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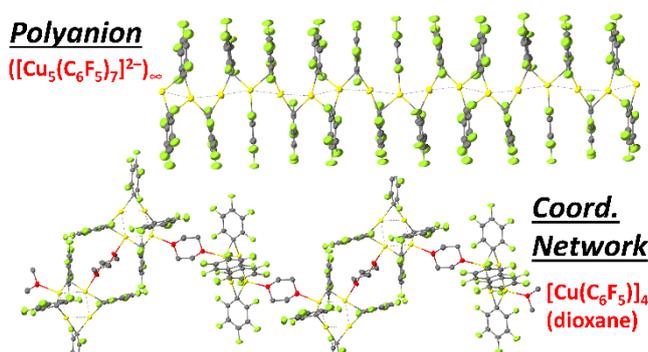
Exploring the Synthesis and Coordination Chemistry of Pentafluorophenyl-Copper: Organocopper Polyanions and Coordination Networks

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Abstract: $[\text{Cu-C}_6\text{F}_5]_4$ is a thermally stable and soluble compound with suitable reactivity for synthetic applications in organic and inorganic chemistry. Here the synthesis of $[\text{Cu-C}_6\text{F}_5]_4$ is explored in different solvents and followed by in-situ ^{19}F NMR spectroscopy. The importance of solvent choice during the synthesis from Grignard reagent $\text{C}_6\text{F}_5\text{MgBr}$ is highlighted, with a range of magnesium cuprate species identified and isolated when THF is used as solvent (rather than Et_2O), including $[\text{Cu}(\text{C}_6\text{F}_5)_2]^-$ and the remarkable organocopper polyanion $([\text{Cu}_5(\text{C}_6\text{F}_5)_7]^{2-})_\infty$. The coordination chemistry of $[\text{Cu-C}_6\text{F}_5]_4$ with 1,4-dioxane is investigated in solution and in the solid state, with an extended coordination network, $[\text{Cu-C}_6\text{F}_5]_4(\text{dioxane})$, structurally resolved for the first time. This structure reveals interwoven linear and zig-zag chains featuring dioxane donors unusually coordinating to adjacent Cu sites of some of the $[\text{Cu-C}_6\text{F}_5]_4$ tetramers.



Introduction

Organocopper compounds are an important class of organometallic reagents.^{1,2} In organic synthesis, they are powerful tools for selective C-C bond forming reactions, often with complementary reactivities compared to organolithium or Grignard reagents.³⁻⁶ Recent examples include C-C couplings using perfluorinated organic groups, which may induce intriguing reactivity trends due to their highly electron withdrawing nature.^{7,8} Furthermore, organocopper reagents are useful synthons for further copper-containing structures,⁹⁻¹¹ including luminescent compounds¹²⁻¹⁵ and ultrasmall Cu or Cu_2O nanoparticles.¹⁶

Organocopper compounds aggregate in solution and in the solid-state through electron-deficient, two-electron, three-centre bonding with bridging organic groups, often as squares or pentagons.⁹ Evidence for weak cuprophillic interactions can be seen in short $\text{Cu}\cdots\text{Cu}$ distances which are less than the sum of the van der Waals radii of two copper atoms (for example, in $[\text{CuC}_6\text{F}_5]_4$ $\text{Cu}\cdots\text{Cu} = 2.44 \text{ \AA}$ ¹⁷ vs $\Sigma r_{\text{vdW}}(\text{Cu}\cdots\text{Cu}) = 2.8 \text{ \AA}$).¹⁸ In combination with more polar organometallic reagents such as organolithiums, organocopper reagents form metal cuprates such as Gilman reagents, $[\text{R}_2\text{CuLi}]_n$.¹⁻³ Copper(I) salts, e.g. CuCl , CuBr or CuCN , are also often used to directly generate mixed aggregates of cuprates by reaction with organolithium, Grignard or even organocopper reagents.^{1-3, 19, 20} The nature of the counter cation, e.g. Li vs Mg, and its interaction with the cuprate, e.g. contact ion pair (CIP) or solvent separated ion pair (SSIP), play important roles in determining the reactivity of the species.^{3, 21} The composition of these aggregates is dependent on the donor abilities of the solvent and may exist as an equilibrium of structures.²² The aggregation state may affect the properties, such as stability, reactivity and enantioselectivity, therefore, knowledge of the aggregation state under reaction

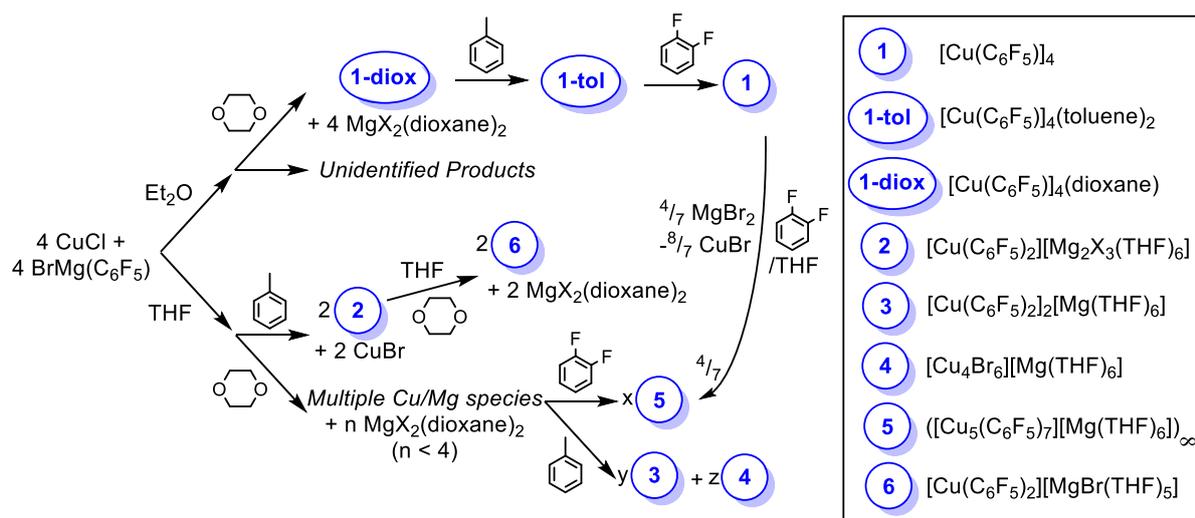
conditions is fundamental to understanding these complexes.³ Despite the wide use of Grignard reagents in combination with copper halides in C-C bond forming reactions, structurally characterised examples of magnesium cuprates remain relatively uncommon,²¹ these include CIPs²³⁻²⁶ and SSIPs^{24, 27} with Cu to Mg ratios varying from 0.5 to 10. Furthermore, there are few examples of structurally characterised diaryl-cuprates with electron withdrawing substituents.

CuC₆F₅ was first prepared in 1968 by Cairncross and Sheppard from CuX (X = Cl or Br) and C₆F₅MgBr in Et₂O. The product was initially formed as a 1,4-dioxane complex described as '[CuC₆F₅]₂·(1,4-dioxane)' using elemental analysis data (but not structurally characterised), the dioxane could be removed by gradual heating up to 100-128°C under vacuum.^{12, 28, 29} It has been suggested that formation from Grignard reagents rather than from (unstable and dangerous) C₆F₅Li is preferable to avoid the formation of cuprates.¹² Since its discovery [CuC₆F₅]₄ has found use in many synthetic processes, especially for C-C couplings.^{30, 31} [CuC₆F₅]₄ has a pronounced ability to form complexes with Lewis bases due to the strongly electron withdrawing nature of the C₆F₅ moieties.^{13, 14, 17, 32} In particular, the binding behaviour of CuC₆F₅ to a 'hard' oxygen donor (in 1,4-dioxane)^{28, 29} is unusual when compared to other organocopper complexes. The enhanced Lewis acidity of the copper centres in CuC₆F₅ also encourages donor interaction with solvents, including with toluene in structurally characterised [CuC₆F₅]₄(toluene)₂,¹⁷ and the donor-free form is only accessed with weakly coordinating solvents such as 1,2-dichloroethane.¹⁷ The electron deficient C₆F₅ groups also lead to interesting supramolecular arrangements in the solid state due to their propensity for 'π-stacking' with more electron rich aromatic groups (via quadrupole-quadrupole) interactions.^{13, 14, 32, 33} Interestingly, the related silver compounds [AgC₆F₅]_∞ and [AgC₆F₅(MeCN)]_∞ occur as linear polymeric chains.^{34, 35}

In this paper the synthesis of [CuC₆F₅]₄ using a Grignard precursor is explored using in-situ ¹⁹F NMR spectroscopy and in different solvents. The results highlight the importance of solvent choice for removing magnesium halide by-products. Despite the well-behaved synthesis observed in Et₂O solvent, we show that changing the solvent to more donating THF allows for a wide range of unusual magnesium cuprate structures to be synthesised which are characterised by single-crystal X-ray diffraction. We also investigate the coordination chemistry of [CuC₆F₅]₄ with 1,4-dioxane both in solution and the solid state, revealing the solid-state structure of an interwoven coordination polymer.

Results and Discussion

The synthesis of [CuC₆F₅]₄ was conducted following the established literature procedure. In brief, the Grignard reagent (C₆F₅)MgBr was generated in Et₂O and added to a suspension of CuCl in Et₂O at 0°C. 1,4-dioxane is added to drive precipitation of MgX₂·(dioxane)₂ (an insoluble 2D coordination polymer),³⁶ at which point the major signal from the solution phase by ¹⁹F NMR spectroscopy is consistent with that of [Cu(C₆F₅)₄(dioxane)_x (x ≥ 2) (which we show by ¹⁹F and ¹⁹F DOSY NMR spectroscopy experiments is the likely form in the presence of excess dioxane, *vide infra*) (Fig. S1, Table S1). The organocopper species can then be extracted using toluene and recrystallised as the colourless complex [Cu(C₆F₅)₄(toluene)₂, **1-tol**.¹⁷ Further recrystallization from 1,2-C₆H₄F₂ (a solvent with reduced π electron density compared to toluene)³⁷ results in the isolation of the [Cu(C₆F₅)₄ unit **1** without donor interactions (Scheme 1, Fig. S2-4). When solvated in 1,2-C₆H₄F₂ the ¹⁹F NMR spectroscopy chemical shifts of **1** are comparable to those reported in CDCl₃, another very weakly-coordinating solvent.¹⁷ The ¹⁹F_{para} NMR spectroscopy signal of **1** is particularly sensitive to the presence of donor interactions and is significantly shifted in the presence of coordinating arene solvents such as toluene (Table S1).¹⁷ The difference between the ¹⁹F_{meta} and ¹⁹F_{para} chemical shifts (Δδ_{m,p}) has been previously shown to decrease as an arene becomes more electron rich and becomes a stronger donor.¹⁷



Scheme 1. Overview of reactivity of CuCl with BrMg(C₆F₅) in different solvents.

The dioxane adduct (**1-diox**) was identified over 50 years ago, and yet has not been structurally characterised.²⁹ To identify the structure of **1-diox** was recrystallized from 1,2-C₆H₄F₂ in the presence of ~1 equivalent of 1,4-dioxane. **1-diox** has an extended structure composed of dioxane molecules bridging between [CuC₆F₅]₄ tetramers, with a formula of [Cu(C₆F₅)₄(dioxane) (Figs. 2, S5-6). Similar coordination polymers of other organometallic compounds with 1,4-dioxane are also known,³⁶ whilst [Cu(C₆F₅)₄] units have been previously linked together by η²-π interactions in binary stacks of [Cu(C₆F₅)₄](naphthalene).³² Oxygen donors typically bind weakly to ‘soft’ Cu(I) centres, and structural examples of ethers coordinating to Cu(I) are restricted to Cu-alkynyl clusters including [Cu₁₀(hfac)₆(C≡CtBu)₄(Et₂O)] (hfac = 1,1,1,5,5,5-hexafluoropentan-2,4-dione),³⁸ and [Cu₁₆(C≡CC≡CTrip)₁₆(THF)₄] (Trip = 2,4,6-triisopropylphenyl).³⁹ In contrast, THF does not coordinate to the Cu centres of mesitylcopper, [CuMes]₄, in the solid-state, instead co-crystallising as a non-coordinated solvent molecule.⁴⁰ The extended solid-state structure of **1-diox** is comprised of interwoven zig-zag and linear chains of [CuC₆F₅]₄(dioxane) running approximately perpendicular to each other (Fig. 1). In some cases, the dioxane linkers coordinate to opposite Cu sites on the [CuC₆F₅]₄ tetramers so that a linear chain occurs, whilst other polymeric strands show some binding of dioxane to adjacent coppers of a tetramer to create a zig-zag in the chain. The Cu₄ units with adjacent donors show a twist in the Cu₄ plane (torsion Cu1-Cu2-Cu3-Cu4 = 10.86(2)°, see Fig 1.), in contrast to the flat Cu₄ geometry of those with opposite donors. In all cases the *trans*-tetramer Cu...Cu distances are greater than 3 Å, and the Cu₄ geometry is not significantly compressed into a rhombus as has been observed with other donors such as toluene.^{17, 32} To the best of our knowledge, there are no other reported examples of two donors selecting an adjacent binding arrangement on to neighbouring coppers of a planar organocopper tetramer, with all other examples displaying coordination to opposite Cu sites.^{17, 32, 41-44} The Cu–O distances range between 2.159(2) and 2.247(2) Å, slightly longer than the Cu–THF bond lengths observed in [Cu₁₆(C≡CC≡CTrip)₁₆(THF)₄] (2.04(2)-2.15(4)Å).³⁹ In solution, the ¹⁹F NMR chemical shifts of the C₆F₅ group in **1** shift upfield as increasing equivalents of dioxane are added to a solution of **1** and the Δδ_{m,p} distance decreases, in line with increasing interaction with a donor species (Table S1, Fig S7).¹⁷ Some precipitation is observed when 0.5-2 equivalents of dioxane are added (to a 0.06 M solution of **1**) but the components become fully soluble when ≥2 equivalents of dioxane are present. This suggests that <2 equivalents of dioxane favours coordination polymerisation (e.g. precipitation of **1-diox**), but a greater content of donor helps break down these extended structures. The spectra suggest that coordination of dioxane occurs as an equilibrium in solution, with excess dioxane favouring coordination of multiple dioxane molecules to a single Cu₄

unit, i.e. generating $[\text{CuC}_6\text{F}_5]_4(\text{dioxane})_x$, where $x \geq 2$. ^{19}F DOSY NMR spectroscopy data comparing **1** with **1** + excess dioxane are consistent with multiple donor molecules per Cu tetramer for the latter, (e.g. $x = 2$ or 3 , see Fig S22). In keeping with reported donor interactions to $[\text{CuR}]_4$ units,^{17, 32, 41-44} and the solid-state structure of **1-diox** it is anticipated that x is most likely equal to two and the expected formula in solution is $[\text{CuC}_6\text{F}_5]_4(\text{dioxane})_2$.

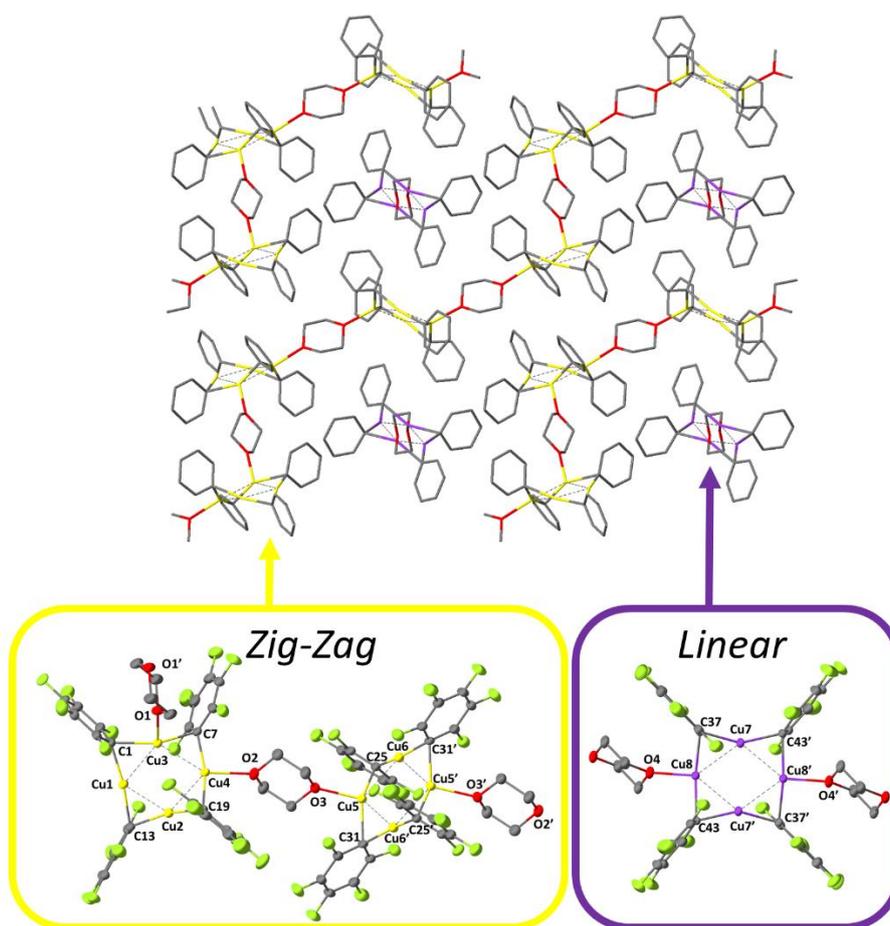


Figure 1. Solid-state structure of **1-diox** (H-atoms omitted for clarity), ellipsoids displayed with 50% probability, packing diagram showing zig-zag (Cu = yellow) and linear (Cu = purple, chain coming out of page) chains (F atoms removed for clarity, structure displayed in stick form). Zig-zag fragment and linear fragment shown below. Selected interatomic distances (Å) and angles (°): Cu1-Cu2, 2.4045(7); Cu2-Cu4, 2.4610(8); Cu3-Cu4, 2.4971(7); Cu3-Cu1, 2.4536(7); Cu5-Cu6, 2.5056(7); Cu5-Cu6', 2.4682(7); Cu7-Cu8, 2.4800(7); Cu7-Cu8', 2.4630(7); Cu3-O1, 2.230(2); Cu4-O2, 2.247(2); Cu5-O3, 2.159(2); Cu8-O4, 2.169(2); Cu-C range (*linear*) 1.954(3) - 2.069(3), (*zig-zag*) 1.975(3)-2.094(3); Cu-C-Cu range (*linear*) 74.62(10) - 77.08(11), (*zig-zag*) 73.48(10) - 75.38(10); Cu1-Cu2-Cu4, 99.38(2); Cu1-Cu3-Cu4, 97.08(3); Cu2-Cu1-Cu3, 81.75(2); Cu2-Cu4-Cu3, 79.22(2); Cu5-Cu6-Cu5', 93.36(2); Cu6-Cu5-Cu6', 86.64(3); Cu7-Cu8-Cu7', 76.08(2); Cu8-Cu7-Cu8', 103.92(2); Cu1-Cu2-Cu4-Cu3 (torsion), 10.86(2); Cu5-Cu6-Cu5'-Cu6' (torsion), 0.00(2); Cu7-Cu8-Cu7'-Cu8' (torsion), 0.00(2).

We investigated the possible synthesis of **1** in THF, a slightly more polar and more strongly donating solvent than Et_2O , but a preferred solvent for the synthesis of other organocopper species such as mesitylcopper.⁴⁰ The process was followed by ^{19}F NMR spectroscopy and compared to the reaction when prepared in Et_2O (Figs S1 & S8). Grignard solutions in either solvent exhibit similar ^{19}F and ^{13}C NMR signals, which are distinct from the starting material BrC_6F_5 (Table S1). After reaction with CuCl

in THF solvent the red/brown products remained soluble and the ^{19}F and ^{13}C NMR spectra of the solution show signals consistent with the chemical shifts (and small $\Delta\delta_{m,p}$ values) found for compounds with the cuprate anion $[\text{Cu}(\text{C}_6\text{F}_5)_2]^-$ (see compounds **2**, **3** and **6** *vide infra*, Table S1, Fig. S8). This initial reaction mixture was concentrated and toluene added – which initiated precipitation of grey solid, later confirmed as CuBr by powder X-ray diffraction (Fig. S9). The remaining solution was concentrated and crystallised at -20°C to yield colourless magnesium cuprate complex $[\text{Cu}(\text{C}_6\text{F}_5)_2][(\text{Mg}_2\text{X}_3(\text{THF})_6)]$ ($\text{X} = \text{Br}$ or Cl) **2** (Scheme 1, Fig. S9). **2** is essentially the direct stoichiometric product of the reaction of $\text{CuX} + 2 (\text{C}_6\text{F}_5)\text{MgBr}$ and can be prepared directly by this reaction (see supporting information).

If 3.3 equivalents of 1,4-dioxane (relative to Cu) are added to the initial THF reaction mixture (i.e. containing a mixture of **2** + CuBr) then precipitation of $\text{MgX}_2 \cdot (\text{dioxane})_2$ is induced (see Fig. S11). However, due to the competing interaction of THF, which has a similar donating ability to 1,4-dioxane, incomplete removal of MgX_2 occurs under these conditions.³⁶ The ^{19}F NMR spectrum of the mixture shows little change after the addition of 1,4-dioxane, i.e. retaining the $[\text{Cu}(\text{C}_6\text{F}_5)_2]^-$ cuprate ion. This finding is in contrast to when using Et_2O as a solvent, as at this stage uncharged **1-diox**_x would be observed (Table S1, Figs. S1 & S8). The solubles of the reaction were extracted and dried to a brown solid. A small quantity of this product proved to be toluene soluble and this fraction was identified as a mixture of crystalline compounds including $[\text{Cu}(\text{C}_6\text{F}_5)_2]_2[\text{Mg}(\text{THF})_6]$, **3** – a cuprate with a reduced Mg:Cu ratio compared to **2**, and $[\text{Cu}_4\text{Br}_6][\text{Mg}(\text{THF})_6]$, **4** – the anion of which is constructed from a tetrahedron of Cu atoms surrounded by an octahedron of bromides, and which exhibits luminescence at ~ 570 nm (Fig. S12).^{45, 46} Both compounds crystallise separately from the reaction mixture and were characterised by X-ray crystallography (Figs. 2, S13). Further extraction of organo-copper species from the remaining (toluene insoluble) reaction mixture was conducted using the polar but weakly coordinating solvent 1,2- $\text{C}_6\text{H}_4\text{F}_2$. This gave a yellow solution which was filtered and concentrated to yield crystals of $([\text{Cu}_5(\text{C}_6\text{F}_5)_7][\text{Mg}(\text{THF})_6] \cdot 2\text{C}_6\text{H}_4\text{F}_2)_\infty$ (**5**) a remarkable polymeric structure comprised of an anionic string of Cu centres with separated Mg cations, which may be referred to as a polysalt (Figs. 3, S14-15). Identification of compounds **2-5** indicates that a rich speciation of Cu/Mg compounds may occur if all Mg is not completely removed from the reaction (Scheme 1), with further complication if both Cl^- and Br^- counterions are present. Addition of 3 equivalents of 1,4-dioxane to a THF solution of **2** yields related cuprate $[\text{Cu}(\text{C}_6\text{F}_5)_2][\text{MgBr}(\text{THF})_5]$ (**6**) via the loss of 1 equivalent of $\text{MgX}_2 \cdot (\text{dioxane})_2$ (Figs. 2, S16-17), note that the complete removal of 1.5 equiv MgX_2 , which would form **3**, does not occur under these conditions.

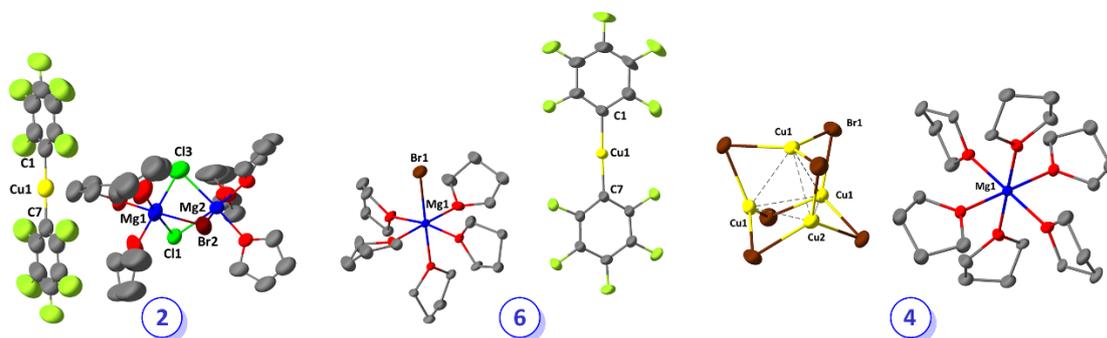


Figure 2. Solid-state structures of **2**, **6** and **4** (H-atoms omitted for clarity), ellipsoids displayed with 50% probability. Representative image of halide composition in **2**, all three halides are a disordered mix of Cl and Br. Unit cell of **2** contains half of two anions, one full anion shown for clarity here. One of two Cu_4 disorder positions of **4** shown. Selected interatomic distances (\AA) and angles ($^\circ$): for **2**; Cu1-C1, 1.912(7); C1-Cu1-C1', 179.994, torsion angles along C-Cu-C axis($^\circ$), 1.5 and 12.54.; for **6**; Cu1-C1,

1.919(5); Cu1-C7, 1.912(5); C1-Cu1-C7, 177.1(2), torsion angle along C-Cu-C axis(°), 7.6; for **4**; Cu1-Cu1', 2.719(4); Cu1-Cu2, 2.730(4); Cu-Br range 2.373(3)-2.411(3).

The solid-state structure of **2** shows that the three halides are disordered over chemically equivalent positions, with each site found to exhibit an occupancy of less than one Br but greater than one Cl, and are best modelled as a disordered mixture of ~2 Cl and ~1 Br. This type of Mg dimer has been shown to act as an electrolyte for Mg ion batteries.^{47, 48} The structures of **2**, **3** & **6** represent the first reported structural characterisation of the dipentafluorophenylcuprate anion, $[\text{Cu}(\text{C}_6\text{F}_5)_2]^-$, which adopts a typical linear geometry (Cu-C bond lengths ~1.91 Å), similar to previously reported $[\text{CuR}_2]^-$ anions.⁴⁹

The unusual solid-state structure of **5** reveals a wavy linear polyanion made of Cu atoms bridged by C_6F_5 units, with the Cu atoms each bonded to two or three C_6F_5 groups (Cu-C distances range 1.971(5)-2.362(5)). The C_6F_5 groups sit parallel to each other but are inclined up or down (Fig. 3d) to ensure a favourable off centred stacking arrangement (with distances between C_6 centroids as low as 3.45 Å, Fig. S18). The Cu...Cu distances are rather short with an average distance of 2.42 Å (ranging = 2.4038(15) – 2.4416(10)) with some distances shorter than those found in **1** (2.44 Å) and the polymeric structure $\text{Cu}_2(\text{C}\equiv\text{CC}\equiv\text{CPh})_2(\text{NH}_3)$ (2.44 Å)³⁹ and significantly shortened compared to intermolecular interactions in 1D chain structures such as $\text{CuC}_6\text{F}_5(\text{Py})$ (2.89 Å), and also $\Sigma r_{\text{vdW}}(\text{Cu}\cdots\text{Cu})$ (2.8 Å).^{13, 14} **5** can be considered as a copper rich cuprate with general formula $[\text{Cu}_x\text{Ar}_{x+y}]^{y-}$ ($y < x$), previous examples of such species include $[\text{Cu}_5\text{Ph}_6][\text{Li}(\text{THF})_4]$ which exhibits a trigonal bipyramidal cluster anion.⁵⁰ Polymeric organocopper chains are very rare, and restricted to neutral alkynyl compounds including ladder like $[\text{Cu}(\text{C}\equiv\text{CPh})]_\infty$ and branched $[\text{Cu}_2(\text{C}\equiv\text{CC}\equiv\text{CPh})_2(\text{NH}_3)]_\infty$.^{39, 51} Shorter structures such as Cu_4 or Cu_6 chains have been reported with multidentate bridging N-donor ligand frameworks.⁵²⁻⁵⁵ These chains and polymers hold interest as potential molecular wires for uses in nanoelectronics.^{18, 55} The closest structural analogue of **5** is probably the germylene supported Cu_4 chain $[\text{LGe}(\text{Me})(\text{CuC}_6\text{F}_5)_2]_2$ (L = $\text{HC}[\text{C}(\text{Me})\text{N}-2,6\text{-iPr}_2\text{C}_6\text{H}_3]_2$), which shows a similar wavy Cu chain with bridging C_6F_5 groups and Cu...Cu distances ranging from 2.4157(7)-2.4919(8).⁵⁶ There is also resemblance to the uncharged organosilver polymer $[\text{AgC}_6\text{F}_5]_\infty$.³⁴ The extended solid-state structure of **5** is arranged as alternating layers of parallel polymers separated by layers of cations and solvent (Figs. 4c,d, S19).

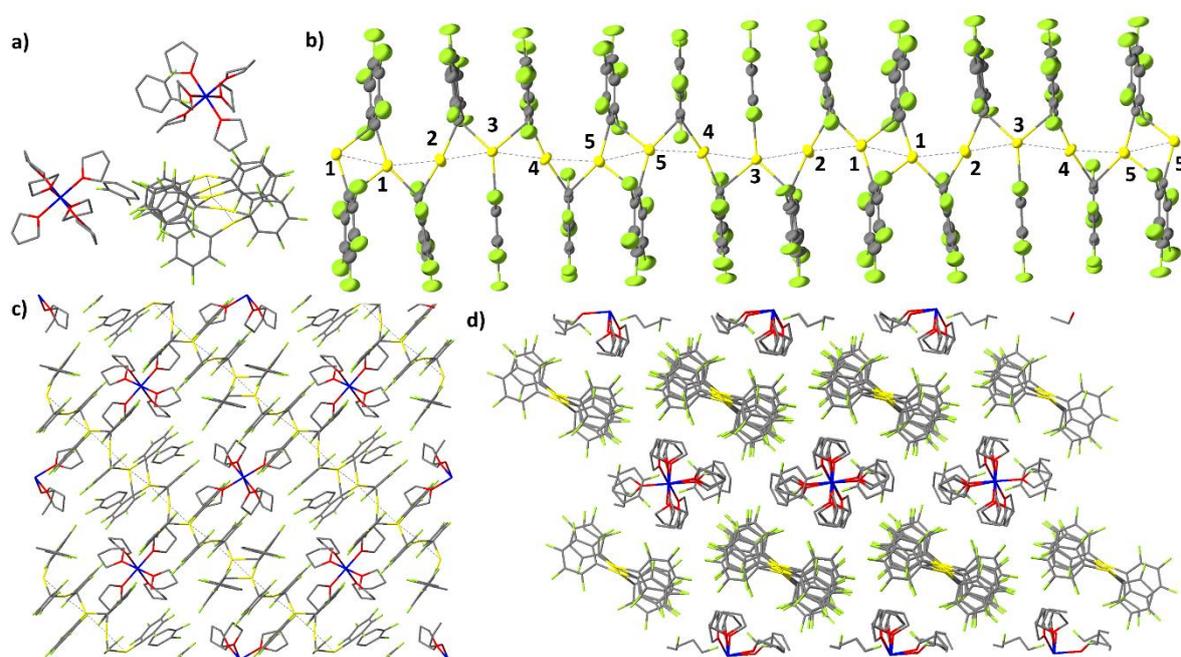


Figure 3. a) Asymmetric unit of solid-state structure of **5** (showing complete cations, H-atoms omitted for clarity), ellipsoids displayed with 50% probability (organic components show in stick from for clarity). b) extended chain of Cu(I) polymer with Cu atom labels. c and d) 2x2x2 unit cells displaying extended along a axis (c) and along axis of polymer chains (d).

5 can be synthesised directly from the addition of a THF solution of MgBr₂ to 7/4 equivalents of **1** dissolved in 1,2-C₆H₄F₂, with a precipitate of by-product CuBr (two equivalents) forming after mixing. The THF is required to solvate oxophilic MgBr₂ which then forms a stable [Mg(THF)₆]²⁺ cation and releases bromide anions. Any initial heterocuprates of the form [Cu_x(C₆F₅)_x(Br)_y]^{y-} which may form as an initial equilibrium mixture are unstable due to the spontaneous precipitation of CuBr under these conditions, resulting in the formation of **5** from the remaining solution components.

Upon dissolution of **5** in 1,2-C₆H₄F₂, the ¹⁹F NMR spectrum shows a single set of broadened signals for the C₆F₅ groups, upon cooling the peaks become even broader (Figs. S15, S20), suggesting that the C₆F₅ groups are fluxional in solution. Upon dissolution of **5** in THF, the ¹⁹F NMR chemical shifts of **5** are consistent with the weighted average of the signals of ¾ **1** and ¼ **3**, and upon cooling to 245 K the signals split into two separate sets resembling neutral **1** and cuprate **3** (Figs. S14, S21), this suggests that in the presence of excess donor solvent the polymer **5** may be decomposed into a fluxional mixture of **1** and **3**. ¹⁹F DOSY NMR spectroscopy analysis was conducted in the weakly coordinating solvent 1,2-C₆H₄F₂ and indicated a minor decrease in diffusion coefficient for **5** compared to **1**, suggesting that short oligomeric chains of **5** may persist in solution, but that extended polyanions (which would exhibit high charges) are unlikely (see Table S2 and Figs. S22-25).

Conclusion

This study emphasises the importance of solvent choice in transmetalation reactions using Grignard reagents; use of Et₂O enables straightforward removal of MgX₂ by-products by addition of 1,4-dioxane to generate the desired organocopper compounds. In contrast, use of more strongly donating THF makes MgX₂ removal difficult (but may instead result in competitive precipitation of CuBr) and generates a range of magnesium cuprate species, with varying Mg:Cu ratios and anions of [Cu(C₆F₅)₂]⁻ or polyanion ([Cu₅(C₆F₅)₇]²⁻)_∞. Understanding the chemistry of organocopper/cuprate species generated in-situ, e.g. by reaction of copper halides with Grignard reagents, is of importance with respect to using these reagents directly in organic synthesis. The electron withdrawing nature of the C₆F₅ group enables [CuC₆F₅]₄ to coordinate to oxygen donor solvents, forming an extended coordination network [**1-diox**] with 1,4-dioxane. In contrast, the arene 1,2-C₆H₄F₂ is sufficiently electron poor to enable the base-free structure of [CuC₆F₅]₄ to exist in the solid-state or in solution and this polar but weakly coordinating solvent is also useful for crystallising compounds **1-diox** and **5**. The organocopper polysalt **5** is very unusual and likely forms in the solid state due to a combination of favourable cuprophilic interactions and off-centred arene-arene stacking interactions. The wide range of possible anion and cation combinations identified in compounds **2-6**, forming from various ratios of Cu, Mg, C₆F₅ and Br show that enormous complexity can occur even in a simple system, and adds further evidence that the presence of s-block halides plays a pivotal role in the speciation and aggregation of organometallic reagents.^{24, 27, 57, 58}

Experimental Section

All manipulations were undertaken using a nitrogen filled glovebox or using a Schlenk line, unless otherwise stated. CuCl (Alfa Aesar, 97%), CuBr (Alfa Aesar, 98%), C₆F₅Br (Acros), Mg turnings (Sigma Aldrich), anhydrous MgBr₂ (Sigma Aldrich, 98%), were used directly from suppliers. THF, hexane and

toluene were dried by refluxing over sodium (and benzophenone for THF), C₆H₄F₂ was washed with alumina and then dried by stirring over CaH₂ followed by trap-to-trap distillation. 1,4-dioxane and d₈-toluene were dried by stirring over CaH₂. All dry solvents were degassed by bubbling with N₂ for 30 minutes or freeze pump thaw cycles and stored over 4Å molecular sieves under nitrogen. The raw data that support the findings of this study are available from the Warwick Research Archive Portal. All reported yields are calculated from isolated solids extracted from the reaction flask in the glovebox.

NMR spectra were recorded on Bruker Avance III HD 300, 400 or 500 MHz instruments and all chemical shifts reported in parts per million (ppm). NMR spectra of samples using 1,2-C₆H₄F₂ as the solvent were locked and shimmed using a separate C₆D₆ sample or an internal capillary. In these spectra ¹⁹F NMR spectra were referenced to the 1,2-C₆H₄F₂ signal at 139.84 ppm. ¹⁹F DOSY NMR analysis was carried out using Bruker's Dynamics Center. Fluorescence spectra were recorded on an Agilent Technologies Cary Eclipse Fluorescence Spectrophotometer. Elemental Analysis was determined using a Perkin Elmer 240 Elemental Analyzer by the Microanalysis Laboratory at the Department of Chemistry, University of Cambridge.

1, [CuC₆F₅]₄·1,2-C₆H₄F₂. 1.0 g (41.1 mmol) of Mg was added to a N₂ filled Schlenk with a stirrer bar and stirred overnight. 5.13 mL (41.1 mmol) of C₆F₅Br was added to a second Schlenk and dissolved in 25 mL Et₂O. 5 mL of the solution was added dropwise to the Mg at 0°C and stirred for 15 minutes. The remainder of the solution was then added slowly and allowed to stir at room temperature to form a brown coloured solution of Grignard BrMgC₆F₅. 3.5 g (35.4 mmol) of CuCl was suspended in 40 mL of Et₂O and the Grignard added dropwise to this at 0°C. The reaction was allowed to stir overnight at room temperature after which it appeared as a dark brown solution with precipitate. 5 mL of 1,4-dioxane was added to 15 mL of Et₂O and this solution added to the reaction mixture, and the flask shaken vigorously, initiating further precipitation such that most of the reaction mixture is thick sludge. The organocopper reagent is extracted using successive toluene (2 x 60 mL) washes. The soluble fraction was filtered, evacuated to dryness and recrystallised from toluene at -20°C repeatedly until a pale yellow colour is achieved. A final -20°C recrystallisation from 1,2-C₆H₄F₂ yields **1** (N.B. a second recrystallisation from 1,2-C₆H₄F₂ may be required to remove all toluene). 1.42 g of **1** was isolated (16% yield).

¹⁹F NMR spectroscopy (470 MHz, 1,2-C₆H₄F₂): -104.9 (m), -142.6 (t), -158.8 (m). ¹³C{¹H} NMR spectroscopy (126 MHz, 1,2-C₆H₄F₂): 154.55 (dd, ¹J(F,C) 236 Hz, ²J(F,C) 20 Hz), 136.71 (dm, ¹J(F,C) 258 Hz), 98.9 (m) (N.B. para carbon was not clearly identified). Elemental Analysis data (predicted for [CuC₆F₅]₄·0.4C₆H₄F₂): % C, 32.72 (32.76); % H, 0.38 (0.17). (note partial occupancy of crystallised solvent, this is consistent with NMR spectra collected from the same material, which predicts ~0.25 C₆H₄F₂ per Cu₄ unit)

1-diox, [Cu(C₆F₅)]₄(dioxane). 100 mg (0.10 mmol) of **1** was dissolved in a minimal amount of 1,2-difluorobenzene. 9 µL (0.10 mmol) of 1,4-dioxane was added and the reaction stirred. The flask was cooled at -20°C overnight to yield a pale yellow crystalline compound. 29 mg **1-diox** isolated (30% isolated yield).

¹H NMR spectroscopy (500 MHz, 1,2-C₆H₄F₂): = 3.36 (s, dioxane). ¹⁹F NMR spectroscopy (470 MHz, 1,2-C₆H₄F₂): = -105.2, -143.7 (m), -159.1 (m). ¹³C{¹H} NMR spectroscopy (126 MHz, 1,2-C₆H₄F₂): 66.6 (s, dioxane) (low solubility hindered accurate location of C-F signals). Elemental Analysis data (predicted for [Cu(C₆F₅)]₄(C₄H₈O₂): % C, 33.09 (33.28); % H, 0.88 (0.80).

2^{Br}, [Cu(C₆F₅)₂][(THF)₆Mg₂Br₃]. 0.5 g (20.6 mmol) of Mg was added to a N₂ filled Schlenk with a stirrer bar and stirred overnight. 2.56 mL of C₆F₅Br (20.6 mmol) was added to a second Schlenk and dissolved

in 12.5 mL THF. The solution was added dropwise to the Mg at 0°C and then allowed to stir at room temperature to form the Grignard BrMgC₆F₅. 1.48 g (10.3 mmol) of CuBr was suspended in 12.5 mL of THF and the Grignard added dropwise to this at 0°C, the Grignard flask was washed with a further 6 mL THF and this added to the reaction flask. The reaction was allowed to stir at room temperature for 3 hours after which time it appeared as a dark brown solution with a little precipitate. The solvent was removed under vacuum and solids were recrystallised from THF/hexane. N.B. the product is difficult to recrystallise as it crystallises quickly, trapping impurities. Repeated manipulation using THF and hexane allowed for purification. 4 g of off-white product was retrieved (35% yield).

Elemental Analysis data (predicted for [Cu(C₆F₅)₂][(C₄H₈O)₆Mg₂X₃], X₃ = Br₃): % C, 38.25 (38.65); % H, 4.57 (4.33). For NMR spectroscopy data see **2** below.

2, [Cu(C₆F₅)₂][(THF)₆Mg₂X₃] (X₃ = Cl₂Br). For a direct stoichiometric synthesis of **2** see the prep for **2^{Br}** above with exchange of CuBr for CuCl. Alternatively, as was initially conducted in this study, **2** forms by the dropwise addition of a slight excess of Grignard (C₆F₅)MgBr (prepared from 0.5 g Mg (20.6 mmol) and 2.56 mL of C₆F₅Br (20.6 mmol) in 12.5 mL THF as described above) to a suspension of CuCl (1.75 g, 17.7 mmol) in 12.5 mL THF at 0°C which was allowed to stir for 3 hours at room temperature. This reaction yields a red/brown solution of **2** + CuX. The solution was concentrated under vacuum and then toluene added to initiate the precipitation of CuBr. The solution was filtered. The remaining soluble fraction was concentrated under vacuum and placed at -20°C to yield 2.5 g (24% yield) colourless crystals of **2**.

¹⁹F NMR spectroscopy (470 MHz, THF): -111.5 (m), -164.6 (t, ³J(F,F) 20 Hz), -165.3 (m). For ¹³C NMR spectroscopy of [Cu(C₆F₅)₂]⁻ see data for compound **6**. Elemental Analysis data (predicted for [Cu(C₆F₅)₂][(C₄H₈O)₆Mg₂X₃], X₃ = Cl₂Br): % C, 42.07 (41.99); % H, 4.79 (4.70).

3, [Cu(C₆F₅)₂]₂[Mg(THF)₆] as an impure mixture with **4.** A slight excess of Grignard (C₆F₅)MgBr (prepared from 0.5 g Mg (20.6 mmol) and 2.56 mL of C₆F₅Br (20.6 mmol) in 12.5 mL THF as described above) was added dropwise to a suspension of CuCl (1.75 g, 17.7 mmol) in 12.5 mL THF at 0°C and allowed to stir for 3 hours at room temperature. This reaction yields a red/brown solution of **2** + CuX. To this 3.3 equivalents of 1,4-dioxane (5 mL, 58.7 mmol) were added and the soluble fraction removed and dried under vacuum. Toluene was added to the solid products to extract a mixture of products, which crystallised at -20°C. Crystals of both **3** and **4** were retrieved and characterised by X-ray crystallography. Further attempts to synthesise a pure batch of **3** were unsuccessful. However, a related cuprate **6** with a different cation, [MgBr(THF)₅]⁺, was straightforwardly prepared (see below). N.B. Addition of excess 1,4-dioxane to **6** in 1,2-C₆H₄F₂ resulted in the spontaneous crystallisation of **5**.

¹⁹F NMR spectroscopy (470 MHz, THF, collected from crude product): -111.6 (m), -164.1 (m), -165.2 (m). For ¹³C NMR spectroscopy of [Cu(C₆F₅)₂]⁻ see data for compound **6**.

4, [Cu₄Br₆][Mg(THF)₆], synthesised as a mixture with CuBr.

467 mg (3.26 mmol) of CuBr was suspended in 10 mL of THF in a Schlenk flask. 150 mg (0.82 mmol) of MgBr₂ was placed in a separate Schlenk flask and dissolved in 10 mL THF. The THF solution of MgBr₂ was added to the suspension of CuBr giving a green solution with precipitates. The mixture was heated to 50°C and stirred overnight. The soluble fraction was then discarded leaving a luminescent colourless solid product. We were not able to remove residual CuBr starting material that is retained in the solid product, elemental analysis suggests that only ~43% of the CuBr starting material has reacted under these conditions. The product is highly air sensitive and loses luminescence under air. 528 mg of the mixed solids collected.

Elemental Analysis data (predicted for a mixture of **4** + 5.4 CuBr = [Cu₄Br₆][Mg(C₄H₈O)₆] + 5.4(CuBr)): % C, 14.70 (14.67); % H, 2.49 (2.46)

5, [Cu₅(C₆F₅)₇][Mg(THF)₆].2C₆H₄F₂. 197 mg (0.19 mmol, *N.B.* 0.76 mmol Cu) of **1** was dissolved in 3 mL THF in a Schlenk flask. In a second Schlenk flask 20 mg (0.11 mmol) MgBr₂ was dissolved in 9 mL THF. The MgBr₂ solution was added dropwise to the organocopper solution at 0°C and stirred, before warming to room temperature and stirring for 30 minutes. The solution was filtered to remove CuBr and the remaining soluble fraction was evacuated to ~ 2 mL and 2 mL of 1,2-C₆H₄F₂ was added. The solution was further concentrated to ~ 1 mL total and allowed to crystallise overnight to yield a yellow powder. The remaining soluble fraction was discarded and the solid dried under vacuum. 65 mg collected (20% yield)

¹⁹F NMR spectroscopy (470 MHz, 1,2-C₆H₄F₂): -106.1 (br), -148.7 (very br), -160.8 (br); ¹⁹F NMR spectroscopy (470 MHz, THF): -110.5 (br), -160.9 (br), -164.2 (m). *N.B.* due to the broadness of the signals no clear signals were observed by ¹³C NMR spectroscopy. Elemental Analysis data (predicted for [Cu₅(C₆F₅)₇][Mg(C₄H₈O)₆], assuming solvent loss under vacuum): % C, 39.92 (40.78); % H, 2.33 (2.49).

6, [Cu(C₆F₅)₂][MgBr(THF)₅]. 0.5 g of Mg (20.6 mmol) was added to a N₂ filled Schlenk with a stirrer bar and stirred overnight. 2.56 mL (20.6 mmol) of C₆F₅Br was added to a second Schlenk and dissolved in 12.5 mL THF. The solution was added dropwise to the Mg at 0°C and then allowed to stir at room temperature to form the Grignard BrMgC₆F₅. 1 g (10.1 mmol) of CuCl was suspended in 12.5 mL of THF and the Grignard added dropwise to this at 0°C, the Grignard flask was washed with a further 6 mL THF and this added to the reaction flask. The reaction was allowed to stir at room temperature for 3 hours after which time it appeared as a dark brown/purple solution with a little precipitate. 2.6 mL (30.5 mmol) of 1,4-dioxane was added to the reaction mixture initiating the precipitation of a pale pink precipitate and leaving a pale yellow solution. The solution was filtered, evacuated to a sticky solid and then recrystallised from THF/hexane twice, removing any brown oily residues, until a colourless crystalline product was achieved. 4.3 g collected (49% yield).

¹⁹F NMR spectroscopy (282 MHz, 1,2-C₆H₄F₂): -111.3 (m), -162.2 (t, ³J(F,F) 20 Hz), -164.2 (m); ¹⁹F NMR spectroscopy (470 MHz, THF): -111.5 (m), -164.2 (t, ³J(F,F) 20 Hz), -165.1 (m). ¹³C{¹H} NMR spectroscopy (126 MHz, THF): 149.5 (dd, ¹J(F,C) 220 Hz, ²J(F,C) 32 Hz), 137.4 (dm, ¹J(F,C) 257 Hz), 135.7 (dm, ¹J(F,C) 252 Hz), 129.5 (t, ²J(F,C) 78 Hz). Elemental Analysis data (predicted for [Cu(C₆F₅)₂][MgBr(C₄H₈O)₅]): % C, 45.37 (44.57); % H, 4.84 (4.68).

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¹H, ¹⁹F, ¹³C and ¹⁹F DOSY NMR spectroscopy data; fluorescence spectrum for **4**; X-ray crystallography details and figures for the solid-state structures of **1** and **3**, and powder X-ray diffraction data.

CCDC 2022727-2022732 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

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