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## COMMUNICATION

# Translation of assembling trajectory by preorganisation: A study of the magnetic properties of 1D polymeric unpaired electrons immobilised on a discrete nanoscopic scaffold†

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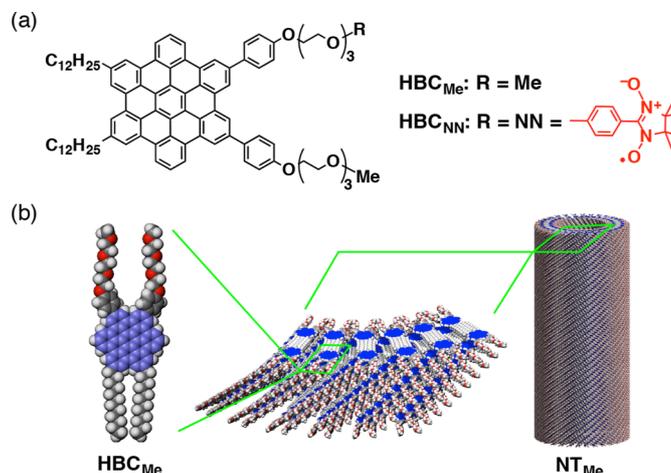
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**A nitronyl nitroxide (NN)-appended hexabenzocoronene (HBC<sub>NN</sub>), when allowed to coassemble with bis(hexafluoroacetylacetonato)cobalt(II), forms a coaxial nanotubular architecture featuring NN-Co(II) coordinated copolymer chains immobilised on the outer and inner nanotube surfaces. Upon lowering the temperature, this nanotube has enhanced magnetic susceptibility below 10 K.**

Self-assembled structures are often considered highly dynamic and only somewhat maintain the trajectory of their assembling events spatiotemporally due to the concomitant occurrence of thermodynamic structural reorganisation.<sup>1</sup> However, in recent years, some intriguing observations that refute this preconceived notion have been reported in which the sequence of assembling events in supramolecular polymerisation is memorised, so that block copolymers are formed in a noncovalent manner.<sup>2</sup> These examples may reveal a new aspect of molecular assembly and indicate the potential of developing particular physical properties originating from a particular assembling trajectory.

Here we report the interesting observation that the magnetic properties of an organic radical-appended metal-coordination copolymer reflect its assembling trajectory (Fig. 2). This coordination copolymer consists of nitronyl nitroxide (NN) units that are coordinated with bis(hexafluoroacetylacetonato)cobalt(II) (Co(hfac)<sub>2</sub>). In the crystalline state, such a NN-Co(II) coordination copolymer is known to exhibit single-chain magnetic behaviour characterised by enhanced magnetic susceptibility below 50 K.<sup>3</sup> In the crystal structure, the copolymer chains adopt an extended conformation and align unidirectionally with spatial insulation from one another. We envisioned that such oriented copolymer chains might spontaneously be formed when allowed to develop on the restricted surface of a 1D nanoscopic scaffold. Thus, we noted the nanotubular assembly of Gemini-shaped hexabenzocoronene derivatives (HBCs) and designed NN-appended HBC (HBC<sub>NN</sub>), shown in Fig. 1a, as an assembling motif.

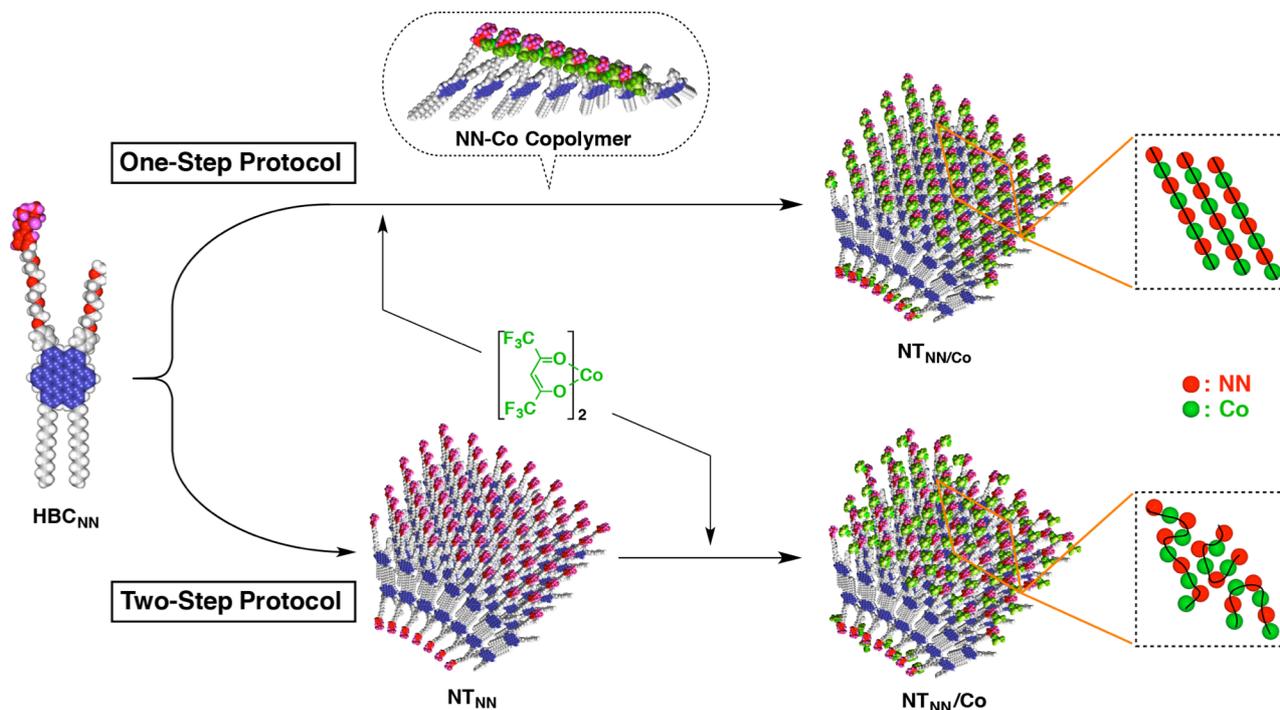
In 2004, we reported that HBC<sub>Me</sub> (Fig. 1a), carrying two alkoxyphenyl groups on one side of its extended  $\pi$ -conjugated core and two dodecyl side chains on the other, self-assembles into a well-defined nanotubular structure (NT<sub>Me</sub>, Fig. 1b).<sup>5a</sup> The typical tubular



**Fig. 1** (a) Chemical structures of HBC<sub>Me</sub> and HBC<sub>NN</sub>. (b) Schematic representations of the hierarchical nanotubular architecture of Gemini-shaped HBC<sub>Me</sub> (NT<sub>Me</sub>).

wall is 3 nm thick, consisting of  $\pi$ -stacked HBC units with a helically twisted *J*-aggregate geometry, and characterised by its bilayer structure supported by interdigitation of the dodecyl side chains.<sup>5,6</sup> Consequently, the alkoxyphenyl side chains cover both the inner and outer nanotube surfaces. If HBC<sub>NN</sub> likewise self-assembles into nanotubular NT<sub>NN</sub>, the NN groups should be well exposed on the nanotube surface<sup>6</sup> and therefore can coordinate with transition metal ions.

Prior to the present study using HBC<sub>NN</sub>, we reported that the assembly of pyridine- and bipyridine-appended HBC derivatives is promoted by coordination of their metal-ligating units with Pt(II) and Cu(II) ions, affording NTs wrapped by metal-coordinated copolymer chains.<sup>2b,7</sup> Through these studies, we found that HBC NTs (Fig. 1b) are not dynamic at ambient temperatures and can maintain for a long time a block copolymer sequence without reshuffling<sup>2b</sup> or a one-handed helical geometry without racemization.<sup>7b</sup> As highlighted in the present paper, the nanotube obtained by the one-step coassembly of HBC<sub>NN</sub> and Co(hfac)<sub>2</sub> (Fig.



**Fig. 2** Schematic representations of the formation of HBC nanotubes with surface-immobilised NN-Co(II) coordination copolymer chains by one-step coassembly of  $\text{HBC}_{\text{NN}}$  with  $\text{Co}(\text{hfac})_2$  ( $\text{NT}_{\text{NN}/\text{Co}}$ ; upper) and two-step coassembly upon post treatment of preassembled metal-free  $\text{NT}_{\text{NN}}$  with  $\text{Co}(\text{hfac})_2$  ( $\text{NT}_{\text{NN}/\text{Co}}$ ; lower).

2, upper) has enhanced magnetic susceptibility below 10 K, reminiscent of the reported single-chain magnetic behaviour of the crystalline NN-Co(II) copolymer,<sup>3,4</sup> although nanotube prepared by post-functionalisation of  $\text{NT}_{\text{NN}}$  with  $\text{Co}(\text{hfac})_2$  (Fig. 2, lower) has no special magnetic properties.

$\text{HBC}_{\text{NN}}$  was synthesised by etherification of the hydroxyl group of precursor **5** with NN derivative **4** bearing a 4-(bromomethyl)phenyl group (Scheme S1 in ESI†). Electronic absorption spectroscopy of a 1,2-dichloroethane (DCE) solution of  $\text{HBC}_{\text{NN}}$  (Fig. 3a) reveals a rather broad absorption band at 550–700 nm due to an  $n-\pi^*$  transition of the NN groups,<sup>8</sup> along with an intense absorption band at 365 nm due to a  $\pi-\pi^*$  transition of the HBC core.<sup>5</sup> Because of the presence of an unpaired electron in the NN groups,  $\text{HBC}_{\text{NN}}$  in electron spin resonance (ESR) spectroscopy displays a well-resolved quintuplet signal in  $\text{CH}_2\text{Cl}_2$  (Fig. S1 in ESI†).<sup>8</sup>

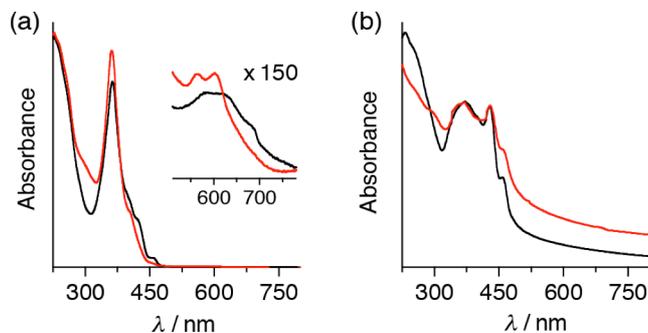
When pentane vapour was allowed to diffuse at 25 °C over a period of 12 h into a DCE solution (1 mL) of a mixture of  $\text{HBC}_{\text{NN}}$  (0.32  $\mu\text{mol}$ ) and  $\text{Co}(\text{hfac})_2$  (0.40  $\mu\text{mol}$ ), nanotube  $\text{NT}_{\text{NN}/\text{Co}}$  formed quantitatively as a precipitate (one-step protocol; Fig. 2, upper). The precipitate was collected by centrifugation and washed twice with DCE/pentane (1/2 v/v) to allow isolation of  $\text{NT}_{\text{NN}/\text{Co}}$ . As confirmed by scanning and transmission electron microscopy (SEM and TEM, respectively; Fig. 4a),  $\text{NT}_{\text{NN}/\text{Co}}$  is uniform in diameter (20 nm) and wall thickness (3 nm).

Electronic absorption spectroscopy of a cast film of  $\text{NT}_{\text{NN}/\text{Co}}$  reveals *J*-aggregated HBC absorption bands at 429 and 462 nm (Fig. 3b). Infrared spectrum displays  $\text{CH}_2$  stretching vibrations at 2917 ( $\nu_{\text{anti}}$ ) and 2848  $\text{cm}^{-1}$  ( $\nu_{\text{sym}}$ ), indicating that the dodecyl side chains of  $\text{HBC}_{\text{NN}}$  adopt an extended conformation and interdigitate with one another to support the bilayer wall structure.<sup>5c,9</sup> The spectral features thus observed are characteristic of previously reported nanotubularly

assembled HBC derivatives.<sup>5–7</sup> Furthermore, the powder X-ray diffraction (XRD) pattern of  $\text{NT}_{\text{NN}/\text{Co}}$  (Fig. S2a in ESI†) is nearly the same as that of  $\text{NT}_{\text{Me}}$ , consisting of helically stranded columnar arrays of  $\pi$ -stacked HBC units (Figs. 1b and S2b in ESI†).<sup>5c</sup>

As determined by inductively coupled plasma–atomic emission spectroscopy (ICP-AES), the  $[\text{Co}(\text{II})]/[\text{HBC}_{\text{NN}}]$  ratio in  $\text{NT}_{\text{NN}/\text{Co}}$ , isolated by precipitation (*vide ante*), is 0.93 (Fig. S3 in ESI†), which is nearly that expected for the ideal case with all NN groups coordinated to Co(II). In support of this metal coordination interaction, the stretching vibration band due to the N–O group (1352  $\text{cm}^{-1}$ ) of  $\text{NT}_{\text{NN}/\text{Co}}$  is shifted by 10  $\text{cm}^{-1}$  from that of  $\text{HBC}_{\text{NN}}$  alone (1362  $\text{cm}^{-1}$ ).<sup>10</sup> This coordination event appears to occur rapidly; as shown in the inset of Fig. 3a, the  $n-\pi^*$  transition due to the NN groups of  $\text{HBC}_{\text{NN}}$  (black curve) displays a blue shift (red curve) as soon as an equimolar amount of  $\text{Co}(\text{hfac})_2$  is added to a DCE solution of  $\text{HBC}_{\text{NN}}$ .<sup>11</sup> Also noteworthy, without pentane vapour under conditions otherwise identical to the above, no spectral change associated with the HBC  $\pi$ -stacking occurs (Fig. 3b, red curve). Therefore, the assembling precursor for  $\text{NT}_{\text{NN}/\text{Co}}$  under vapour diffusion conditions is most likely a Co(II)-bridged coordination oligomer of  $\text{HBC}_{\text{NN}}$  rather than metal-free  $\text{HBC}_{\text{NN}}$ .

We also found that, even in the absence of  $\text{Co}(\text{hfac})_2$ ,  $\text{HBC}_{\text{NN}}$  under analogous vapour diffusion conditions can self-assemble into nanotube  $\text{NT}_{\text{NN}}$ , whose spectral (Fig. 3b, black curve) and dimensional (Fig. 4c) features as well as XRD pattern (Fig. S2 in ESI†), are substantially identical to those of  $\text{NT}_{\text{NN}/\text{Co}}$ . However, in the absence of  $\text{Co}(\text{hfac})_2$ , the assembly proceeded very sluggishly. For example, a DCE solution of  $\text{HBC}_{\text{NN}}$  under the diffusion of pentane vapour was immersed for 12 h at 25 °C, and an aliquot of the mixture, after being air-dried, was subjected to SEM microscopy, where no nanotubular assembly but only irregular aggregates, presumably formed in the air-drying process, were detected (Fig. 4b).



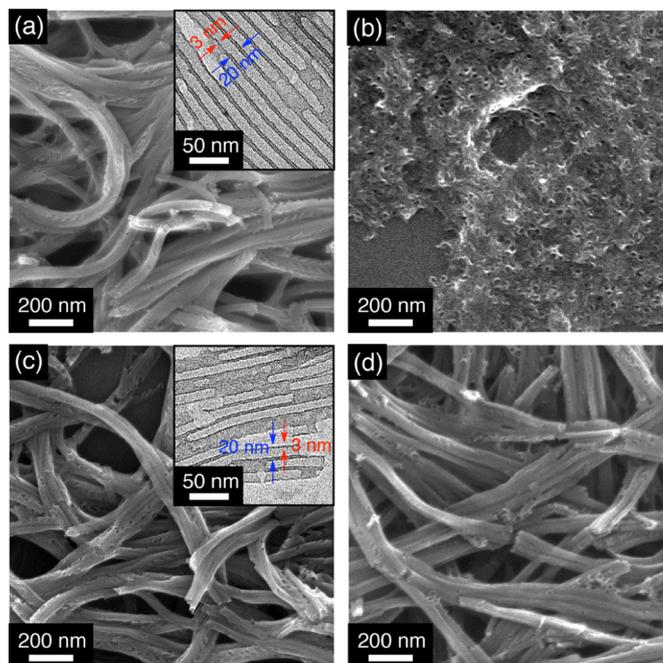
**Fig. 3** (a) Electronic absorption spectra at 25 °C of DCE solutions of HBC<sub>NN</sub> (0.32 mM, black) and a 1:1 mixture of HBC<sub>NN</sub> and Co(hfac)<sub>2</sub> (0.32 mM for each, red). Inset shows magnified spectra in the range of 510–780 nm. (b) Electronic absorption spectra at 25 °C of cast films of NT<sub>NN</sub> (black) and NT<sub>NN/Co</sub> (red) on a quartz plate.

In contrast, when the immersion was carried out for a much longer period, such as 96 h, only nanotubes (NT<sub>NN</sub>) were detected (Fig. 4c).

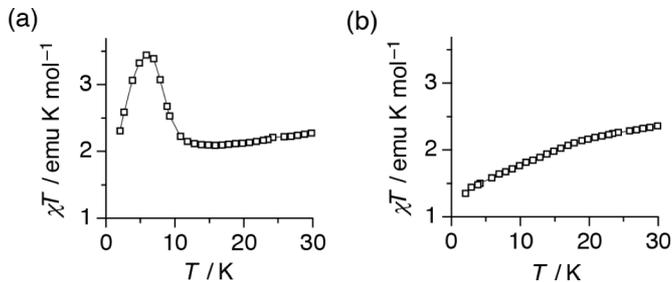
According to the two-step protocol (Fig. 2, lower), metal-free NT<sub>NN</sub> is converted into NT<sub>NN/Co</sub> by treatment with Co(hfac)<sub>2</sub>. For example, NT<sub>NN</sub> (0.32 mM) was mixed with Co(hfac)<sub>2</sub> (0.40 mM) in DCE/pentane (1/2 v/v), and the mixture was gently stirred at 25 °C for 72 h. Then, the reaction mixture was centrifuged, and a precipitate, after being washed twice with DCE/pentane (1/2 v/v), was collected. As observed by SEM (Fig. 4d), the resulting nanotubes (NT<sub>NN/Co</sub>) maintain high structural integrity comparable to that of NT<sub>NN</sub>. The ratio [Co(II)]/[HBC<sub>NN</sub>], as determined by ICP-AES, is 0.92 (Fig. S3 in ESI<sup>†</sup>), which is virtually identical to that of NT<sub>NN/Co</sub> prepared by the coassembly of HBC<sub>NN</sub> with Co(hfac)<sub>2</sub> ([Co(II)]/[HBC<sub>NN</sub>] = 0.93). Together with a clear shift of the N–O stretching vibration from 1362 to 1352 cm<sup>-1</sup>,<sup>10</sup> we conclude that almost all NN groups in NT<sub>NN</sub> accommodate a Co(II) ion.

Analogous to HBC<sub>NN</sub>, its nanotubular assembly NT<sub>NN</sub> is ESR-active due to an unpaired electron at the NN groups (Fig. S4c in ESI<sup>†</sup>). Upon lowering the temperature, the ESR signal of solid-state NT<sub>NN</sub> becomes intensive monotonically. As expected, NT<sub>NN/Co</sub> and NT<sub>NN/Co</sub> are both ESR-active, and their spectral profiles are virtually identical even in a low temperature range (Figs. S4a and S4b in ESI<sup>†</sup>). However, distinctly different from the case of NT<sub>NN</sub>, the ESR signals of both NT<sub>NN/Co</sub> and NT<sub>NN/Co</sub>, upon cooling, becomes initially enhanced but deteriorate suddenly when the temperature reaches approximately 50 K.<sup>12</sup> This difference is caused by a NN–Co(II) spin-spin interaction, as also supported below by the ESR spectral profile due to Co(II). Co(hfac)<sub>2</sub> as a reference is ESR-silent at 300 K but displays a set of rather broad split signals at a lower temperature such as 40 K (Fig. S4d in ESI<sup>†</sup>). As in the case of Co(hfac)<sub>2</sub>, the Co(II) centres in both NT<sub>NN/Co</sub> and NT<sub>NN/Co</sub> are ESR-silent at 300 K but are ESR-active upon cooling, displaying a broad signal (Figs. S4a and S4b in ESI<sup>†</sup>).<sup>13</sup>

As described above, no substantial difference in ESR is present between NT<sub>NN/Co</sub> and NT<sub>NN/Co</sub>. However, their magnetic susceptibilities are clearly different. As shown in Fig. S5a in ESI<sup>†</sup>, the  $\chi T$  values ( $\chi$ : molar magnetic susceptibility) of NT<sub>NN/Co</sub> and NT<sub>NN/Co</sub> at 300 K are 3.18 and 3.12 emu K mol<sup>-1</sup>, respectively. These values are close to that (3.30 emu K mol<sup>-1</sup>) expected for an equimolar mixture of magnetically non-coupled Co(II) ( $S = 3/2$ ,  $g_{Co} = 2.5$ ) and NN radicals ( $S = 1/2$ ,  $g_{NN} = 2.0$ ).<sup>14</sup> Upon cooling, the  $\chi T$  values of NT<sub>NN/Co</sub> and NT<sub>NN/Co</sub> gradually decrease, with a Weiss constant ( $\theta$ ) of -17.2 and -13.1 K, respectively (Figs. S5b and S5c in ESI<sup>†</sup>). Notably, at a temperature below 10 K, NT<sub>NN/Co</sub> exhibits an



**Fig. 4** SEM micrographs of cast films of (a) HBC<sub>NN</sub> (0.32 μmol) assembled in DCE (1.0 mL) upon diffusion of pentane vapour for 12 h in the presence of Co(hfac)<sub>2</sub> (0.40 μmol) [NT<sub>NN/Co</sub>], (b, c) HBC<sub>NN</sub> (0.32 μmol) assembled in DCE (1.0 mL) upon diffusion of pentane vapour for 12 h (b; ill-defined aggregates) and 96 h (c; NT<sub>NN</sub>), and (d) metal-free NT<sub>NN</sub> immersed for 72 h in a DCE/pentane (1/2 v/v) solution of Co(hfac)<sub>2</sub> (0.40 μmol) [NT<sub>NN/Co</sub>]. Insets in (a) and (c) show TEM micrographs of NT<sub>NN/Co</sub> and NT<sub>NN</sub>, respectively. Blue and red remarks indicate diameters and wall thicknesses of the nanotubes.



**Fig. 5**  $\chi T$ - $T$  plots of (a) NT<sub>NN/Co</sub> and (b) NT<sub>NN/Co</sub> under a magnetic field of 100 Oe.

abrupt increase in  $\chi T$  (Fig. 5a),<sup>13,15</sup> whereas NT<sub>NN/Co</sub> displays only a monotonic and moderate decrease (Fig. 5b).

The observed difference in magnetic susceptibility between NT<sub>NN/Co</sub> and NT<sub>NN/Co</sub> most likely reflects a possible difference in the orientational integrity of their NN–Co(II) coordination copolymer chains. For such coordination polymer chains to exert the property of so-called ‘single-chain magnet’ upon clustering, they must unidirectionally align and be insulated from one another, as previously described.<sup>3,4</sup> Although the magnetic behaviour of NT<sub>NN/Co</sub> in Fig. 5a is merely a small sign of ferrimagnetic spin coupling, we assume that its NN–Co(II) coordination copolymer chains are, to some extent, unidirectionally oriented, considering that their construction is driven by a  $\pi$ -stacking interaction among the

HBC pendants (Fig. 2, upper). In contrast, the NN-Co(II) coordination copolymer chains in  $\text{NT}_{\text{NN/Co}}$ , which are not interesting magnetically (Fig. 5b), should form via random positioning of Co(II) ions on the nanotube surface to connect the NN groups (Fig. 2, lower), where unidirectional orientation of the coordination copolymer chains is unlikely.

In summary, coassembly of NN-containing HBC ( $\text{HBC}_{\text{NN}}$ ) and  $\text{Co}(\text{hfac})_2$  forms nanotube  $\text{NT}_{\text{NN/Co}}$ , with NN-Co(II) coordination copolymer chains immobilised on the outer and inner surfaces. At a temperature below 10 K, this nanotube shows an abrupt enhancement in  $\chi T$ . Although a nanotube with substantially identical chemical composition and dimensional aspect ( $\text{NT}_{\text{NN/Co}}$ ) is available by post-functionalisation of a metal-free  $\text{HBC}_{\text{NN}}$  nanotube with  $\text{Co}(\text{hfac})_2$ , no particular magnetic features exist, even at very low temperatures. From these contrasting results, together with the reported single-chain magnetic crystal of NN-Co(II) copolymers, we conclude that the assembling trajectory for  $\text{NT}_{\text{NN/Co}}$  has a critical role in the emergence of its unique magnetic feature.

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## Notes and references

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