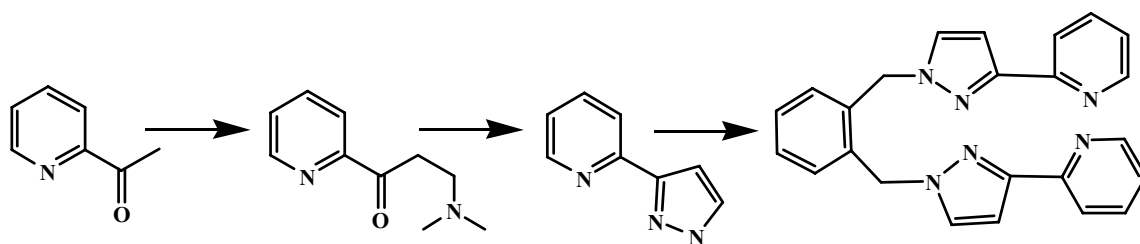

Keywords Cyano-bridged · Semi-rigid · Steric exclusion · Tunable assembly

Introduction

Rational design molecules assembly has always been a hot topic in coordination chemistry. In the research of molecule-based magnetic materials, cyano-bridged

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Scheme 1 Preparation of semi-rigid tetradentate ligand bpmb

bimetallic assemblies have attracted considerable attention due to their predictable structures and fascinating magnetic properties [1–4]. In the meanwhile, it becomes an efficient way to control the nuclearity of complexes via introducing rigid ligands to occupy active sites of the metal centers in the heterobimetallic system [5–9]. Using this strategy, lots of compounds with *cis* or *trans* arrangement have been prepared, such as *cis* mode of trinuclear complexes [10] and *trans* mode of 1D chains [11]. In our previous work, the *cis* or *trans* arrangements of Fe$_2$Cu complexes have been successfully controlled with different steric hindrance building blocks, wherein ferromagnetic and antiferromagnetic interactions dominate respectively [12]. We intend to control the nuclearity via tune the steric effect. Herein, a semi-rigid tetradentate ligand bpmb (1,2-bis(3-(2-pyridyl)pyrazol-1-ylmethyl)benzenes) was adopted to occupy the four coordination sites of the Co^{II} center with two sites in *cis* position be vacant. The remained two *cis* sites were further linked by two building blocks with different steric effect. One trinuclear complex was obtained for building blocks with smaller steric hindrance [(Tp)Fe^{III}(CN)$_3$]$^-$ (Tp = hydrotris(pyrazolyl) borate), whereas one tetranuclear compound was obtained for building block with larger steric hindrance effect [(pzTp)Fe^{III}(CN)$_3$]$^-$ (pzTp = tetrakis(pyrazolyl)borate). Both complexes were characterized by the spectroscopic, structural, and magnetic measurements. Our results provide an effective strategy to control the nuclearity and magnetic properties utilizing steric effect.

Experimental Section

Chemicals and Measurements

Unless the otherwise specified, materials were acquired from the suppliers and could be used with no in-depth purification. 1,2-bis(3-(2-pyridyl)pyrazol-1-ylmethyl) benzenes was synthesized according to method reported previously in the reference.

Synthesis of 1,2-bis(3-(2-pyridyl)pyrazol-1-ylmethyl) benzenes

The semi-rigid ligand bpmb was achieved by three steps (Scheme 1). A mixture of 2-acetylpyridinc (12.1 g, 0.1 mol) and DMF-dimethylacetal (20 cm^3) was refluxed in methol for 16 h. After concentration in vacuo, the resulting crude solid was recrystallised from CHC1$_3$. Then hydrazine hydrate (20 cm^3) and ethanol (20 cm^3) was added and stirred at 60 °C with stirring for 60 min. After addition of water (100 cm^3) the resulting off-white precipitate was filtered off, dried and recrystallised from CH$_2$C1$_2$-hexane to give 5.8 g (63%) of 3-(2-pyridyl)pyrazole. Element analysis, calculated for C$_8$H$_7$N$_3$: C, 66.19; H, 4.86; N, 28.95%. Found: C, 66.57; H, 4.66; N, 28.73%. EIMS *m/z* 145 (*M*$^+$). A mixture of 1,4-bis(bromomethyl)benzene (2.00 g, 7.60 mmol), 3-(2-pyridyl)pyrazole (2.43 g, 16.7 mmol), aqueous NaOH (10 M, 20 cm^3), benzene (50 cm^3) and Bu$_4$NOH (40% aqueous solution, 1 drops) was heated to 80 °C for 24 h. Then the mixture was diluted with H$_2$O (100 cm^3) and the organic layer separated, dried over MgSO$_4$, concentrated and purified by alumina column to give bpmb as a white solid (Yield: 1.34 g, 45%). Anal.Calcd for C$_{24}$H$_{20}$N$_6$: C, 73.45; H, 5.14; N, 21.41%. Found: C, 73.34; H, 5.37; N, 21.39%. EIMS *m/z* 392 (*M*$^+$).

Synthesis of Compounds [(Tp)Fe^{III}(CN)$_3$]$_2$Co^{II}(bpmb)·2H$_2$O (1) and {[(pzTp)Fe^{III}(CN)$_3$]$_2$[Co^{II}(bpmb)]$_2$}·[(pzTp)Fe^{III}(CN)$_3$]$_2$·4H$_2$O (2)

One triangular (**1**) and a tetranuclear (**2**) were synthesized by a diffusion method. The compounds **1** and **2** were synthesized by a diffusion method in an H-shaped tube. 4.0 mL methanol solution of 0.1 mmol (36.6 mg) of Co(ClO$_4$)$_2$·6H$_2$O and 0.1 mmol (39.2 mg) of bpmb ligand were placed at the bottom in one side of an H-shaped tube, while 4.0 mL methanol solution of 0.2 mmol (117.8 mg) of Bu$_4$N[(Tp)Fe^{III}(CN)$_3$] in the other side. Then 8.0 mL methanol solution was layered upon solutions of both sides to provide diffusion pathway. Crystallization took several weeks and gave red crystals of **1** in a yield of 35% based on Co(ClO$_4$)$_2$·6H$_2$O. Anal.Calcd for

$C_{48}H_{44}B_2CoFe_2N_{24}O_2$: C 48.80, H 3.75, N 28.46%; Found: C 48.71, H 3.69, N 28.34%. IR (solid KBr pellet ν/cm^{-1}): 3422 br, 2925 w, 2532 w, 2122 s, 1634 s, 1618 s, 1534 m, 1384 s, 1270 w, 1203 m, 1161 s, 1066 s, 1042 s, 978 w, 902 m, 874 m, 771 s, 688 m. The preparation of compound **2** was carried out using 0.1 mmol (65.5 mg) Bu$_4$N[(pzTp) Fe^{III}(CN)$_3$] instead of Bu$_4$N[(Tp)Fe^{III}(CN)$_3$] and also gave red crystals in a yield of 43% based on Co(ClO$_4$)$_2$·6H$_2$O. Anal.Calcd for $C_{108}H_{96}B_4Co_2Fe_4N_{56}O_4$: C 49.38, H 3.68, N 29.86%; Found: C 49.34, H 3.59, N 29.82%. IR (solid KBr pellet ν/cm^{-1}): 3411 br, 3129 m, 2937 m, 2529 m, 2151 s, 2115 s, 1623 s, 1543 s, 1387 s, 1314 w, 1204 s, 1151 w, 1069 s, 1055 s, 817 m, 783 s, 694 m.

Results and Discussion

Description of Crystal Structures

Single-crystal X-ray diffraction analysis collected at 296 K reveals that **1** and **2** both crystallize in a monoclinic $P2_1/c$ space group. The crystallographic data are presented in Table.S1. The selected bonds and angles are listed in Table. S2 (for compound **1**) and Table. S3 (for compound **2**).

As shown in Fig. 1a, the structure has a cyanide-bridged *cis* trinuclear core. Two crystallographically independent [(Tp)Fe^{III}(CN)$_3$]$^-$ units are linked to [Co^{II}(bpmb)]$^{2+}$ unit via cyanide bridges, forming a *cis* neutral [(Tp) Fe^{III}(CN)$_3$]$_2$Co^{II}(bpmb) trinulcear. Uncoordinated water molecules are located between the complexes. In the [(Tp) Fe^{III}(CN)$_3$]$^-$ units, each Fe center adopts a distorted octahedral geometry with a C_{3v} symmetry. Coordination bond lengths of Fe1–C are in the range of 1.918(6)–1.928(7) Å,

while those of Fe1–N are 1.976(5)–1.981(5) Å, respectively. The coordination environment of Fe2 ion is very similar to that of Fe1 center, and coordination bond lengths are 1.908(8)–1.916(6) Å and 1.969(5)–1.981(5) Å for Fe2–C and Fe2–N, respectively, in good agreement with those observed in other low-spin Fe (III) compounds [13, 14]. The Fe–C≡N linkages are close to linearity with bond angles of 173.4–177.4°. The Cobalt ion in [Co^{II}(bpmb)]$^{2+}$ unit is located in the octahedral environment with four nitrogen atoms from tetradentate bpmb and two cyanide nitrogen atoms from the bridging cyanide ions. The Co–N$_{cyanide}$ bonds [2.083(5)–2.095(4) Å] are slightly shorter than the bpmb ones, which range from 2.116(4) to 2.196(4) Å. Three metal centers are in an approximate right angle with a Fe1···Co1···Fe2 angle of 87.2°, while the Co–N≡C bond angles are obviously deviate from linearity with the same bond angles of 160.5°, suggesting large steric hindrances occurred between the [(Tp)Fe^{III}(CN)$_3$]$^-$ and bpmb ligand. Each molecule then interacts with other adjacent molecule by π···π stacking between aromatic rings of the bpmb ligand at a centroid distance of 3.72 Å, thus forming a dimer structure (Figure. S1). The intramolecular Fe1···Co1, Fe2···Co1, and Fe1···Fe2 distances are 5.078(1), 5.034(2) and 6.972(1) Å, respectively, while the closest intermolecular Fe···Co, Co···Co, and Fe···Fe distances are 8.593(1), 7.825(1) and 11.748(2) Å, respectively, indicating the weak intermolecular magnetic interactions (Figure. S2).

Single-crystal X-ray diffraction analysis show that compound **2** containing [(pzTp)Fe^{III}(CN)$_3$]$^-$ instead of [(Tp) Fe^{III}(CN)$_3$]$^-$. This change increases the steric effect between the building blocks and adjacent bpmb ligand, leading to a larger Fe1···Co1···Fe2 angle of 92.7°, forming a centrosymmetrical tetranuclear square. The crystal structure consists
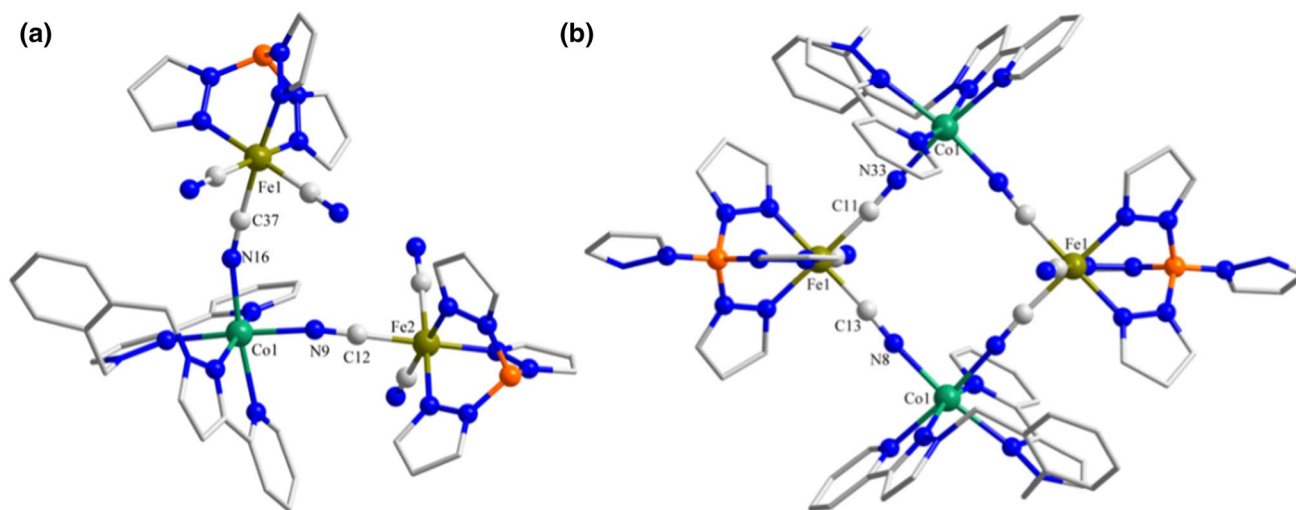

Fig. 1 Crystal structure of **1** (**a**) and **2** (**b**), H and O atoms have been omitted for clarity (Fe, dark yellow, Co, sea green, C, gray, N, blue, B, orange) (Color figure online)

of one discrete tetranuclear mixed metal unit, two [(pzTp) $Fe^{III}(CN)_3$]$^-$ anions, and four free water molecules. Two [(pzTp)$Fe^{III}(CN)_3$]$^-$ units are linked by two [Co^{II}(bpmb)]$^{2+}$ via bridging cyanide ions to form [2 + 2]-type discrete molecular square. Similar with **1**, each Fe center adopts a slightly distorted octahedral geometry, formed by three N atoms from pzTp and three cyanide-carbon atoms. The Fe–C bond lengths are 1.904(5)–1.914(5) Å and the Fe–N distances are 1.951(5)–1.978(5) Å, respectively. The Co center employs the same coordination geometry with **1**. In contrast, The Co–$N_{cyanide}$ bonds [2.078(5)–2.079(5) Å] are slightly shorter while the Co–N_{bpmb} bonds are increased to 2.211(5) Å. Because of the larger steric building block [(pzTp) $Fe^{III}(CN)_3$]$^-$, the Co–N≡C angle tends to be linear to 174.8°, making longer intramolecular Fe···Co and Fe···Fe distances of 5.149(1) and 7.058(1) Å. These values are similar to those observed in the related tetranuclear square compounds [15]. Weak intermolecular π···π interactions also formed between free [(pzTp)$Fe^{III}(CN)_3$]$^-$ anions (3.59 Å) and between adjacent bpmb ligands and free [(pzTp)$Fe^{III}(CN)_3$]$^-$ anions (3.42 Å), leading to a supramolecular chainlike structure along the *c* axis (Figure S3).

Magnetic Properties

Temperature-dependent magnetic susceptibilities for **1** and **2** were measured between 300 and 2 K under a dc field of 1000 Oe. The resulting plots of χT versus T for **1** were given in Fig. 2a. As shown in the figure, the χT value is 4.40 cm^3 mol^{-1} K at room temperature, which is obviously larger than the spin-only value of $\chi T = 2.9$ cm^3 mol^{-1} K for the two magnetically isolated low-spin Fe^{III} (S = 1/2) and one magnetically isolated high-spin Co^{II} (S = 3/2) assuming $g_{Fe} = g_{Co} = 2.0$. The larger value probably due to the orbital contributions of Co center and afford *g* values to

deviate significantly from 2.0 (normally ca. 2.5) [16]. Later it decreased gradually with lowering temperature and then abruptly dropped to 1.49 cm^3 mol^{-1} K at $T = 2$ K. Such a magnetic behavior indicates the dominant antiferromagnetic couplings between the Fe^{III} and Co^{II} ions, which could be observed in other complexes exhibiting similar antiferromagnetic behaviors [17]. The Curie–Weiss law [$\chi T = C/ (T - \theta)$] is applied in the temperature range of 2–300 K to afford the Curie constant $C = 4.70$ cm^3 mol^{-1} K and Weiss temperature $\theta = -25.71$ K. The negative Weiss temperature further suggests that antiferromagnetic interactions are dominant in the trinuclear complex. According to the distorted trinuclear structure, the magnetic data have been simulated with the MAGPACK program [18] based on an exchange Hamiltonian $H = -2J_1 \cdot S_{Fe1} \cdot S_{Co1} -2J_2 \cdot S_{Fe2} \cdot S_{Co1}$, where J_1 and J_2 represent the exchange magnetic coupling constants between Fe^{III} ions and Co^{II} ions through the cyano-bridges. The best fitting results above 48 K give the $J_1 = -10.5$ cm^{-1}, $J_2 = -8.4$ cm^{-1}, $g = 2.64$ with the $R = 1.37 \times 10^{-4}$, which is consistent with other Fe^{III}–Co^{II} assemblies based on cyanometalate precursors [19]. The negative *J* value confirms the antiferromagnetic couplings dominate between Fe^{III} and Co^{II} ions. The *M* versus *H* dc data measured at 1.8 K shown in Figure. S4. As the applied magnetic field increased, the magnetization increased steeply and reached to 1.3 Nβ at 50 kOe. Ac susceptibility measurements were performed at various frequencies (Figure.S5) but no slow relaxation of the magnetization was detected above 2 K, leading to a fast quantum tunneling which may be due to the small energy gap between the ground and excited states [20].

The χT vs *T* data for **2** show the similar magnetic behavior and also suggest the antiferromagnetic couplings with **1**. At 300 K, the χT value is 7.70 cm^3 mol^{-1} K, corresponding to four low-spin Fe^{III} ions and two high-spin Co^{II} ions with $g = 2.31$. Firstly this curve gradually decreased to 6.92
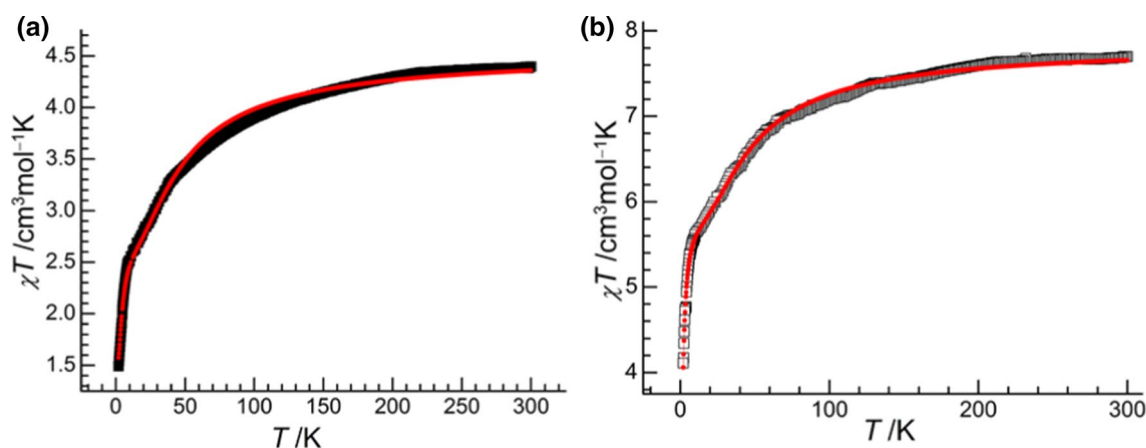

Fig. 2 Temperature-dependent magnetic susceptibility for **1 (a)** and **2 (b)**. The red lines represent the best fit of the experimental results (Color figure online)

cm^3 mol^{-1} K at 65 K, then it sharply dropt and reached the minimum value of 4.11 cm^3 mol^{-1} K at 2 K, indicting the dominant antiferromagnetic behavior. The Curie–Weiss law is also applied in the temperature range of 2–300 K to afford the Curie constant $C = 7.93$ cm^3 mol^{-1} K and Weiss temperature $\theta = -8.72$ K. The negative Weiss temperature further suggests the dominant antiferromagnetic interactions exist in the tetranuclear complex. The fitting results above 25 K of the magnetic data for **2** are similar with **1** and the best-fit parameters for χT vs T are $J = -10.5$ cm^{-1}, $g = 2.44$ and $R = 3.8 \times 10^{-5}$. The large J value indicates the dominant antiferromagnetic interactions between Fe^{III} and Co^{II} ions. Further confirmation of the dominant antiferromagnetic couplings is obtained in the field-dependent magnetization at 1.8 K (Figure. S6) because the magnetization is 4.7 Nβ at 50 kOe, far from the saturated value of 6 Nβ ($g = 2.0$). No out-of-phase signal was observed in ac susceptibility studies above 2 K (Figure. S7), indicating the absence of SMM properties.

Both compounds exhibit *cis* arrangements due to the fact that large steric exclusion in the distorted [Co^{II}(bpmb)]$^{2+}$ unit prevents cyanide nitrogen atoms bridging the Co^{II} center from opposite direction but with an approximate right angle. However, they still form structures with different nuclearities because of distinct steric hindrance of building blocks. In comparison, the Co–N≡C angle of compound **2** is larger than **1**, the longer intramolecular Fe···Co and Fe···Fe distances lead to greater interspace between Fe centers, which is beneficial to the formation of square unit. On the other hand, the magnetic simulations were performed to discuss the correlations between structure and magnetic properties. As judged from the magnetic simulation data, the J value in compound **2** is larger than **1**, which may be due to more linear Co–N≡C angle. It seems that the overlap degree of the magnetic orbitals between Fe^{III} and Co^{II} ions is positively relative to Co–N≡C bond angles. The larger orbitals overlap will result in the stronger Fe^{III}–CN–Co^{II} magnetic interactions [21].

Conclusions

In summary, a cyano-bridged Fe$_2$Co triangular unit **1** and a Fe$_2$Co$_2$ square unit **2** were successfully synthesized via tunable assembly. The semi-rigid ligand bpmb adopts a distorted coordination configuration with Co center, leading to the *cis* arrangement of two compounds. At the same time, the larger steric exclusion of [(pzTp)Fe^{III}(CN)$_3$]$^-$ increases the Fe1···Co1···Fe2 angle, forming tetranuclear square of **2**. The magnetic-structural correlations indicate a positive correlation exists between J values and the Co–N≡C bond angles. This strategy provides a feasible way in the tunable assembly process.

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