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A tetranuclear $Cu^{II}_2Dy^{III}_2$ coordination cluster as a Suzuki (C–C) coupling reaction promoter†

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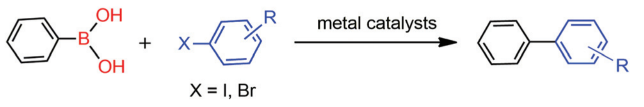
The air-stable tetranuclear coordination cluster $[Cu^{II}_2Dy^{III}_2L_4(NO_3)_2(CH_3CN)_2]\cdot 2(CH_3CN)$, which can be obtained in high yield, promotes the Suzuki coupling reaction of phenylboronic acid with substituted aryl halides under environmentally benign conditions.

Long term research is required to achieve synthetic control in combining 3d and 4f centres with organic ligands as well as to understand the influence of each centre on the studied properties; however this methodology has yielded entities with exceptional magnetic[1] or luminescent behaviour.[2] The development of Earth-abundant metal-based catalytic methodologies to replace the existing practices that use noble and rare elements is a key target in modern science.[3] In this direction, 3d/4f *in situ*[4–6] or well-characterised coordination clusters have recently emerged as sustainable catalytic platforms with advantages of ease of synthesis, good abundance (in spite of belonging to the so-called rare earths) and low cost.[7] Our group has established the efficacy of a series of tetranuclear coordination clusters $[M^{II}_2Ln^{III}_2L_4(X)_2(solv)_2]$ (M = Ni, Co, Cu, Zn, X = Cl, NO_3, Ln = Y, Dy, Gd) for domino-electrocyclization and Lewis acid reactions,[8–11] whereas other groups have, successfully, used them in redox,[12–14] co-polymerization[15] and carbon dioxide fixation reactions.[16,17]

Metal-promoted Suzuki–Miyaura coupling includes organoboron derivatives and carbon electrophiles and represents a valuable procedure for C–C bond formation (Scheme 1).[18] This synthetic protocol uses commercially available boron reactants, which are relatively stable and non-toxic and can be easily functionalized. The initial reports involved noble and expensive Pd-based catalysts; however several methodologies, based on Earth-abundant, low cost, first row transition elements such as Fe,[19] Co,[20] Ni[21] and Cu[22] have been identified. In the case of Cu promoted catalysis,[23,24] the high loading required to achieve the C–C bond-formation in high yields is considered a significant drawback.

In our quest to investigate and expand the applicability of the $[M^{II}_2Ln^{III}_2L_4]$ 3d/4f catalytic species further and given the successful use of Cu^{II} based compounds in the Suzuki–Miyaura reaction, we synthesised the compound $[Cu^{II}_2Dy^{III}_2L_4(NO_3)_2(CH_3CN)_2]\cdot 2(CH_3CN)$, **1**·2($CH_3CN$), where H_2L is the Schiff base ligand (*E*)-2-(2-hydroxy-3-methoxybenzylidene-amino)phenol. Compound **1** is synthesized in two high-yielding steps (overall yield: 93%), under ambient conditions, using commercially available starting materials, from the reaction of $Cu(NO_3)_2\cdot 3H_2O$, $Dy(NO_3)_3\cdot 6H_2O$, H_2L and Et_3N in MeCN (20 mL) in a molar ratio of 2 : 4 : 4 : 9. After mixing, the resulting solution was filtered and greenish crystals of **1**·2(CH_3CN) were obtained in 3 days from the mother liquor and collected by filtration, washed with Et_2O, and dried in air. Compound **1** crystallizes in the orthorhombic space group *Pbca*. Its core topology is of the well-known tetranuclear defect dicubane or the butterfly type (Fig. 1). The Cu^{II} ions are in the central "body" positions and the Dy^{III} ions are at the "wingtip" positions with a separation of 3.4105(9) Å, whereas the Cu–Cu distance is 3.411 Å. The coordination environment of both the metals is almost saturated; five out of six and six out of eight coordination sites of the Cu^{II} and Dy^{III} centres, respectively, are occupied by the ligand. The final coordination site on the Cu^{II} ion is occupied by a solvent MeCN molecule and the remaining two sites on the Dy^{III} ion are occupied by two



Scheme 1 A representative example of the Suzuki C–C coupling reaction.

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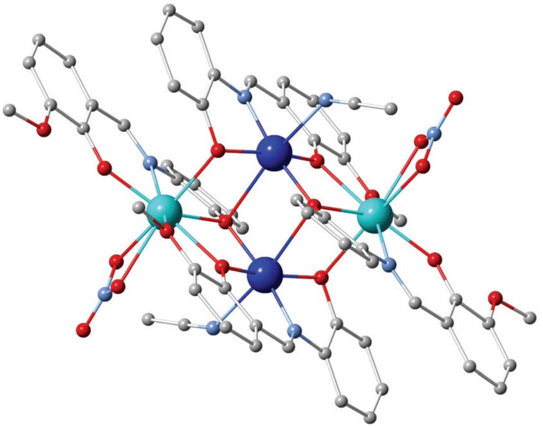


Fig. 1 The molecular structure of compound **1** in the crystal. Color codes: Cu^{II} (dark blue), Dy^{III} (cyan), oxygen (red), nitrogen (light blue), and carbon (grey). H-atoms are omitted for clarity.

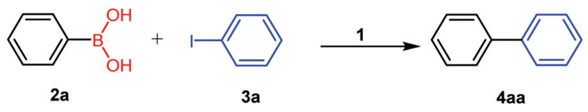
oxygen atoms from a chelating nitrate anion. This compound is isoskeletal to the previously reported tetranuclear compounds and more specifically to $[Cu^{II}_2Y^{III}_2L_4(NO_3)_2(DMF)_2]$, which was found to be an efficient cooperative catalyst in the Michael addition reaction.[8] Thermal studies under a N_2 atmosphere (Fig. S1†) identify a partial loss of the solvent molecules (9.83%) and that compound **1** is stable up to 250 °C. At this point the framework collapses to yield the corresponding $Cu^{II}_2Dy^{III}_2O_5$ residue (calculated: 31.20%, found: 31.01%). To further confirm the identity of compound **1** in solution we recorded a UV-Vis spectrum in CH_3CN. This revealed a broad peak (500 to 700 nm), characteristic of Cu^{II} in this coordination environment (Fig. S2†). Preliminary magnetic studies identify the paramagnetic character of compound **1** and that the Cu centres are in oxidation state II.

With the catalyst in hand, we chose phenylboronic acid and iodobenzene as model substrates and attempted to identify environmentally friendly solvents[25] to perform the reaction (Table 1). The completion of the reaction was monitored by TLC. Two experiments in the absence of compound **1** were performed as blank to exclude the release of Pd nanoparticles from the magnetic stirrer. After 24 h, compound **1** showed higher activity in the DME : water mixture (1 : 1 ratio) with 89% yield of the desired 1,1′-biphenyl product (Table 1, entry 4). The reaction was performed in other solvents such as water, ethanol, DME (dimethoxyethane), DMF (dimethylformamide), DMF : water (1 : 1), THF (tetrahydrofuran), and THF : water (1 : 1); however the corresponding compound was obtained in lower yield. Therefore, the DME : water mixture (1 : 1) was chosen as the solvent for the subsequent experiments.

Furthermore, the effect of a base on the reaction performance was studied using different bases such as K_2CO_3, KOH, Na_2CO_3, NaOH, Et_3N, Cs_2CO_3 and KO^{t}Bu in a mixed DME and water solvent (Fig. S2†). We identified that K_2CO_3 is the desirable base for the reaction with higher product yield for this reaction. In the absence of a catalyst, the coupling product is formed in very low yield (>2%) using K_2CO_3 as the base. Therefore, we may envisage that the presence of the base is essential to activate boronic acid *via* enhancing the polarization of the organic ligand, thus facilitating transmetallation. The next step was to use different loadings of the catalyst. As shown in Table 2, the initial experiment of 5.0 mol% is the optimum condition.

Then, we investigated the influence of temperature on the coupling reaction between phenylboronic acid and iodobenzene in a range of temperatures (0 °C–120 °C). Control experiments showed that **1** can show good conversion at 80 °C but is inactive at temperatures lower than 40 °C (Fig. S3†). At 100 and 120 °C, the catalyst affords the corresponding compound in lower yield; therefore we concluded that the temperature of 80 °C was the optimum temperature. Moreover, experiments in the presence of Cu salts under similar catalytic conditions yielded the expected product with significantly higher loadings when compared to those with **1**. For example, various Cu(II) salts (Table S1†) show up to 33% conversion, whereas the use of $Dy(NO_3)_3$ does not promote the organic transformation. The use of Cu(I) salts yields the corresponding product in 40% yield, which is slightly higher than that for the Cu(II) salts,

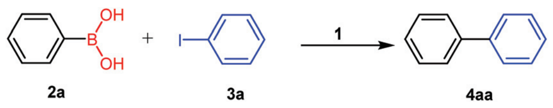
Table 1 Influence of solvents[a]



Entry	Solvent	Yield[b]
1	Water	10
2	Ethanol	12
3	DME	46
4	**DME : water(1 : 1)**	**89**
5	DMF	66
6	DMF : water(1 : 1)	79
7	THF	36
8	THF : water(1 : 1)	48

[a] Iodobenzene (1.0 mmol), phenylboronic acid (1.1 mmol), PPh_3 (2.0 mol%), K_2CO_3 (5.0 mmol), Cu_2Dy_2 (5.0 mol%), 80 °C. [b] Isolated yield.

Table 2 Optimization experiments for the coupling reaction of phenyl boronic acid and iodobenzene catalysed by compound **1**[a]



Entry	Catalyst (mol%)	Yield[b]
1	1	48
2	2	56
3	**5**	**89**
4	10	72
5	20	69

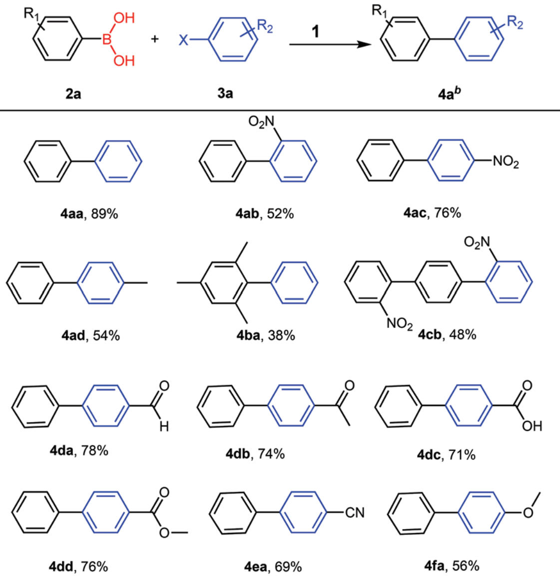
[a] Iodobenzene (1.0 mmol), phenylboronic acid (1.1mmol), PPh_3 (2.0 mmol), K_2CO_3 (5.0 mmol), DME : water (1 : 1), 80 °C. [b] Isolated yield.

while the *in situ* combination of $\mathrm{Cu(NO_3)_2/Dy(NO_3)_3/H_2L}$ gave a poor outcome (entry 7, Table S1†), showcasing the advantage of the use of the well-characterised material.

With the optimal reaction conditions in hand, we then extended the scope of the reaction and performed the coupling reactions between different aryl halides and phenylboronic acid. As a first step, we investigated the influence of the substitution on the aromatic ring of the aryl halide. The reactions with substitution in the *ortho* and *para* positions of the aryl halide ($-\mathrm{NO_2}$) yielded the corresponding products in moderate to good yields. The electron-withdrawing group ($-\mathrm{NO_2}$) of the aryl halide enhanced the rate of cross-coupling. For example, the nitro ($-\mathrm{NO_2}$) group at the *para* position of the aromatic aryl halide furnished the desired product **4ac** in 76% yield (Table 3) and the electron-donating group ($-\mathrm{CH_3}$) at the *para* position of the aryl halide produced the corresponding product **4ad** in 54% yield (Table 3). Furthermore, the reaction of sterically hindered halides with phenylboronic acid afforded **4ba** in 38% yield (Table 3). The slight increase in the yield of **4ac** when compared with that of **4ab** may be attributed to the influence of the strong electron-withdrawing group ($\mathrm{NO_2}$) that results in the reductive halogenation of the aryl halides.

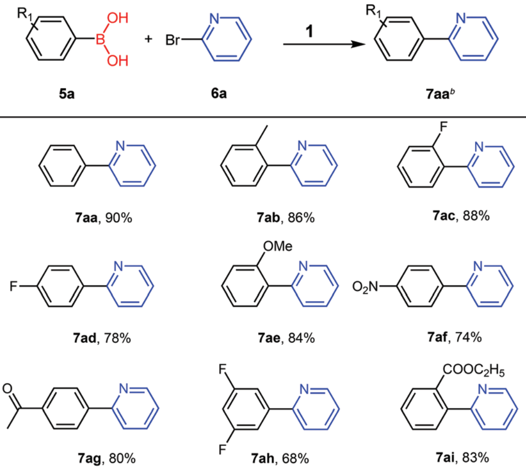
Furthermore, we explored different substituted aryl boronic acids and nitrogen-based heteroaryl halides (2-bromopyridine) using **1** as a precatalyst under the same reaction conditions and the results are summarized in Table 4. Reactions with both electron-rich and electron-poor aryl boronic acids proceeded smoothly. A quantitative yield of 2-phenylpyridine was obtained in the presence of 5.0 mol% of catalyst **1** at 80 °C in 8 h (Table 4, **7aa**). Electron withdrawing and electron donating groups at the *ortho*/*para* position afforded the corresponding products in good yield as compared to that of the *meta*-position (Table 4).

Table 3 Reaction of phenylboronic acid with different aryl halides[a]



[a] Aryl halide (1.0 mmol), phenylboronic acid (1.1 mmol), $\mathrm{PPh_3}$ (2.0 mol%), $\mathrm{K_2CO_3}$ (5.0 mmol), $\mathrm{Cu_2Dy_2}$ (5.0 mol%), 80 °C. [b] Isolated yield.

Table 4 Reaction of 2-bromopyridine with different phenylboronic acids[a]



[a] Aryl halide (1.0 mmol), phenylboronic acid (1.1 mmol), $\mathrm{PPh_3}$ (2.0 mol%), $\mathrm{K_2CO_3}$ (5.0 mmol), $\mathrm{Cu_2Dy_2}$ (5.0 mol%), 80 °C. [b] Isolated yield.

Finally, for an initial understanding of the catalyst's role we also tested this coupling reaction with other topologically equivalent catalysts, varying the 3d part *i.e.* $\mathrm{Co^{II}_2Dy_2}$, $\mathrm{Ni^{II}_2Dy_2}$ and $\mathrm{Zn^{II}_2Dy_2}$.[8,26,27] However, all the reactions failed to produce the desired product **4aa** as compared to **1**, thus identifying the suitability and superiority of **1** as the catalyst for the Suzuki Coupling reaction under these reaction conditions and justifying our selection.

Conclusions

Extending our studies in exploring the use of 3d/4f coordination clusters as organic transformation promoters, in this work we report, for the first time, the cross-coupling activity of compound **1**. The very promising results highlight the richness of the reactivity of the 3d/4f chemistry and its potential applications. The catalytic conversion proceeds under environmentally benign conditions and thus the current methodology has a sustainable character. More experiments are required to fully understand the role of **1** in the present organic transformation and these experiments are under investigation. The present results open new research avenues for the chemistry of Cu/4f coordination clusters.

Conflicts of interest

There are no conflicts to declare.

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