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Introduction

In recent years, the field of molecular magnetism has been a hot research topic, in which great progress has been achieved.^{1,2} The design and synthesis of molecule-based magnets, especially one-dimensional (1D) magnets (so-called single-chain magnets (SCMs)), with organic bridging ligands and transition metals continues to be a productive area due to their intriguing structures, unique physical characteristics, and promising novel applications, such as magnetic sensors, magnetic switches and multifunctional magnetic devices.^{3,4} Coordination chemistry is a powerful tool for accessing such systems, and a common strategy is to connect paramagnetic metal centers with short bridging groups ($C_2O_4^{2-}$, CN^- , SCN^- , N_3^- , *etc.*) to transmit magnetic coupling.⁵ There is a clear

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Effect of phenylacetic acid coligands on the structures and magnetic properties of azido-bridged copper(II)-chain compounds†

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To explore and alter the structures of azido–copper(II) chain compounds, as well as investigate how their magnetic properties are influenced by substituents on the phenylacetic acid coligands, three new azido-bridged Cu(II) compounds, [Cu(o-npa)(N₃)(H₂O)]_n (1), [Cu(p-npa)(N₃)]_n (2) and [Cu(p-mpa)(N₃)]_n (3) (o-Hnpa = o-nitrophenylacetic acid, p-Hnpa = p-nitrophenylacetic acid, and p-Hmpa = p-methylphenylacetic acid), have been successfully obtained, and structurally and magnetically characterized. Single-crystal structure analyses indicate that the azido ligands adopt the single end-on (EO) mode to connect adjacent Cu(II) centers in all three compounds. In compounds 1 and 2, the carboxylate groups exhibit the same μ_2 -bridging bidentate mode. Although compound 2 exhibits a 2D layer-structure formed through connections between the p-NO₂ groups on the aromatic rings and 1D Cu(III)-chains, 2 shows similar intrachain ferromagnetic coupling to 1. When p-methylphenylacetic acid is employed as a coligand, compound 3 exhibits a 2D layer-structure, in which the carboxylate adopts a μ_3 -bridging tridentate mode to shorten the distance between Cu(III)-chains. Due to the counter-complementarity of the superexchange pathways in this system, compound 3 behaves as a magnet with a spontaneous magnetization temperature of 7 K.

relationship between the coordination mode of azido and the way in which coupling is transmitted: the μ -1,1 (end-on, EO) and µ-1,3 (end-to-end, EE) coordination modes generally transmit ferromagnetic (FM) and antiferromagnetic (AFM) exchange interactions respectively, which is helpful for predicting the magnetism of the compounds,⁵ although there are several exceptions.⁶ In addition, plenty of compounds feature mixed azido bridging modes and also show interesting magnetic properties.⁷ Among metal-azido-bridged systems, transition metal-azido-bridged compounds have attracted considerable attention, especially Cu(II)-azido-bridged coordination polymers.8 Recently, combining azido and coligands in one system has been an interesting approach for constructing new structures and modulating magnetic behaviour.9 Considering that the carboxylate group can also efficiently transmit magnetic exchange, introducing carboxylate into metal-azido systems would increase the structural diversity and modulate the magnetic behaviour of the compounds, giving a large number of coordination polymers with diverse topologies and magnetic properties,9 for example, pyridylcarboxylates,^{10a} pyridylacrylates,^{10b} pyridine carboxylate N-oxide,^{10c} dicarboxylates,^{10d} and aromatic carboxylate derivatives.^{11a} Similarly, non-coordinating substituents in the o, m, or p position of the aromatic ring of the benzoic acid coligand could influence the structural properties of the compounds, such as Cu--Cu distances, Cu-N-Cu angles and intrachain



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[†] Electronic supplementary information (ESI) available: Selected bond lengths and angles are listed in Tables S1–S3. Fig. S3 shows XRPD graphs of compounds 1–3. CCDC reference numbers are 972618 (1), 972616 (2) and 972617 (3). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3ce42532k

separations of the Cu(n) ions, and further affect the magnetic behaviour of the compounds.¹¹ Extending the idea above, if phenylacetic acid is selected as coligand instead of benzoic acid, do the substituents on the aromatic ring affect the coordination mode of the carboxylate groups? Furthermore, how do the intrachain structure and the magnetic behaviour of the Cu(n)-azido system change?

In order to answer the questions above, three phenylacetate coligands with o-nitro, p-nitro and p-methyl substituents were introduced into the Cu(II)-azido system. Herein we report the synthesis and characterization of three new azido-Cu(II) compounds which are formulated as $[Cu(o-npa)(N_3)(H_2O)]_n$ (1), $[Cu(p-npa)(N_3)]_n$ (2) and $[Cu(p-mpa)(N_3)]_n$ (3). Compounds 1 and 2, in which nitro groups are located at the o and p positions of the phenylacetic acids, respectively, display similar intrachain structures with mixed EO-azido and syn-syn carboxylate bridges. 1 is an infinite 1D chain, while 2 has a 2D layer-structure. Magnetic data indicate that both 1 and 2 exhibit intrachain ferromagnetic interactions. Interestingly, compound 3 behaves as a 2D ordered magnet with a phase transition temperature of about 7 K because the carboxylate groups adopt a μ_3 -bridging tridentate mode due to the methyl group in the phenylacetic acid.

Experimental section

Physical measurements

Elemental analyses (C, H, N) were performed on a Perkin-Elmer 2400 CHN elemental analyzer. The FT-IR spectra were recorded in the range 400-4000 cm⁻¹ using KBr pellets on an EQUINOX55 FT/IR spectrophotometer. The phase purity of the bulk or polycrystalline samples was verified by X-ray powder diffraction (XRPD) measurements performed on a Rigaku RU200 diffractometer at 60 kV and 300 mA, with Cu K α radiation (λ = 1.5406 Å), a scan speed of 5° min⁻¹ and a 2θ step size of 0.02°. Temperature-dependent magnetic measurements were performed on a Quantum Design MPMS XL-7 SQUID magnetometer. Magnetic susceptibility measurements were collected in the range of 2-300 K, under an applied field of 1 kOe, and ac magnetization measurements were taken at 1.8 K from 0 to 50 kOe. All data were corrected for diamagnetism estimated from Pascal's constants, and an experimental correction for the sample holder was applied.

Materials and methods

All of the solvents and reagents for synthesis are of analytical grade and are commercially available. $CuCl_2 \cdot 6H_2O$, *o*-nitrophenylacetic acid (*o*-Hnpa), *p*-nitrophenylacetic acid (*p*-Hnpa), *p*-methylphenylacetic acid (*p*-Hmpa) and NaN₃ were purchased from commercial sources and used without further purification.

Caution! Although we have not experienced any problems in our experiments, azido and its compounds are potentially explosive; only a small amount of material should be prepared, and should be handled with care.

Synthesis

Preparation of $[Cu(o-npa)(N_3)(H_2O)]_n$ (1). Compound 1 was hydrothermally synthesized under autogenous pressure. A mixture of CuCl₂·6H₂O (0.0517 g, 0.3 mmol), NaN₃ (0.0196 g, 0.3 mmol), and *o*-Hnpa (0.0908 g, 0.5 mmol) in 6 mL H₂O was sealed in a Teflon-lined stainless steel autoclave and heated to 140 °C. After 72 h, the reaction vessel was cooled to room temperature at 10 °C h⁻¹. Large block-like dark green crystals were collected. Yield: 68% (based on Cu). Anal. calcd for C₈H₈CuN₄O₅ (%): C, 31.61; H, 2.63; N, 18.44. Found (%): C, 31.71; H, 2.59; N, 18.49. IR (KBr, cm⁻¹): 3497 (m), 2968 (s), 2085 (vs), 1684 (vs), 1568 (s), 1523 (s), 1394 (s), 1292 (w), 791 (w), 719 (m), 690 (w), 494 (w).

Preparation of $[Cu(p-npa)(N_3)]_n$ (2). A mixture of CuCl₂·6H₂O (0.0342 g, 0.2 mmol), *p*-Hnpa (0.0362 g, 0.2 mmol), and NaN₃ (0.0131 g, 0.2 mmol) in 15 mL H₂O was stirred for 2 h at room temperature. A deep green solution was formed and filtered, and then the filtrate was left to slowly evaporate at room temperature. Dark green crystals of 2 were obtained within two weeks. Yield: 52% (based on Cu). Anal. calcd for C₈H₆CuN₄O₄ (%): C, 33.60; H, 2.10; N, 19.60. Found (%): C, 33.56; H, 2.02; N, 19.69. IR (KBr, cm⁻¹): 3458 (m), 2916 (w), 2080 (vs), 1649 (s), 1551 (s), 1409 (s), 1229 (w), 732 (m), 598 (w), 534 (w).

Preparation of $[Cu(p-mpa)(N_3)]_n$ (3). The synthetic procedure for 3 was similar to that for 2, but *p*-Hnpa was replaced with *p*-Hmpa. Dark green crystals were collected after a week. Yield: 42% (based on Cu). Anal. calcd for C₉H₉CuN₃O₂ (%): C, 42.40; H, 3.53; N, 16.49. Found (%): C, 42.50; H, 3.46; N, 16.58. IR (KBr, cm⁻¹): 3447 (m), 2926 (w), 2093 (vs), 1634 (s), 1531 (s), 1400 (s), 1269 (w), 723 (m), 588 (w), 513 (w).

Crystallographic data collection and refinement

Suitable single crystals of the three compounds were mounted on glass fibers for X-ray measurements. Reflection data were collected at room temperature on a Bruker SMART APEX-CCD-based diffractometer using graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å). An empirical absorption correction was applied using the SADABS program.¹² Data processing was accomplished with the SAINT processing program. The structures were solved by direct methods and refined on F^2 with full-matrix least-squares using the SHELXTL 97 program.¹³ All non-hydrogen atoms were refined with anisotropic displacement parameters. Selected crystallographic data and structural refinement details for 1, 2 and 3 are summarized in Table 1. Selected bond lengths and bond angles are listed in Tables S1–S3.†

Results and discussion

Description of structures

Crystal structure of $[Cu(o-npa)(N_3)(H_2O)]_n$ (1). Single-crystal X-ray diffraction analysis reveals that compound 1 crystallizes in the monoclinic space group $P2_1/n$. The asymmetric unit of 1 consists of one Cu(π) ion, one azido ligand, one *o*-npa ligand and one coordinated water molecule. As shown in Fig. S1(a),†

Table 1 Selected crystallographic data for the three compounds 1, 2 and 3

Compound	1	2	3
Empirical formula	C ₈ H ₈ CuN ₄ O ₅	C ₈ H ₆ CuN ₄ O ₄	C ₉ H ₉ CuN ₃ O ₂
Formula weight	303.72	285.71	254.73
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/c$
a (Å)	13.5498(16)	6.785(5)	17.787(3)
b (Å)	6.5985(8)	7.594(6)	6.6764(13)
c (Å)	13.6226(16)	10.591(8)	8.4841(16)
α (°)	90	70.714(15)	90
$\beta(\circ)$	116.118(2)	77.11(14)	102.003(3)
γ (°)	90	88.869(14)	90
$V(Å^3)$	1093.6(2)	501.3(7)	985.5(3)
Z	4	2	4
$D (g \text{ cm}^{-3})$	1.845	1.893	1.717
$Mu(mm^{-1})$	2.018	2.188	2.197
$F(0 \ 0 \ 0)$	612	286	516
Unique reflections	1937	1736	1816
Observed reflections	5269	1736	4869
R _{int}	0.0358	0.0000	0.0696
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0331, wR_2 = 0.0795$	$R_1 = 0.0858, wR_2 = 0.1803$	$R_1 = 0.0508, wR_2 = 0.1210$
<i>R</i> indices (all data)	$R_1 = 0.0439, wR_2 = 0.0855$	$R_1 = 0.1716, wR_2 = 0.2360$	$R_1 = 0.0907, wR_2 = 0.1628$
Goodness-of-fit on F^2	1.075	1.049	1.003

the Cu(n) ion has a slightly distorted octahedral geometry. The equatorial square is composed of two nitrogen atoms (Cu1–N1 = 2.004 Å, Cu1–N1A = 2.021 Å) from two azido ligands and two oxygen atoms (Cu1–O1 = 1.922 Å, Cu1–O1A = 1.939 Å) from two carboxylate groups of the *o*-npa ligands. The apical positions are occupied by two oxygen atoms (Cu1–O2 = 2.807 Å, Cu1–O2A = 2.427 Å) from two coordinated water molecules. Adjacent Cu(n) ions are bridged by EO-azido, μ_2 -bridging bidentate carboxylate bridges and water oxygen atoms, with a Cu–N–Cu angle of 110.3°, a Cu–O–Cu angle of 77.9° and a Cu···Cu distance of 3.303 Å to form an isolated 1D mixed carboxylate/EO-azido/H₂O bridged copper chain along the *b* direction (Fig. 1).

Crystal structure of $[Cu(p-npa)(N_3)]_n$ (2). Compound 2 crystallizes in the triclinic space group $P\bar{1}$ and contains two types of crystallographically independent Cu(II) ions, Cu1 and Cu2, each lying at an inversion center but possessing different geometries. As illustrated in Fig. S1(b),† Cu1 adopts a slightly distorted octahedral geometry, while Cu2 is in a square-planar environment. The equatorial plane of Cu1 consists of two nitrogen atoms (Cu1–N1 = 1.917 Å, Cu1–N1A = 1.917 Å) from two equivalent single EO mode azido ligands

and two oxygen atoms (Cu1-O1 = 1.917 Å, Cu1-O1A = 1.917 Å) from two equivalent carboxylate groups. Two nitro oxygen atoms (Cu1-O2 = 2.514 Å, Cu1-O2A = 2.514 Å) from another two *p*-npa ligands occupy the axial sites. Cu2 is equatorially coordinated by two nitrogen atoms (Cu2-N1A = 1.993 Å, Cu2-N1B = 1.993 Å) from two azido ligands and two oxygen atoms (Cu2-O3 = 1.934 Å, Cu2-O3A = 1.934 Å) from two carboxylate groups. In 2, one carboxylate group bridges two $Cu(\pi)$ ions via a μ_2 -bridging bidentate mode. Unlike in compound 1, one nitro group of the *p*-npa ligand binds another $Cu(\pi)$ ion *via* a monodentate mode. This may be attributed to a steric hindrance effect resulting from the different position of the nitro group. The metal ions alternate in the Cu1-Cu2-Cu1 sequence to generate a 1D mixed carboxylate/EO-azido bridged chain along the *a* direction (Fig. 2) in 2. The intrachain Cu…Cu separation is 3.393 Å, and the Cu1-N1-Cu2 angle is 120.4°, which is much larger than the 108° Cu-N-Cu angles in other Cu(II)-EO-azido systems.^{5c,8b,11a,14,15} Furthermore, neighbouring chains are cross-linked by coordinated nitro groups from the *p*-npa ligands to afford a 2D layer along the ac plane (Fig. S2[†]), with the nearest interchain Cu…Cu separation of 10.375 Å spanned by the *p*-npa ligands.



Fig. 1 The Cu(μ)-chain in compound 1 with mixed water oxygen, carboxylate and azido bridges. Benzene rings and H atoms have been omitted for clarity.



Fig. 2 The uniform chain with mixed double bridges (*syn-syn* carboxylate and EO-azido) in compound 2. Benzene rings and H atoms have been omitted for clarity.

Crystal structure of $[Cu(p-mpa)(N_3)]_n$ (3). Although obtained by the same synthetic method, compound 3 displays an entirely different structure compared to 2. The single-crystal X-ray diffraction analysis suggests that compound 3 crystallizes in the monoclinic space group $P2_1/c$ and adopts a 2D coordination network structure. The asymmetric unit is built up from one Cu(II) ion, one azido ligand and one p-mpa ligand. All Cu(II) ions are fivecoordinate with a slightly distorted square-based pyramidal geometry (Fig. S1(c)[†]). The apical position of Cu1 is occupied by one oxygen atom (Cu1-O1 = 2.594 Å) from one carboxylate group, and the equatorial plane is formed by two oxygen atoms (Cu1-O2 = 1.926 Å, Cu1-O3 = 1.960 Å) from another two carboxylate groups and two nitrogen atoms (Cu1-N1 = 1.979 Å, Cu1-N1A = 1.973 Å) from two azido ligands. Single EO-azido and carboxylate bridges link two Cu(II) ions to form a 1D Cu(II) chain (Fig. 3), in which the Cu1-N-Cu1A angle is 122.4° and the Cu1…Cu1A distance is 3.463 Å. Furthermore, the carboxylate groups link the Cu1B ions in these 1D Cu(II) chains to form a 2D coordination network (Fig. 4). The carboxylate groups adopt the μ_3 -bridging tridentate coordination mode, which significantly lessens the distance between two neighbouring chains. The shortest $Cu(\pi)$ ion separation between two neighbouring chains is 3.662 Å. For 3, the methyl groups on the p-mpa ligands affect the coordination mode of the carboxylate groups and the conformation of the 2D layers, which may stem from the electronic effect of the substituent on the coligand.



Fig. 4 The μ_3 -bridging tridentate carboxylate groups connect adjacent chains, forming a 2D sheet in compound 3. Benzene rings and H atoms have been omitted for clarity.

increases smoothly between room temperature and 50 K, and then sharply reaches a maximum value of 6.86 cm³ K mol⁻¹ at 2.58 K. Eventually, it decreases rapidly to 6.40 cm³ K mol⁻¹ at 2 K. This type of curve is typical of strong ferromagnetic coupling between Cu(π) ions, noticeable at very low temperatures. The final decrease in $\chi_M T$ may be attributed to the saturation effect or the presence of interchain AFM interactions. The data above 70 K follow the Curie–Weiss law with a Curie constant *C* of 0.55 cm³ K mol⁻¹ and a Weiss constant Θ of 37.68 K (Fig. 5, inset). The positive Θ value confirms the ferromagnetic coupling between the Cu(π) centers, and the *C* value falls in the usual range expected for Cu(π) ions. The magnetic data of 1 were fitted using the following equations:⁷

$$\chi = \frac{Ng^2\beta^2}{4kT} \left[\frac{1+5.7979916x+16.902653x^2+29.376885x^3+29.832959x^4+14.036918x^5}{1+2.7979916x+7.008678x^2+8.6538644x^3+4.5743114x^4} \right]^{\frac{1}{3}}$$
(1)

Magnetic studies

The crystalline samples of 1–3 were all phase-pure, as confirmed by XRPD (see Fig. S3 in the ESI†). According to the obtained data, a dominant ferromagnetic coupling between the $Cu(\pi)$ ions in compounds 1–3 can be suggested.

Magnetic properties of $[Cu(o-npa)(N_3)(H_2O)]_n$ (1). The magnetic properties of 1 are shown in Fig. 5 in the form of a $\chi_M T$ versus T plot (χ_M is the molar magnetic susceptibility per Cu(n) ion). The $\chi_M T$ value at 300 K is equal to 0.55 cm³ K mol⁻¹, which is higher than the expected value (0.375 cm³ K mol⁻¹) for magnetically isolated Cu(n) ions (S = 1/2, g = 2.0). Upon cooling, the $\chi_M T$ value



Fig. 3 The mixed carboxylate/EO-azido bridges form a 1D chain in compound 3. Benzene rings and H atoms have been omitted for clarity.

$$\chi_{\rm M}T = \frac{\chi T}{1 - (zJ'/Ng^2\beta^2)\chi}$$
(2)

$$x = J/2kT \tag{3}$$

The best fit of the magnetic susceptibility data resulted in $g = 2.26, J = 35.44 \text{ cm}^{-1}$, and $zJ' = -0.13 \text{ cm}^{-1} (zJ' \text{ describes the})$ interchain antiferromagnetic interaction). The large J value confirms the strong ferromagnetic coupling between the $Cu(\pi)$ centers, while the small negative zJ' value indicates the presence of weak interchain AFM interactions over the long interchain distance, consistent with the drop in the $\chi_M T$ product at low temperature. Magnetization versus field data were collected for 1 at 2 K (Fig. S4[†]). The M value increases very rapidly in the low field region and rises gradually as the field increases, reaching a saturation value of $1.18N\beta$ at higher fields, as expected for one Cu(II) ion with g = 2.0, demonstrating ferromagnetic coupling along the $Cu(\pi)$ chain. To corroborate the existence of ferromagnetic long-range ordering, measurements of the ac susceptibility and hysteresis loop were carried out, but showed negative results.



Fig. 5 $\chi_M T$ vs. T plot for compound 1. The solid line is the fit to the experimental data. Inset: $1/\chi_M$ vs. T plot; the red solid line is the best fit to the Curie-Weiss law.

According to the structural data, the system can be treated as an infinite uniform chain in which magnetic coupling is mediated through the triple bridges (one EO-azido, one syn-syn carboxylate and one coordinated water molecule bridge). It is well known that a syn-syn carboxylate bridge can transmit AFM interactions between neighbouring metal ions.⁷ EO-azido is certainly one of the most interesting magnetic couplers in molecular magnetism, and the magnitude of the J parameter depends on several factors, but mainly the Cu-N-Cu angle (θ). The single EO azido bridge should also mediate FM coupling, according to a number of studies on Cu(II) systems with such bridges. According to previous reports,⁸ EO-azido bridging of Cu(II) ions with low θ results in ferromagnetic coupling, but the coupling is antiferromagnetic if the angle is above a critical θ value, which has been evaluated to be about 108°.5c,8b,11a,14,15 However, compound 1 displays ferromagnetic behaviour and has a Cu-N-Cu angle of 110.3°, which is similar to some refuted reports.^{11a} For two metal ions linked by multiple bridges, the overall coupling cannot be simply described as an algebraic sum of the contributions arising from each bridge, which may exhibit counter-complementarity of the superexchange pathways in such systems.¹⁶⁻¹⁸ Thus the AFM contributions of each bridge in 1 cancel each other out, resulting in strong intrachain FM exchange between the Cu(II) ions.

Magnetic properties of $[Cu(p-npa)(N_3)]_n$ (2). The magnetic behaviour of 2 is similar to that of 1, suggesting ferromagnetic coupling. As shown in Fig. 6, the $\chi_M T$ value per Cu(II) at room temperature is about 0.40 cm³ K mol⁻¹, close to the value expected for a magnetically isolated Cu(II) ion. As the temperature is lowered, the $\chi_M T$ value increases smoothly to a maximum at about 5.095 cm³ K mol⁻¹ at 3 K, and then decreases rapidly to 4.266 cm³ K mol⁻¹ at 1.8 K. This indicates that the magnetic interactions among the Cu(II) centers are ferromagnetic, which is further confirmed by a positive Weiss constant Θ of 19.66 K and a Curie constant *C* of 0.365 cm³ K mol⁻¹ obtained by fitting the data to the Curie–Weiss law above 25 K (Fig. 6, inset). Considering that



Fig. 6 $\chi_M T$ vs. T plot for compound 2. The solid line is the fit to the experimental data. Inset: $1/\chi_M$ vs. T plot; the red solid line is the best fit to the Curie-Weiss law.

the interchain magnetic interactions through the long *p*-npa ligands should be much weaker than the intrachain interactions through the short EO-azido and syn-syn carboxylate bridges, the 2D structural framework can be regarded as quasi-1D chains from a magnetic point of view.¹⁹ Thus, using the same simulation equations as for 1, the fit yields g = 2.28, J = 52.25 cm⁻¹, and zJ' = -0.36 cm⁻¹. The positive J value can be interpreted as a consequence of the EO-azido bridges, which result in ferromagnetic coupling. The small negative zJ' value indicates the presence of interchain antiferromagnetic interactions, consistent with the drop in the $\chi_{\rm M}T$ value at 1.8 K. The reduced magnetization is shown in Fig. S5.† The magnetization rises very quickly as the field increases and tends towards saturation at higher fields, as expected for one Cu(II) ion. Indeed, the rapid and abrupt increase in $M/N\beta$ at low field indicates a ferromagnetically ordered state. No hysteresis was observed, and ac magnetic measurements revealed no out-of-phase ac susceptibility signals (Fig. S6 in ESI†), suggesting no long-range ordering or SCM behaviour.

In compound 2, the 2D layers actually consist of 1D chains cross-linked by the ligands, where the 1D chains are created by double syn-syn carboxylate and symmetric EO-azido bridges, which link two consecutive $Cu(\pi)$ ions. Magnetically, the system can be treated as a uniform chain in which magnetic exchange is mediated through the EO-azido and syn-syn carboxylate double bridges, in spite of the fact that adjacent Cu(II)-chains are also connected by nitro groups. The nearest interchain Cu-Cu separation spanned by the p-npa ligands is 10.375 Å. In general, the EO-azido bridge will enable ferromagnetic exchange, while the syn-syn carboxylate will provide a pathway for antiferromagnetic coupling between the Cu(II) centers. However, compound 2 seems to be in disagreement with the expectations mentioned above, exhibiting intrachain ferromagnetic exchange between the Cu(II) ions ($J = 52.25 \text{ cm}^{-1}$). With expansion of the distance between two chains, the interchain antiferromagnetic coupling is weak. In 2, the Cu-N-Cu angle of the EO-azido bridge is 120.4°, which is much larger than the above-mentioned

range of bond angles, 5c,8b,11a,14,15 but overall ferromagnetic behaviour is observed. In addition, the *J* parameter confirms that the ferromagnetic interactions are enabled by the single EO-azido bridges in compound 2.

Magnetic properties of [Cu(p-mpa)(N₃)]_n (3). The magnetic behaviour of compound 3 is remarkably different from that of 1 and 2. The temperature dependence of $\chi_M T$ for compound 3 is shown in Fig. 7 as a $\chi_{M}T$ versus T plot. The value of $\chi_{\rm M}T$ at 300 K is 0.534 cm³ K mol⁻¹, larger than the predicted value of 0.375 cm³ K mol⁻¹ for an isolated Cu(II) ion (S = 1/2) with g = 2.0. As the temperature is lowered from room temperature, the $\chi_{M}T$ value continuously increases to reach a maximum value of 1.418 cm³ K mol⁻¹ at 18 K, and then it decreases rapidly to a value of 0.424 cm³ K mol⁻¹ at 1.9 K, which is attributed to zero-field splitting of the Cu(II)ions or AFM interactions between the chains. As the temperature decreases, the $\chi_{M}T$ product increases, indicating ferromagnetic coupling between the Cu(II) ions within the chains in 3. The Curie–Weiss fit of χ_{M}^{-1} above 60 K results in a Curie constant $C = 0.48 \text{ cm}^3 \text{ K mol}^{-1}$ and a Weiss constant Θ = 33.45 K (Fig. 7, inset). The positive Θ value suggests the presence of dominant ferromagnetic coupling between the Cu(II) ions. Within this compound, the main Cu-bridge-Cu coupling pathways are listed as follows: Cu1-N1-Cu1A, Cu1-(COO)-Cu1A, and Cu1A-O2-Cu1B. With no appropriate magnetic model for a system with various bridges, it is difficult to simulate the magnetic behaviour and calculate the J values from experimental data. At 1.8 K, the field-dependent magnetization increases linearly to a maximum value of $0.75N\beta$ (Fig. S7[†]), indicating that the magnetic moment is still unsaturated (the expected saturated value is $M_s = nSg =$ $1N\beta$). This behaviour is probably due to the significant antiferromagnetic interactions between the Cu(II) ions, since the Cu(II) ions are less anisotropic.²⁰ The field-cooled (FC) and zero-field-cooled (ZFC) magnetization measurements were performed at a low applied field of 10 Oe in the temperature range of 1.8-10 K (Fig. 8). The data diverge below 7 K and the magnetization increases continuously with decreasing



Fig. 7 $\chi_M T$ vs. T plot for compound 3. The solid line is the fit to the experimental data. Inset: $1/\chi_M$ vs. T plot; the red solid line is the best fit to the Curie–Weiss law.





temperature. To corroborate the existence of ferromagnetic long-range ordering, measurements of the ac magnetic susceptibility and hysteresis loop were also carried out for 3. The ac susceptibility measurements were performed in the range 1.8–10 K at frequencies of 1, 10, 100 and 1000 Hz. Fig. 9 shows a peak in the in-phase ($\chi'_{\rm M}$) signal and an out-of-phase ($\chi''_{\rm M}$) signal that is non-zero below 7 K, defining $T_{\rm c}$ for this magnet. No frequency dependence was observed in the ac measurements, thus excluding the possibility of any glassy behaviour in compound 3. Furthermore, as shown in Fig. 10, the hysteresis magnetization was measured at 2 K, 4 K and 10 K within ±6 kOe. A characteristic hysteresis loop with a narrow gap is observed at 4 K, which strongly supports the bulk ferromagnetic ordering of 3.

For 3, the methyl groups of the coligand affect the carboxylate groups linkages, and thus the magnetic behaviour of the compound. In contrast to 1 and 2, the chains are linked *via* tridentate-bridging carboxylate groups, which strengthen the global ferromagnetic behaviour. Compared to 1 and 2, the carboxylate groups in 3 significantly lessen the distance between two neighbouring chains, with a nearest Cu···Cu separation of 3.662 Å. According to the chain topology, there are three sets of magnetic exchange pathways: one *syn–syn* carboxylate bridge, one EO-azido bridge (intrachain) and two



Fig. 9 χ'_{M} and χ''_{M} vs. T plots for compound 3.



Cu–O–Cu bridges from two carboxylate groups (interchain). Antiferromagnetic coupling would be expected for 3, due to the presence of EO-azido bridges, displaying a large Cu–N–Cu angle, together with the *syn–syn* carboxylate bridges featured in the chain. In fact, regardless of the Cu–N–Cu bond angle (122.4°), there is an intrachain ferromagnetic coupling between the Cu(π) ions in 3. Indeed, the strong ferromagnetic coupling behaviour is similar to that of 1. In other words, compound 3 behaves as a 2D ordered magnet.

To deduce a general magneto-structural relationship, we have made a comprehensive comparison of the Cu(II)–azido– benzoate compounds reported in recent years, as shown in Table S4.^{10b,c,11a,c,15a,16,17,21,22}† EO-azido compounds with Cu–N–Cu angles of 126.8°,^{11a} 108.2°,^{11a} 116.8°,^{11a} 109.4°,^{11c} 101.1°,^{11c} 111.9°,¹⁶ and 105.5°^{21d} exhibit strong ferromagnetic coupling. Similarly, in our work, the Cu–N–Cu angles are 110.3°, 120.4° and 122.4°, and the corresponding compounds show ferromagnetic interactions. The coupling constant (*J*) values of compounds 1 and 2 are 35.44 cm⁻¹ and 52.25 cm⁻¹ respectively, which are close to previous results in the literature.^{11a,c,16,21d}

Conclusions

Our interests are to probe how flexible aromatic carboxylate coligands with different substituents influence the structure and magnetism of Cu(π)-azido compounds. Diverse structures and magnetic properties have been observed in the three compounds. Structural analyses show that compound 1 features a 1D three-fold bridged copper chain. Compound 2 exhibits 2D layers in which the Cu(π)-azido chains are interlinked by nitro groups on the *p*-npa ligands. Compound 3 shows 2D layers in which the carboxylate groups adopt a μ_3 -bridging tridentate coordination mode. The magnetic investigations reveal that compounds 1 and 2 show dominant intrachain ferromagnetic coupling, while compound 3 behaves as a magnet. Extension of the carboxylate group

in phenylacetic acid compared to benzoic acid. The different substituents on the aromatic ring may fine-tune the structures and further affect the magnetic properties of the compounds.

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