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## Introduction

Carbon-based nanomaterials, including carbon nanotubes (CNTs), graphene, carbon dots, fullerene, *etc.* have attracted much attention due to their novel structure and unique properties.<sup>1</sup> Among them, magnetic carbon nanocomposites (MCNs) are important functional materials for a wide range of applications, such as catalysis,<sup>2</sup> information storage,<sup>3</sup> microwave absorption,<sup>4</sup> environmental treatment,<sup>5</sup> and biomedical science.<sup>6</sup> In MCNs, the magnetic nanoparticles well wrapped in carbonaceous species can possess excellent stability, dispersibility and biocompatibility.<sup>7</sup> Various approaches such as chemical vapor deposition, electric arc discharge, hydrothermal/solvothermal treatment and the pyrolysis procedure have been successfully applied for the fabrication of functional MCNs.<sup>8</sup> And the prepared

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# Controllable preparation of magnetic carbon nanocomposites by pyrolysis of organometallic precursors, similar molecular structure but very different morphology, composition and properties<sup>†</sup>

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Four cobalt-containing organometallic compounds were synthesized for solid-state pyrolysis (SSP) to study the structure-property relationship between the precursors and the as-synthesized magnetic carbon nanocomposites (MCNs). In this research, the only saturated carbon atom in  $M_C$  was replaced by a N, O or S atom, to produce precursors  $M_N$ ,  $M_O$  and  $M_S$ , respectively. It was found that the crystal phase of cobalt generated upon pyrolysis is dependent on the kind of heteroatom introduced into the precursor: fcc-Co for  $M_C/M_N$ , while the fcc/hcp-Co hybrid for  $M_O/M_S$ . Metal cobalt with different crystal phases has its special catalytic and magnetic properties. Thus, MCNs with very different morphologies, compositions and properties could be prepared by just altering one heteroatom in the precursors upon SSP. Uniform nanotubes were generated from pyrolysis of  $M_C/M_N$ , while nanospheres were generated from  $M_O/M_S$ . The obtained MCNs all show good magnetic properties with  $M_s$  ranging from 47.6 to 54.5 emu g<sup>-1</sup>. Due to the magnetic difference between fcc-Co and hcp-Co, the  $M_s$  values of MCNs obtained from  $M_O/M_S$  are slightly lower than those of  $M_C/M_N$ , but the  $M_r$  and  $H_c$  values of the former are 2 to 5 times higher than those of the latter.

nanocomposites with different morphologies and compositions have their specific properties and application fields.<sup>9</sup> Recently, great achievements of Sahoo *et al.* demonstrated that pyrolysis of cheaper and commercially available precursors is a very powerful and economical method to produce functional magnetic nanomaterials for a wide range of applications, such as optical limiting, photodetection, magnetorheological and electromagnetic interference shielding. Furthermore, the morphology, composition, crystal phase and properties of the nanomaterials can be tuned by changing the synthesis parameters, *i.e.*, reaction temperatures, heating rate, carbon source, concentration of precursors *etc.*<sup>10</sup> Despite the many fabrication methods, the controllable preparation of MCNs with a desired morphology and properties is still a challenge. More importantly, the growth mechanism of these nanocomposites is still ambiguous.

Organometallic complexes including both metal and carbon sources are excellent raw materials for the preparation of MCNs.<sup>11</sup> The metal-containing moieties could be transformed into metal nanoparticles under pyrolysis. Then, the generated metal catalyst could catalyze the formation of carbon nanoparticles (CNPs).<sup>12</sup> Meanwhile, the magnetic metal NPs formed in the pyrolysis process could be well wrapped by the

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#### Paper

carbonaceous materials, which could hinder the oxidation and agglomeration of metal NPs.13 Recently, Vollhardt and Müllen et al. demonstrated that solid-state pyrolysis (SSP) of organometallic complexes is promising for the preparation of MCNs.<sup>14</sup> In SSP, powders of organometallic precursors were sealed in quartz tubes under high vacuum. Placed in a furnace, the precursors underwent stepwise thermolysis without the need of feedstock gases, an inert atmosphere, extra catalysts, and expensive equipment. Especially, the well-defined organometallic compounds played a vital role in regulating the properties and structure of the corresponding CNPs formed in SSP.<sup>15</sup> In the process, the molecular structure of organic precursors could be subtly modified to control the morphology and properties of the obtained CNPs. Thus, it is urgent to know more about the structure-property relationship between the organometallic precursors and the pyrolysis products.

In the present work, four organometallic compounds (i.e.,  $M_C$ ,  $M_N$ ,  $M_O$  and  $M_S$ ) precise in the molecular structure were synthesized to study the structure-property relationship between the precursors and the as-synthesized MCNs as well as the inherent mechanism. Surprisingly, just changing one heteroatom in the precursors could lead to a completely different morphology, composition and properties of the assynthesized MCNs (Fig. 1). After pyrolysis, the Co-containing moieties in  $M_C/M_N$  were transformed into fcc-Co, but it was converted to the fcc-Co/hcp-Co hybrid in Mo/Ms. Subsequently, the morphology of the MCNs could be well controlled as nanotubes (for  $M_C/M_N$ ) or nanospheres (for  $M_O/M_S$ ) with adjustable sizes and magnetic properties. The experimental results indicate that the heteroatom in the precursor could regulate the crystal phase of metal Co (possesses different catalytic activities and magnetic properties), thereby controlling the morphology and magnetic properties of the resulting MCNs upon SSP. The results confirm the power of the concept of precursor-controlled pyrolysis towards defined MCNs, and provide a possible route for the partially controllable preparation of MCNs.

### **Results and discussion**

#### Synthesis and characterization

M.: X = !

(OC)<sub>3</sub>Co

co(CO)

X: C、N

 $M_0: X = 0;$ 

Co(CO)<sub>2</sub>

Solid-State Pyrolysis

(OC)<sub>3</sub>C

 $M_C$  was synthesized using fluorene as the basic unit. Then, replacing the only saturated carbon atom in  $M_C$  with a N, O or S



atom,  $M_N$ ,  $M_O$  and  $M_S$  were obtained, respectively. Scheme S1 (ESI<sup>†</sup>) illustrates the synthetic routes to the intermediates and final products. Firstly, alkynyl-functionalized compounds 1–4 were synthesized by the palladium-catalyzed Sonogashira coupling reaction. Then, organometallic compounds  $M_C$ ,  $M_N$ ,  $M_O$  and  $M_S$  were all prepared *via* the reaction between the alkynyl-functionalized 1–4 and an excess of  $Co_2(CO)_8$ , affording [CCCo<sub>2</sub>(CO)<sub>6</sub>] moieties with satisfactory yield.<sup>16</sup> All the compounds were well characterized by nuclear magnetic resonance (NMR), elemental analysis (EA), mass spectroscopy, and Fourier transform infrared (FTIR) spectroscopy, which well confirmed their explicit molecular structures (Fig. S7–S22, ESI<sup>†</sup>).

Fig. 2 shows the IR spectra of 1, 2,  $M_C$  and  $M_N$ . The stretching vibration of the  $C \equiv C$  of 1 and 2 appears at about 2210 cm<sup>-1</sup>, which completely disappears in the spectra of  $M_{\rm C}$ and  $M_N$ . However, in the spectra of  $M_C$  and  $M_N$ , three strong absorption bands appear in the range of 2010 to 2090 cm<sup>-1</sup>, which are the typical absorptions of  $[CCCo_2(CO)_6]$ , confirming that alkynyl group has been completely reacted with Co<sub>2</sub>(CO)<sub>8</sub>.<sup>17</sup> Meanwhile, due to the presence of the N-H bond in 2 and  $M_N$ , they also show an absorption peak at about 3400 cm<sup>-1</sup>. The IR spectra of the four organometallic compounds and their intermediates are given in Fig. S1 (ESI<sup>+</sup>), and similar results are obtained. Fig. 3 shows the <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of 3 and Mo. After the incorporation of the  $[Co_2(CO)_6]$  unit, the <sup>13</sup>C NMR spectra demonstrate an obvious signal shift for the carbons of the alkynyl group. The signals assigned to  $C \equiv C$  (Ca) shift from 89.4/89.9 to 91.9/92.3 ppm (Ca'). In addition, a strong singlet assigned to the carbonyl carbon (Cb) of [CCCo<sub>2</sub>(CO)<sub>6</sub>] appears at about 199.4 ppm.<sup>18</sup> Moreover, in both the <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra, great changes have also been observed in the aromatic areas close to the  $[CCCo_2(CO)_6]$  unit.

#### Thermal properties and pyrolysis process

In SSP, samples would generally undergo a program of stepwise pyrolysis. The precursors were first heated to the decomposition temperature of metal carbonyl groups and held at this



Fig. 2 IR spectra of compounds  $1,\ 2$  and organometallic precursors  $M_{C},\ M_{N}.$ 

Co@C nanospheres

High Mr and Hc

**Carbon nanotubes** 

Low Mr and Hc

fcc-Co

fcc-Co/hcp-Co hybrids



Fig. 3  $^{1}$ H NMR and  $^{13}$ C NMR spectra of **3** and **M**<sub>O</sub> (in CDCl<sub>3</sub>), the solvent peaks are marked with asterisks.

temperature for several hours to ensure complete decomposition of the cobalt complexes before further heating at a higher temperature for a longer period. We investigated the thermal properties of the organometallic compounds  $(M_C-M_S)$  by TGA. The temperatures  $(T_d)$  for thermal decomposition of the compounds were about 170 °C (corresponding to a weight loss of 5%) (Fig. S2, ESI<sup>†</sup>). Thus, the pyrolysis procedure was as follows: powder of an organometallic compound was vacuum sealed in a quartz tube, and then placed in a furnace. The other three compounds were handled similarly, and all four underwent the same heating program in one furnace at the same time. The samples were first slowly heated to 170  $^\circ C$  at a rate of 1.9  $^\circ C$  $\mathrm{min}^{-1}$  and held for two hours. Then they were heated to 700  $^\circ\mathrm{C}$ at a rate of 5.2 °C min<sup>-1</sup> and held for eight hours. After natural cooling to room temperature, the produced products were well characterized by powder X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), vibrating sample magnetometry (VSM), and energydispersive spectroscopy (EDX).

#### Morphological characterization of the MCNs

As discussed above, the precursor-controlled pyrolysis method is an effective way to produce defined CNPs. Following the same pyrolysis procedure, the prepared organometallic precursors could be well converted to two completely different types of MCNs, viz. nanotubes and nanospheres, with high yield. Upon SSP, M<sub>C</sub> and M<sub>N</sub> produced multiwalled CNTs (Fig. 4a-f). TEM analysis showed that the average inner and outer diameters of the CNTs are about 20 and 40 nm for M<sub>C</sub>, respectively (Fig. 4b), and the length of these CNTs is  $>10 \ \mu m$ . From the high-resolution TEM (HRTEM) images, the nanotubes are well graphitized, made up of  $\sim 25$  layers, and the space between the layers is 3.51 Å (Fig. 4c and Fig. S3a, ESI<sup>+</sup>), consistent with the range reported for the interplanar spacings of graphite ( $d_{002} = 0.34-0.39$  Å).<sup>19</sup> As for the CNTs produced from  $M_N$ , they are with length  $<1 \mu m$ , and with inner and outer diameters of about 30 nm and 60 nm, respectively (Fig. 4d and e). Compared with the CNTs obtained from  $M_C$ , there is a reduction of the length and enlargement of the diameter size. The wall of the CNTs is comprised of *ca.* 40 graphene layers with  $d_{002} = 3.47$  Å (Fig. 4f). As shown in Fig. 5b and Fig. S3d (ESI†), the top of the CNT precisely demonstrates its multilayer tubular structure.

Surprisingly, unlike the cases of M<sub>C</sub> and M<sub>N</sub>, as just changing one heteroatom in the precursors (from N to O or S), MCNs totally different in the morphology are obtained from  $M_0$  and M<sub>s</sub>, both giving nanospheres with a Co@C core-shell structure. For Mo, the TEM and SEM images showed that the diameters of the obtained nanospheres are mainly about 10-15 nm (Fig. 4g-i). And Co NPs are well embedded in amorphous and graphitized carbon with a thickness of 5-10 nm. As shown in Fig. 5c and Fig. S4 (ESI<sup>†</sup>), the Co NPs embedded in graphitized carbon ( $d_{002}$  = 3.43 Å) display a clear lattice structure. The spacing between the lattice planes is, respectively, 0.174 nm and 0.216 nm corresponding to the (111) planes of face centered cubic (fcc) and (100) planes of hexagonal-closed-packed (hcp) phases of cobalt.<sup>20</sup> The results illustrate the coexistence of the fcc (area circled by blue dashed line, Fig. 5c) and the hcp (in green dashed line) structures. Moreover, the fcc phase locating at the center was surrounded by the hcp phase.

As to precursor  $M_s$ , the TEM and SEM analysis showed that the diameters of the nanospheres mainly range from 35 to 55 nm, and the Co NPs are well encapsulated in carbonaceous materials (Fig. 4j–l). And the lattice fringes of Co could be clearly observed in the HRTEM image (Fig. 4l). Interestingly, a special phenomenon was observed in the case of precursor  $M_s$ : in addition to nanospheres (the main products), a few cobalt core/carbon sheath nanocables with a diameter of about 200 nm and a length of 7 µm are obtained (Fig. 5d and Fig. S5, ESI†). The TEM-EDX technique was applied to analyze the element distribution of the nanocable (Fig. 5e). When the electron beam passed through the core (label 1–1 in Fig. 5d) and the sheath (label 1–2) of the nanocable, Co and C are the main elements detected (Cu was from the copper grid), confirming its cobalt core/carbon sheath architecture.

It is interesting to find out how the change of just one atom could lead to the formation of MCNs that have a completely different morphology. Generally, fcc and hcp are the two main crystalline structures of metallic cobalt. Among them, the hcp-Co is stable at room temperature, while the fcc-Co is a metastable phase formed at temperature above 450 °C.<sup>21</sup> In pyrolysis, cobalt mainly existed in the fcc phase at high temperature, especially for the production of CNTs.<sup>22</sup> Despite cobalt being a common catalyst for the synthesis of CNTs, and that its morphology, density and size effect extensively studied,<sup>23</sup> the impact of the crystal phase on catalytic performance was rarely considered, mainly because of the absence of the hcp phase during pyrolysis. Although hcp-Co could exist under specific conditions in pyrolysis, the main pyrolysis products were carbon-encapsulated cobalt NPs.<sup>10g,24</sup> The result imply that fcc-Co is a phase catalytically active for the fabrication of CNTs, while hcp-Co is conducive to the generation of carbonencapsulated cobalt NPs.

Importantly, in classic cobalt-catalyzed Fischer–Tropsch reactions, it was demonstrated that hcp-Co has higher catalytic



Fig. 4 SEM (a, d, g and j), TEM (b, e, h and k) and HRTEM (c, f, i and l) images of the materials obtained through pyrolysis of M<sub>C</sub> (a-c), M<sub>N</sub> (d-f), M<sub>O</sub> (g-i) and M<sub>S</sub> (j-l).

activity than fcc-Co.<sup>25</sup> This is mainly due to the special surface structure of the hcp crystal phase, which has higher intrinsic activity and density of active sites. So it is more beneficial to the decomposition, diffusion and recombination of carbon sources on its surface.<sup>26</sup> Likewise, during catalytic pyrolysis, hydro-carbons were adsorbed and underwent decomposition on the metal catalyst, and then the carbon species diffused and restructured to carbon NPs.<sup>27</sup> In the present work, based on the experimental results and inspired by the above information, it is envisioned that there is fast diffusion and deposition of the carbon source on hcp-Co, leading to complete encapsulation of cobalt NPs by carbon (*i.e.*, formation of cobalt core–carbon shell

composites), rather than nucleation and growth of CNTs. In contrast, the moderate catalytic activity of fcc-Co favors the gradual nucleation and growth of CNTs.

On the other hand, according to previous reports, stacking fault is an important aspect for the production of hcp-Co. Thus, the presence of oxygen or sulfur in precursors perhaps could reduce the activation energy for the formation of stacking faults, thus facilitating the formation of the hcp-phase at high temperature.<sup>10g,24</sup> Overall, in this work, for the first time, we found that a heteroatom (even just changing one atom) in the organometallic precursors could regulate the crystal phase of metal Co, thereby controlling the morphology and properties of



Fig. 5 HRTEM images of the materials obtained through pyrolysis of  $M_c$  (a) and  $M_N$  (b) and  $M_o$  (c). TEM images of the cobalt core/carbon sheath nanocable obtained through pyrolysis of  $M_s$  (d), and its corresponding TEM-EDX spectra (e).

the resulting MCNs upon SSP, providing an effective approach to prepare MCNs controllably.

#### Composition of the MCNs

Powder XRD was used to further study the crystal phase of the produced MCNs (Fig. 6). To differentiate the pyrolysis products from their organometallic precursors, the MCNs obtained from  $M_C$ ,  $M_N$ ,  $M_O$  and  $M_s$  are hereinafter named as  $M_C$ -S,  $M_N$ -S,  $M_O$ -S and  $M_S$ -S, respectively.  $M_C$ -S and  $M_N$ -S exhibited Bragg reflections at  $2\theta$  of 44.3, 51.6 and 75.9°, which could be assigned to



Fig. 6 XRD diffractograms of M<sub>C</sub>-S, M<sub>N</sub>-S, M<sub>O</sub>-S and M<sub>S</sub>-S.

the (111), (200) and (220) planes of the fcc-Co.<sup>28</sup> Due to the presence of the broad signal of the amorphous matrix and impurities covering on the as-synthesized CNTs, the peak at about 26° corresponding to the (002) planes of graphite structure is weak.<sup>29</sup> In agreement with the HRTEM results, fcc and hcp phases coexist in Mo-S and Ms-S, because in addition to the peaks of the fcc phase, there are peaks at  $41.6^{\circ}$  and  $47.5^{\circ}$  that correspond to the (100) and (101) planes of the hcp phase observed over the two samples.<sup>30</sup> Meanwhile, in comparison with those of Mo-S, the intensity of the diffraction peaks for the hcp phase in M<sub>s</sub>-S became much narrower and sharper, indicating an improvement in crystallinity and enlargement of the cobalt size.<sup>31</sup> XRD results showed that cobalt mainly exists in elemental Co without forming a complex with the heteroatom. Actually, heteroatoms in the organometallic precursors are almost not present in the pyrolysis products due to their low content and easy conversion into gaseous substances at high temperatures.<sup>15,22</sup> According to the results of SEM-EDX analysis, except the presence of a small amount of sulfur in Ms-S, the main compositions of all the MCNs are Co and C elements, and the cobalt contents are around 30% (Fig. S6, ESI<sup>+</sup>).

#### Magnetism of the MCNs

All the Co enriched carbon nanocomposites are magnetizable and could be attracted to a magnet at room temperature quickly. Thus, to study the magnetism of the obtained MCNs, especially highlight the impact of hcp-Co on the magnetic anisotropy, VSM was utilized to quantitatively investigate their



Fig. 7 Plots of magnetization (*M*) versus applied magnetic field (*H*) at 300 K for  $M_C$ -S,  $M_N$ -S,  $M_O$ -S and  $M_S$ -S. Inset is the enlarged portion of the M-H plot close to the origin.

 Table 1
 Magnetization data for various samples measured at 300 K

Sample	$M_{\rm s}$ (emu g <sup>-1</sup> )	$M_{\rm r} ({\rm emu}~{\rm g}^{-1})$	$M_{\rm r}/M_{\rm s}$	$H_{\rm c}$ (Oe)
M <sub>C</sub> -S	54.5	6.8	0.12	150
M <sub>N</sub> -S	51.7	5.9	0.11	190
Mo-S	50.6	12.6	0.25	760
M <sub>S</sub> -S	47.6	14.2	0.30	610

magnetic properties at 300 K. Fig. 7 shows the magnetization curves of the MCNs, all the samples exhibited a soft ferromagnetic behavior with high magnetizability. The magnetization rapidly increased with an increase in the strength of the applied field before 5 kOe, with relatively low magnetic remanence  $(M_r)$ and coercivity  $(H_c)$ . The magnetization data are summarized in Table 1. With saturation magnetization  $(M_s)$  ranging from 47.6 to 54.5 emu  $g^{-1}$ , the produced MCNs are endowed with good magnetic properties. Analyzing carefully, the  $M_s$  values of  $M_0$ -S/  $M_{s}$ -S are slightly lower than those of  $M_{c}$ -S/ $M_{N}$ -S, but, their  $M_{r}$ and  $H_c$  values were 2 to 5 times higher than those of the latter. The  $M_{\rm s}$  and  $H_{\rm c}$  values of  $M_{\rm C}$ -S/M<sub>N</sub>-S are 6.8/5.9 emu g<sup>-1</sup> and 150/190 Oe, respectively. However, as to Mo-S/Ms-S, these values significantly increased to 12.6/14.2 emu g<sup>-1</sup> and 760/610 Oe, respectively. Considering the presence of hcp-Co in Mo-S and M<sub>s</sub>-S, those results are understandable: compared with fcc-Co, hcp-Co has a slightly lower  $M_s$  value but much stronger  $M_{\rm r}$  and  $H_{\rm c}$  values.<sup>32</sup> Therefore, the hcp-Co generated in Mo-S and Ms-S leads to the unique magnetism across the prepared MCNs.

### Conclusions

Through rational molecular design, four organometallic precursors were synthesized for solid-state pyrolysis (SSP) to study the structure–property relationship between the precursors and the as-synthesized MCNs. It was found that the crystal phase of the cobalt catalyst could be regulated by the introduction of a heteroatom into the precursor molecule, leading to MCNs that are different in the morphology, composition, and magnetic properties upon SSP. Using such an approach, uniform nanotubes and nanospheres with an adjustable size and magnetic properties could be efficiently fabricated with high selectivity. The obtained MCNs all show good and differentiated magnetic properties, their magnetic properties display a good accordance with their structure, and they could be promising candidates for practical magnetic and catalytic applications. Thus, the results demonstrate the power and workability of precursorcontrolled SSP, and could provide useful information for the partially controllable preparation of MCNs.

### Experimental

#### Materials and instrumentation

Compounds 1-4 were synthesized according to the literature.<sup>33</sup> Octacarbonyldicobalt  $(Co_2(CO)_8)$  was purchased from Alfa Aesar. Dichloromethane (DCM) was dried over and distilled from calcium hydride. Tetrahydrofuran (THF) was dried over and distilled from the K-Na alloy under an atmosphere of dry nitrogen. All other reagents were purchased from commercial suppliers and used as received without further purification. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectroscopy studies were conducted with a Varian Mercury-300 spectrometer and Bruker Avance-400 NMR spectrometer using tetramethylsilane (TMS;  $\delta = 0$  ppm) as the internal standard. MS spectra were acquired with a ZAB 3F-HF mass spectrometer. The Fourier transform infrared (FTIR) spectra were recorded on a Nicolet NEXUS-6700 FTIR spectrophotometer in the region of 400-4000 cm<sup>-1</sup>. Elemental analyses of hydrogen, carbon and nitrogen were performed over a CARLOERBA-1106 micro-elemental analyzer. Thermogravimetric analysis (TGA) was performed on a SQT Q600 TA thermal analyzer at a heating rate of 10  $^{\circ}$ C min<sup>-1</sup> in N<sub>2</sub> with a flow rate of 20 cm<sup>3</sup> min<sup>-1</sup>. The X-ray diffraction (XRD) analyses were performed on a SHIMADZU XRD-6100 diffractometer with CuK $\alpha$  radiation ( $\lambda$  = 1.5418 Å). Scanning electron microscopy (SEM) was conducted with a ZEISS-SIGMA scanning electron microscope. Transmission electron microscopy (TEM) was measured with JEM-2010HT and JEM-2010FEF microscopes at an accelerating voltage of 200 kV. TEM samples were prepared by drying a droplet of the suspension on a TEM copper micrograte mounted with a carbon film. Energy-dispersive Xray spectra (EDX) were recorded using the TEM or SEM. Magnetization curves were recorded on a physical property measurement system (PPMS-9T) with the vibrating sample magnetometer (VSM) option at 300 K.

#### Synthesis of the organometallic compounds

General method for the synthesis of organometallic compounds  $M_C$ ,  $M_N$ ,  $M_O$  and  $M_S$ :  $Co_2(CO)_8$  (6.0 equiv.) and compound 1, 2, 3 or 4 (1.0 equiv.) were dissolved in dry THF under a nitrogen atmosphere. The mixture was stirred overnight at 25 °C and then the solvent was removed under vacuum. The residue was

purified by column chromatography on neutral  $Al_2O_3$  using petroleum ether–DCM mixture as an eluent.

Compound  $\mathbf{M}_{\rm C}$ : black solid was obtained in 68% yield. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 7.78 (m, 4H, ArH), 7.65 (m, 6H, ArH), 7.39 (m, 6H, ArH), and 3.98 (s, 2H, -CH<sub>2</sub>-). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 199.5, 144.5, 141.4, 138.6, 137.3, 129.4, 129.2, 128.7, 128.1, 125.8, 120.6, 92.5, 92.4, and 36.9. FTIR (thin film),  $\nu$  (cm<sup>-1</sup>): 2016.2, 2052.4, and 2088.6 (Co<sub>2</sub>(CO)<sub>6</sub>). Anal. calcd for C<sub>41</sub>H<sub>18</sub>Co<sub>4</sub>O<sub>12</sub>: C 52.48, H 1.93; found: C 52.93, H 2.11.

Compound  $\mathbf{M_N}$ : black solid was obtained in 80% yield. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 8.32 (br, 3H, ArH), 7.64 (br, 6H, ArH), and 7.39 (br, 8H, ArH). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 199.6, 139.8, 138.9, 129.8, 129.4, 129.1, 128.3, 127.9, 123.6, 121.2, 93.5, and 92.3. FTIR (thin film),  $\nu$  (cm<sup>-1</sup>): 2018.0, 2050.6, 2088.6 (Co<sub>2</sub>(CO)<sub>6</sub>), and 3409.5 (N–H). Anal. calcd for C<sub>40</sub>H<sub>17</sub>Co<sub>4</sub>NO<sub>12</sub>: C 51.15, H 1.82, and N 1.49; found: C 52.03, H 1.74, and N 1.57.

Compound **M**<sub>0</sub>: black solid was obtained in 76% yield. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 8.15 (s, 2H, ArH), 7.54 (d, J = 8.4 Hz, 2H, ArH), 7.63 (m, 6H, ArH), and 7.38 (m, 6H, ArH). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 199.6, 156.6, 138.5, 133.6, 129.5, 129.4, 129.2, 128.2, 124.6, 121.1, 92.3, and 91.9. FTIR (thin film),  $\nu$  (cm<sup>-1</sup>): 2019.8, 2051.1, and 2089.5 (Co<sub>2</sub>(CO)<sub>6</sub>). Anal. calcd for C<sub>40</sub>H<sub>16</sub>Co<sub>4</sub>O<sub>13</sub>: C 51.09, H 1.72; found: C 51.69, H 1.61.

Compound **M**<sub>s</sub>: black solid was obtained in 65% yield. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 8.36 (s, 2H, ArH), 7.85 (d, *J* = 8.1 Hz, 2H, ArH), 7.65 (m, 6H, ArH), and 7.36 (m, 6H, ArH). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 199.4, 139.8, 138.5, 136.0, 135.5, 129.3, 128.7, 128.2, 128.0, 123.6, 122.6, 92.5, and 91.8. FTIR (thin film),  $\nu$  (cm<sup>-1</sup>): 2019.6, 2051.5, and 2088.5 (Co<sub>2</sub>(CO)<sub>6</sub>). Anal. calcd for C<sub>40</sub>H<sub>16</sub>Co<sub>4</sub>O<sub>12</sub>S: C 50.24, H 1.69; found: C 50.86, H 1.51.

## Author contributions

Z. R. contributed in conceptualization, formal analysis, writing – original draft, and writing – review & editing. J. R. contributed in formal analysis. S. L. contributed in formal analysis and resources. Y. C.: contributed in funding acquisition and supervision. X. W. contributed in formal analysis. J. S. contributed in conceptualization, investigation, and writing – review & editing. L. Z. contributed in formal analysis. S. Z. contributed in formal analysis and resources. J. L.: contributed in conceptualization and project administration.

# Conflicts of interest

There are no conflicts to declare.

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