

Supplementary material to

Cu^IBiOI is an efficient novel catalyst in Ullmann-type C–N couplings with wide scope – A rare non-photocatalytic application

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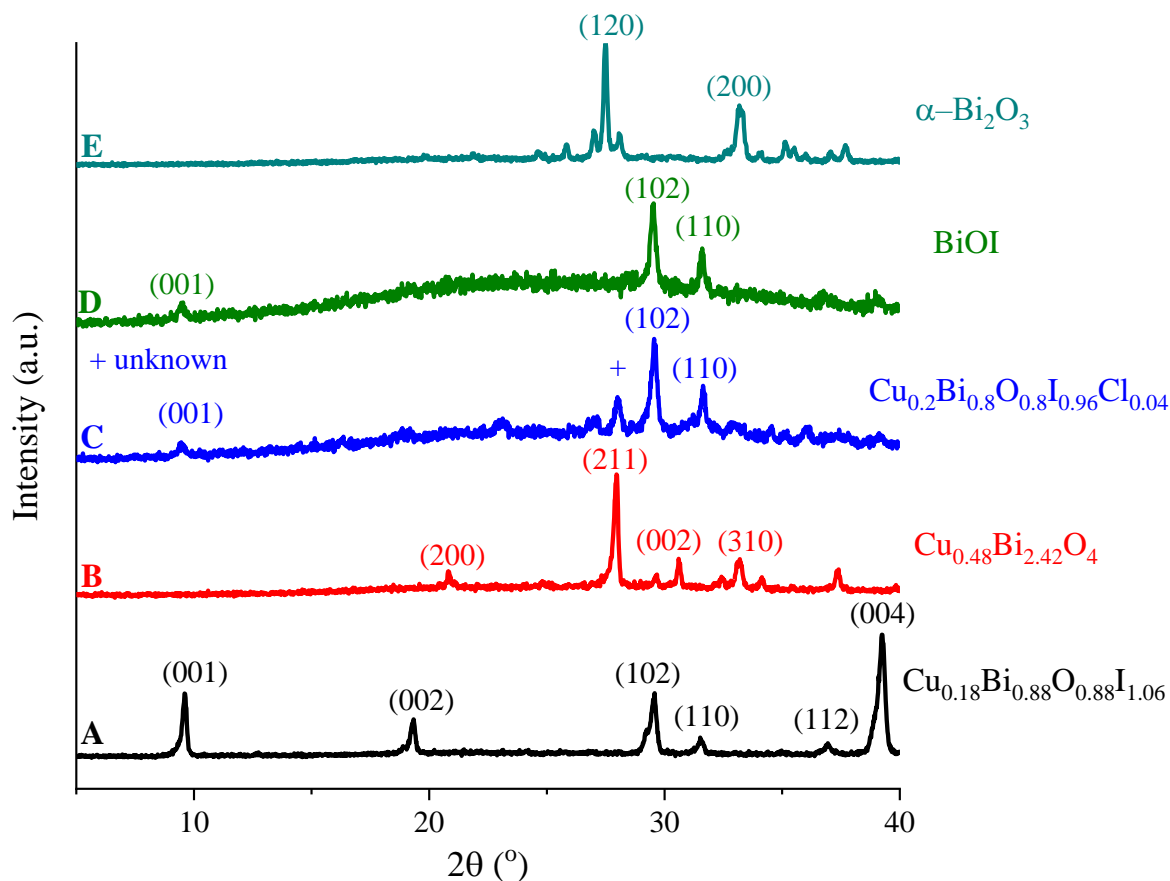


Fig. S1. XRD patterns of (A) the as-prepared; (B) the heat-treated (at 550°C for 2 h), (C) the used Cu^IBiOI catalyst, (D) the as-prepared BiOI and (E) the heat-treated BiOI (at 750°C for 2 h).

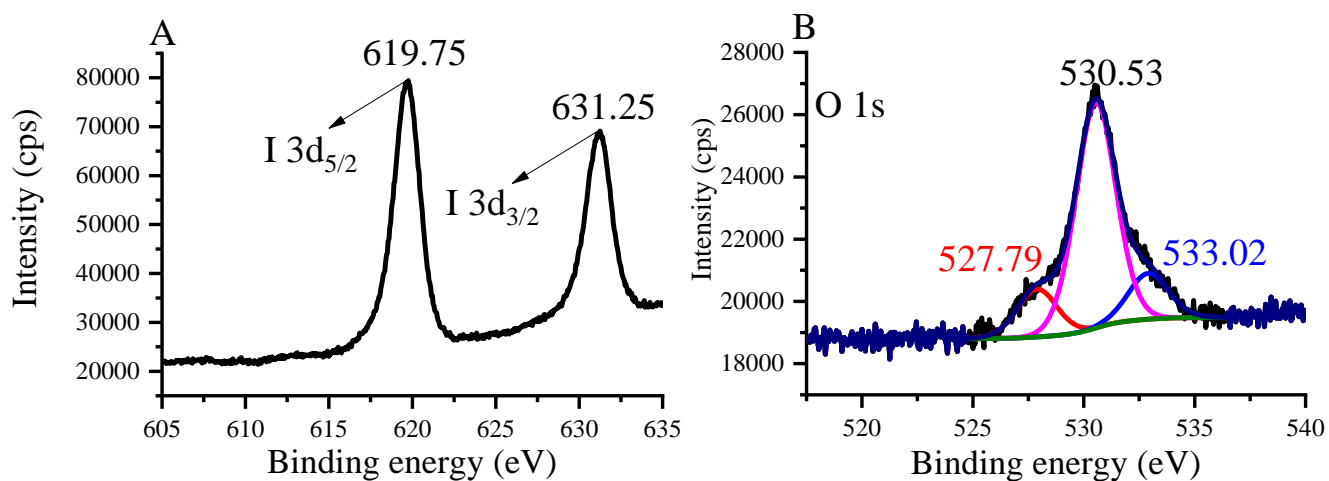


Fig. S2. Deconvoluted XP spectra of the A: I 3d and B: O 1s regions for the as-prepared phase-pure Cu^IBiOI.

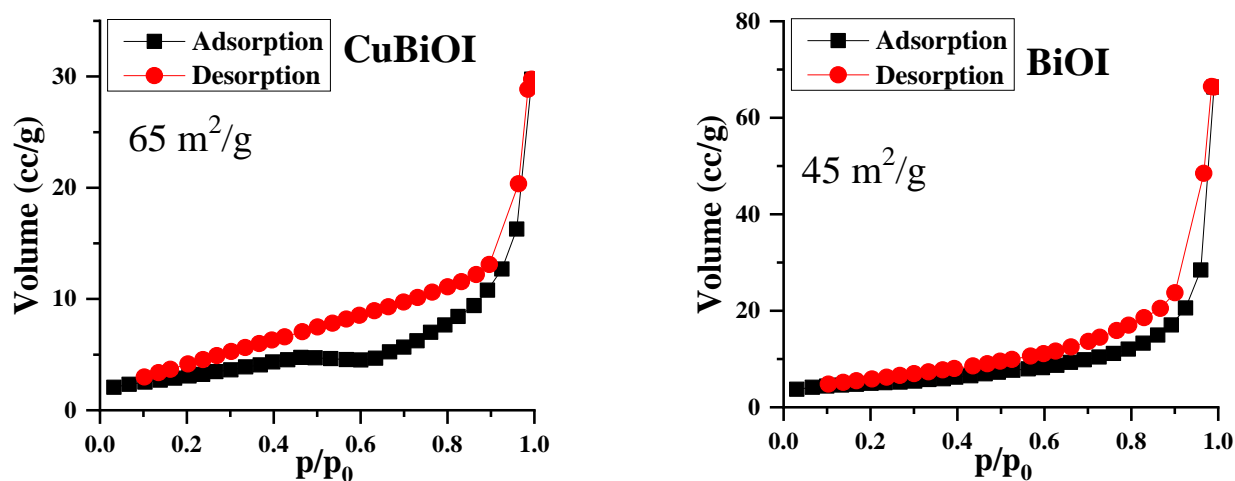


Fig. S3. BET isotherms for the Cu^IBiOI and the BiOI oxohalides.

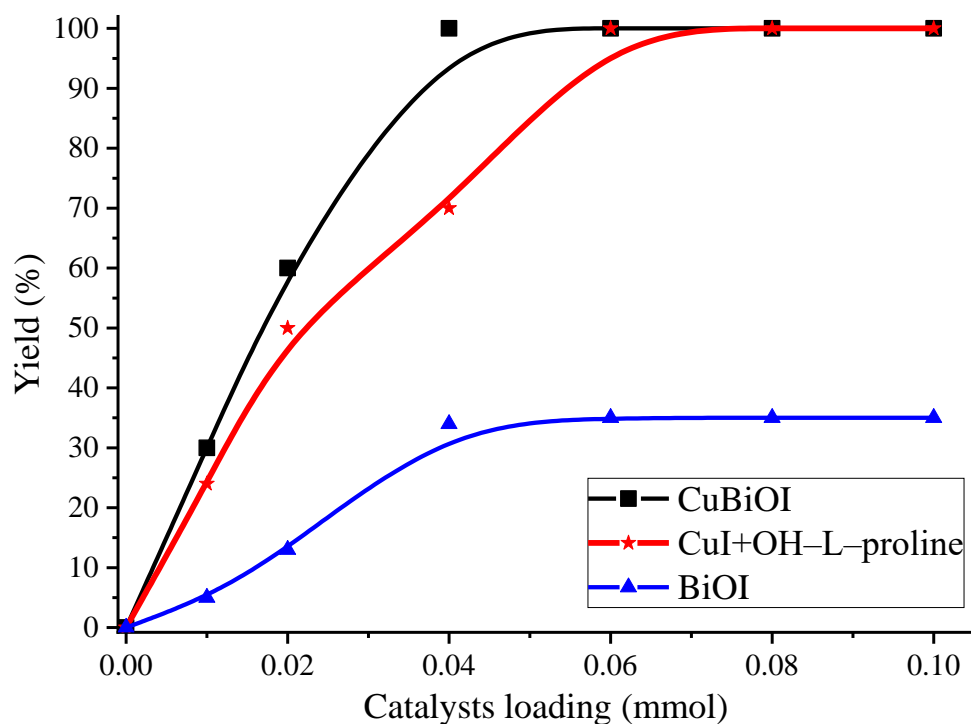


Fig. S4. Optimization of catalyst loading for Ullmann-type C–N coupling reaction between chlorobenzene and aqueous ammonia. Reaction conditions: 1.0 mmol aqueous ammonia; 0.5 mmol chlorobenzene; 0.5 mmol K₃PO₄; 3.0 ml DMSO; 0.05 mmol organic additive (hydroxy-L-proline, if it is necessary); T = 110 °C; t = 24 h.

Table S1

Cu^IBiOI catalyzed coupling of chlorobenzene and aqueous ammonia in the presence of various bases.^a

Bases	Yield (%)
K ₂ CO ₃	79
K ₃ PO ₄	100
Cs ₂ CO ₃	93
pyridine	59
piperidine	54

^a1.0 mmol aqueous ammonia; 0.5 mmol chlorobenzene; 0.04 mmol catalyst; 0.5 mmol base; 3.0 ml DMSO; T = 110 °C; t = 24 h

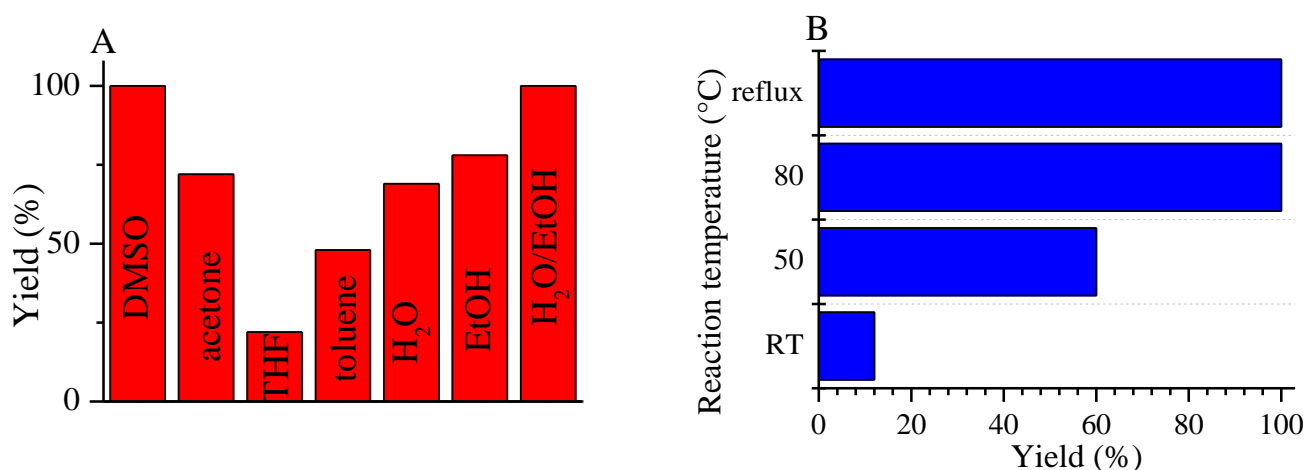


Fig. S5. Investigating various solvents and reaction temperatures in the Cu^IBiOI catalyzed Ullmann-type reaction. Reaction conditions: 1.0 mmol aqueous ammonia; 0.5 mmol chlorobenzene; 0.04 mmol catalysts; 0.5 mmol K₃PO₄; 3.0 ml solvent (H₂O/EtOH mixture for Fig. S5.(B)); t = 24 h; reflux temperature (except for DMSO; T = 110 °C).

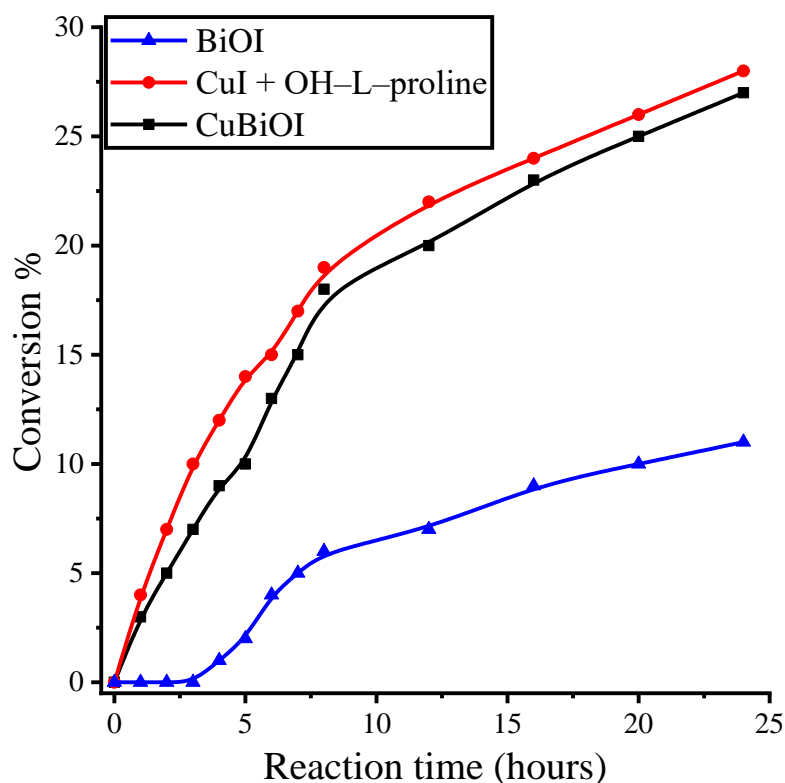


Fig. S6. Ullmann-type C–N coupling reaction between chlorobenzene and aqueous ammonia. Reaction conditions: 1.0 mmol of aqueous ammonia; 0.5 mmol of chlorobenzene; 0.04 mmol (0.06 mmol in the homogeneous case) of catalyst; 0.5 mmol of K_3PO_4 ; 3.0 ml of DMSO; 0.05 mmol of organic additive (hydroxy–L–proline, if it is necessary); $T = 80\text{ }^\circ\text{C}$.

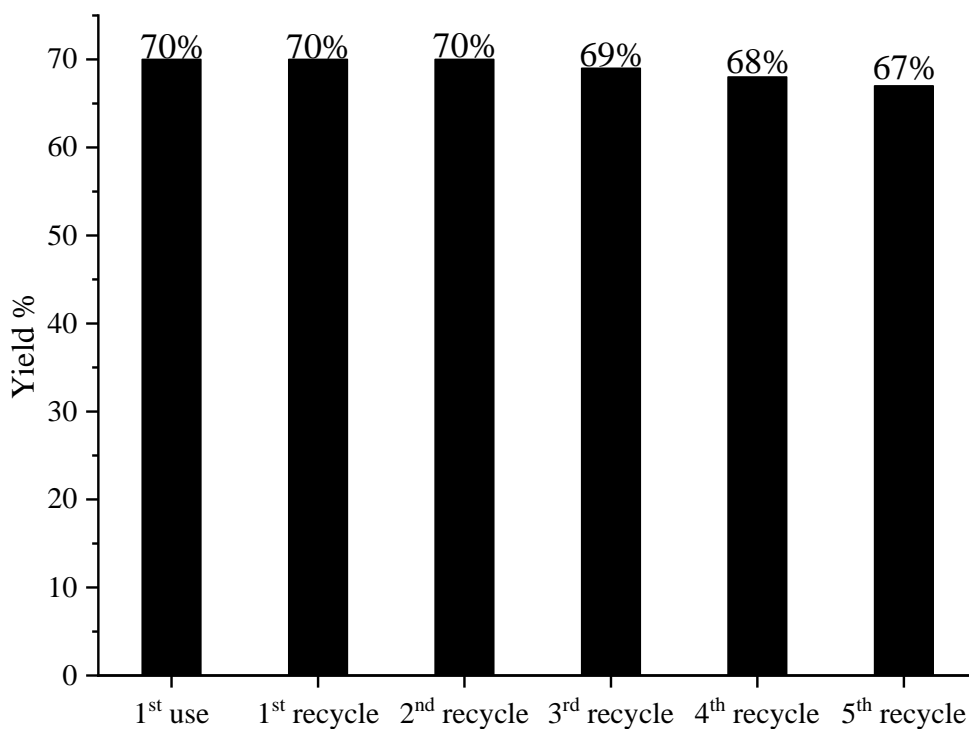


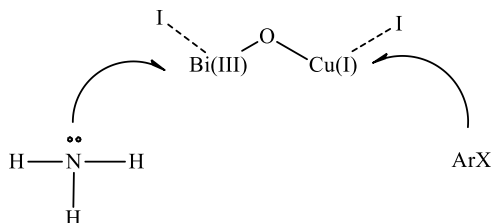
Fig. S7. Recyclability of the as-prepared $Cu^I BiOI$ material tested in Ullmann-type C–N coupling reaction between chlorobenzene and aqueous ammonia. The optimized conditions: 1.0

mmol aqueous ammonia; 0.5 mmol chlorobenzene; 0.02 mmol catalysts; 0.5 mmol K_3PO_4 ; 3 ml EtOH/water (1:1; v/v%); T = 80 °C; t = 20 h.

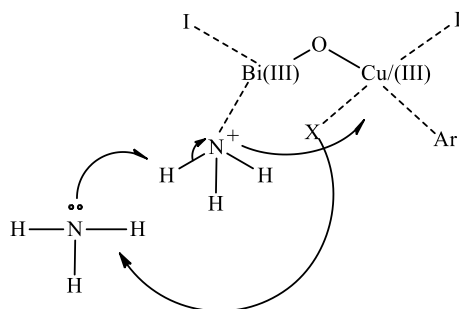
Mechanistic proposal

It is reasonable to assume that Cu(I) is the key active centre in the catalytic cycle for the $Cu^I BiOI$ structure. The bismuth(III) component, as a Lewis acid centre, may accelerate the catalytic cycle through coordinating an ammonia molecule. Possible steps are as follows: step I – oxidative addition of aryl halide over Cu(I); step II – coordination of ammonia to the Bi(III) centre followed by proton abstraction by another ammonia molecule; step III – anionoid migration to the Cu(III) reducing to Cu(II) followed by reductive elimination producing the product and regenerating the Cu(I) centre.

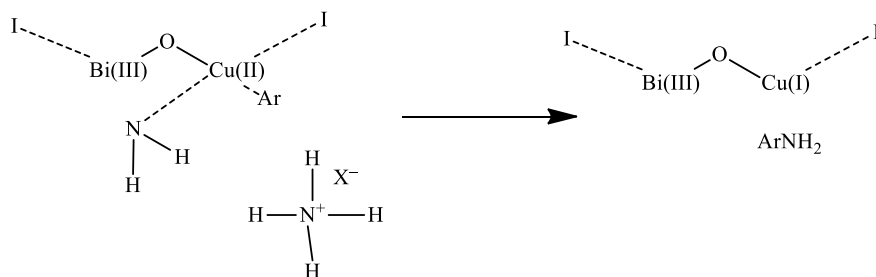
step I: oxidative addition



step II: coordination/proton abstraction



step III: anionoid migration/reductive elimination



Scheme S1 The schematic representation of the possible reaction mechanism of $\text{Cu}^{\text{I}}\text{BiOI}$ catalysed Ullmann-type C–N coupling reaction between aryl halides and ammonia