SUPPORTING INFORMATION

Tunable Prussian blue analogues for the selective synthesis of propargylamines through A^3 coupling

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Experimental

Synthesis of PBAs

A series of PBAs were synthesized following previously reported procedures [1,2]. In short, 15 ml of a 0.1 M aqueous solution of $K_3[Co(CN)_6]$ was added dropwise, under continuous stirring, to 150 ml of a 0.1 M aqueous solution of a $M^1Cl_2.xH_2O$ salt ($FeCl_2.4H_2O$, $CoCl_2$, $NiCl_2.6H_2O$, $CuCl_2.2H_2O$ or $ZnCl_2$) containing 1.5 mmol of poly(tetramethylene ether) glycol (PTMEG). After both solutions were mixed, 37.5 ml of *tert*-butanol (^{t}BuOH) was added and the mixture was stirred for 3 h at room temperature. The precipitate was recovered by centrifugation, washed three times with 50 ml of a 50 : 50 mixture of water : tBuOH and dried at 333 K overnight. The solids Fe-Co, Co-Co, Ni-Co, Cu-Co and Zn-Co PBA were obtained using the respective M^1 sources.

Synthesis of multi-metal Cu_xZn_{1-x}-Co PBAs

A series of multi-metal complexes, Cu_xZn_{1-x}-Co PBAs, were obtained by tuning the initial synthesis molar ratio of $CuCl_2.2H_2O$ and $ZnCl_2$. Briefly, an aqueous solution of $K_3[Co(CN)_6]$ (0.1 M, 15 ml) was added dropwise, under continuous stirring, to another aqueous solution (150 ml) containing 1.5 mmol of PTMEG and specific amounts of $CuCl_2.2H_2O$ and $ZnCl_2$ (15 mmol in total). Then, 37.5 mL of ^{t}BuOH were added and the mixture was stirred for 3 h at room temperature. The precipitate was recovered by centrifugation, washed three times with a 50 : 50 mixture of water : ^{t}BuOH and dried at 333 K overnight.

Characterization

ICP-OES analyses were used to determine the metal content of the catalysts using a Varian 720-ES equipped with a double-pass glass cyclonic spray chamber, a Sea Spray concentric glass nebulizer and a high solids torch. The digestion of the samples was done following a previously reported procedure [3]. PXRD patterns were collected over a 5-60° 2θ range on a STOE Stadi MP diffractometer (in transmission mode) using an image plate detector and focusing Ge(111) monochromator ($CuK\alpha_1$ radiation, λ = 1.54060 Å). Additional high resolution PXRD patterns for the samples Cu-Co, Zn-Co and CuZn-Co PBA were collected at the I11 beamline (Diamond Light Source, Oxfordshire, UK) using the Mythen2 PSD detector over the range 2-92 °2θ. The wavelength of the radiation was obtained by refining a Si NIST

640c standard. Prior to measurements, the samples were finely ground and loaded into borosilicate capillaries (0.5 mm diameter). Pawley refinements of these powder diffraction patterns were performed using the TOPAS-Academic structure refinement software (version 5) [4,5]. N_2 physisorption isotherms were collected at 77 K on a Micromeritics 3Flex Surface Analyzer. The specific surface area (S_{BET}) was determined using the BET method (0.05 – 0.3 p/p_0 range) and the specific external surface area (S_{ext}) and micropore volume (V_{micro}) were obtained using *t*-plot analysis. Before analyses the samples were after evacuated at 423 K for 16 h. FTIR spectra of KBr wafers (1 wt.% of sample) were collected on a Bruker IFS 66 v/S Vacuum FTIR spectrometer. The acid nature and acid site density were determined by pyridine adsorption followed by FTIR spectroscopy (Py-FTIR) using a Nicolet 6700 FTIR spectrometer. To this end, a self-supporting wafer (~ 10 $mg.cm^{-2}$) was placed in a cell under vacuum and activated at 523 K for 1 h. The cell was then cooled down and the probe molecule was adsorbed onto the wafer at 323 K until saturation (25 mbar). The physisorbed and excess pyridine were removed by evacuation for 30 min before reheating to 423 K to record the IR spectrum. The acid site density was calculated from the areas of the absorption bands around 1450 cm^{-1}, which correspond to pyridine coordinated to Lewis acid sites and using the integrated molar extinction coefficient from Emeis [6]. High angle annular dark field (HAADF) images and EDX maps were obtained in a JEOL ARM-200F TEM with a probe Cs corrector operated at 200 kV. Prior to imaging, the samples were suspended in ethanol and dropped onto a Cu grid (300 Mesh, Pacific Grid Tech, USA) coated with a Lacey carbon layer.

A^3 coupling reaction

Prior to reaction, the catalyst was activated at 353 K under vacuum overnight. Glass crimp cap reaction vials were loaded with 10 mg of the catalyst, phenylacetylene (0.05 mmol), piperidine (0.1 mmol), benzaldehyde (0.1 mmol), 2-butanol (0.5 ml) as solvent (unless otherwise specified) and dodecane (0.1 mmol) as internal standard. The vials were placed in a heated copper block at 383 K and stirred at 500 rpm using a magnetic stirring bar. After reaction, the catalyst was removed by centrifugation and the liquid supernatant was analyzed by GC (Shimadzu 2014 GC equipped with a FID detector and a CP-Sil 5 CB column) and GC-MS (Agilent 6890 gas chromatograph, equipped with a HP-5MS column, coupled to a 5973 MSD mass spectrometer). Recycling test reactions were carried out after recovery and re-activation of the sample before each run. Further reactions varying the initial concentration of phenylacetylene and piperidine were carried out in order to assess the kinetics of the reaction.

Moreover, the effect of the solvent was studied by repeating the reaction using toluene, dioxane and DMSO (dimethyl sulfoxide) as solvents.

Table S1. Elemental analysis of selected PBA samples.

PBA	$Cu/Zn_{initial}$ [a]	Cu (wt.%)	Zn (wt.%)	Co (wt.%)	M^1/Co [b]	Cu/Zn_{PBA} [c]
Zn-Co	-	-	31.3	19.0	1.80	-
$Cu_{0.14}Zn_{0.86}$-Co	0.05	5.8	28.8	17.9	1.74 [d]	0.17
$Cu_{0.26}Zn_{0.74}$-Co	0.10	9.5	24.9	18.0	1.72 [d]	0.35
$Cu_{0.41}Zn_{0.59}$-Co	0.15	15.0	21.3	17.4	1.89 [d]	0.71
$Cu_{0.67}Zn_{0.33}$-Co	0.3	23.5	12.6	17.5	1.90 [d]	2.0
$Cu_{0.86}Zn_{0.14}$-Co	1.0	30.8	5.8	17.3	1.98[d]	6.0
$Cu_{0.86}Zn_{0.14}$-Co[e]	1.0	30.8	5.8	17.3	1.98[d]	6.0
$Cu_{0.96}Zn_{0.04}$-Co	9.0	32.9	1.5	18.0	1.77 [d]	25.5
Cu-Co	-	30.7	-	19.0	1.60	-

[a] Initial $CuCl_2.2H_2O$: $ZnCl_2$ molar ratios used during synthesis. [b] Molar ratios determined by ICP. [c] Cu/Zn molar ratios in the multi-metal PBA complex determined by ICP. [d] (Cu+Zn)/Co molar ratio. [e] Elemental analysis after one reaction cycle.

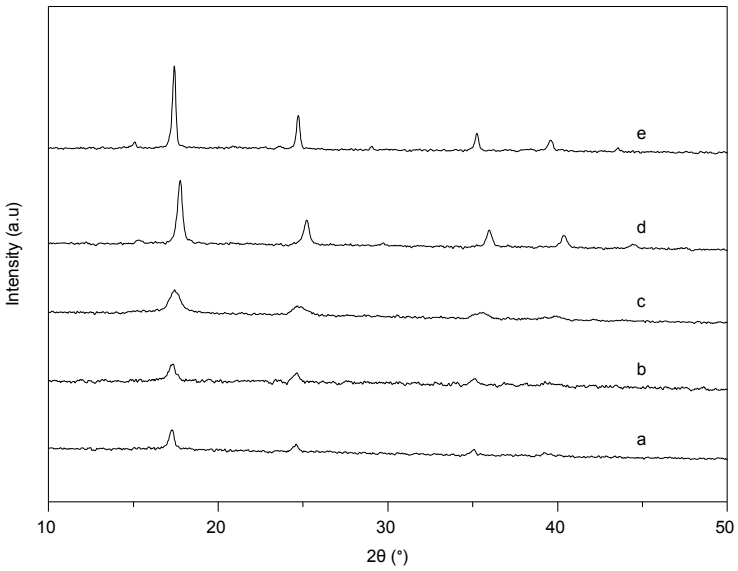

Fig. S1. PXRD patterns for PBA samples: a) Fe-Co, b) Co-Co, c) Ni-Co, d) Cu-Co and e) Zn-Co.

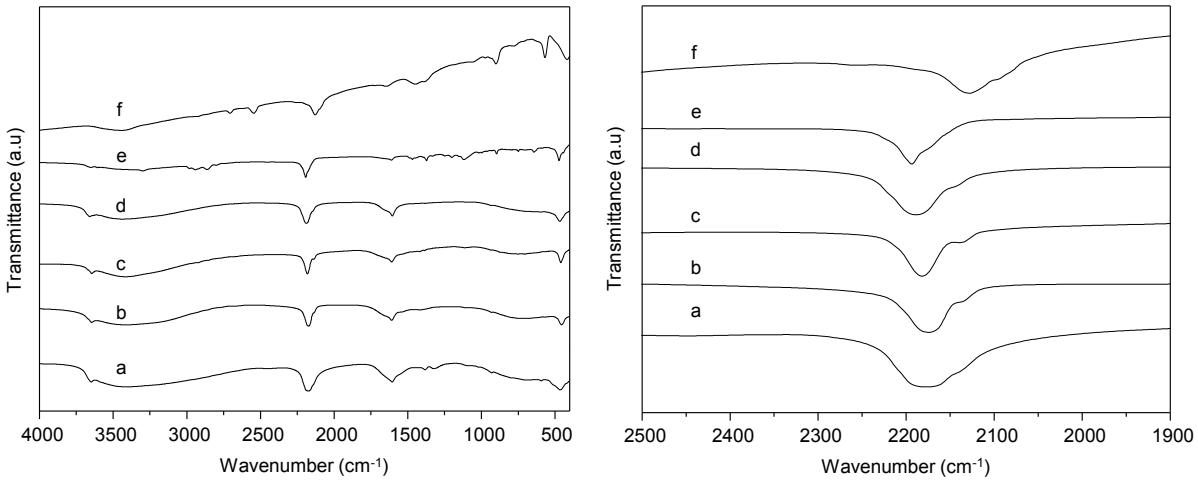

Fig. S2. FTIR spectra (left) and C≡N stretching region of the FTIR spectra (right) of: (a) Fe-Co PBA, (b) Co-Co PBA, (c) Ni-Co PBA, (d) Cu-Co PBA, (e) Zn-Co PBA and (f) $K_3Co(CN)_6$.

Table S2. Textural properties of the PBA samples determined from N_2 physisorption at 77 K and Lewis acid properties determined by pyridine adsorption followed by FTIR spectroscopy.

PBA	S_{BET} (m^2/g)	S_{ext} (m^2/g)	V_{micro} (cm^3/g)	LAS (mmol/g)[a]
Fe-Co	641	311	0.168	-
Co-Co	1076	327	0.382	-
Ni-Co	114	39	0.038	-
Cu-Co	540	147	0.201	0.044
$Cu_{0.86}Zn_{0.14}$-Co	567	147	0.222	0.053
Zn-Co	666	138	0.270	0.073

[a] Amount of pyridine adsorbed on Lewis acid sites (LAS) per gram of PBA. IR spectra recorded at 423 K.

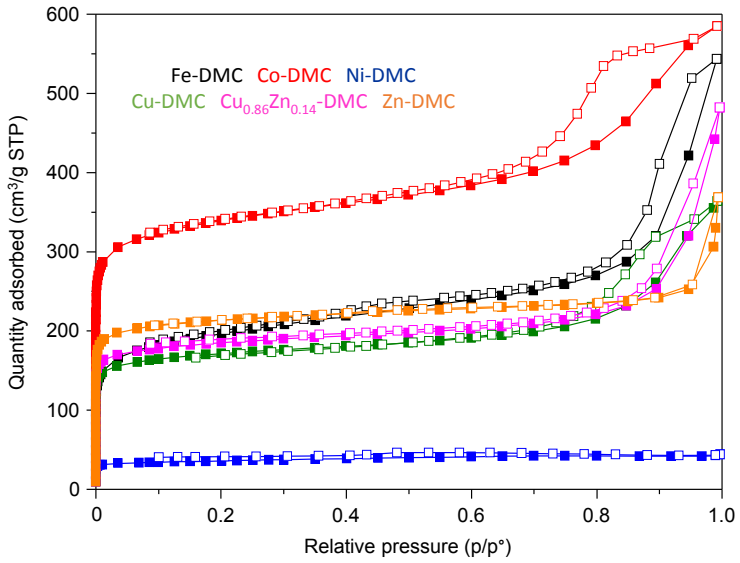

Fig. S3. Nitrogen physisorption isotherms of PBA samples. Filled symbols denote adsorption and open symbols denote desorption.

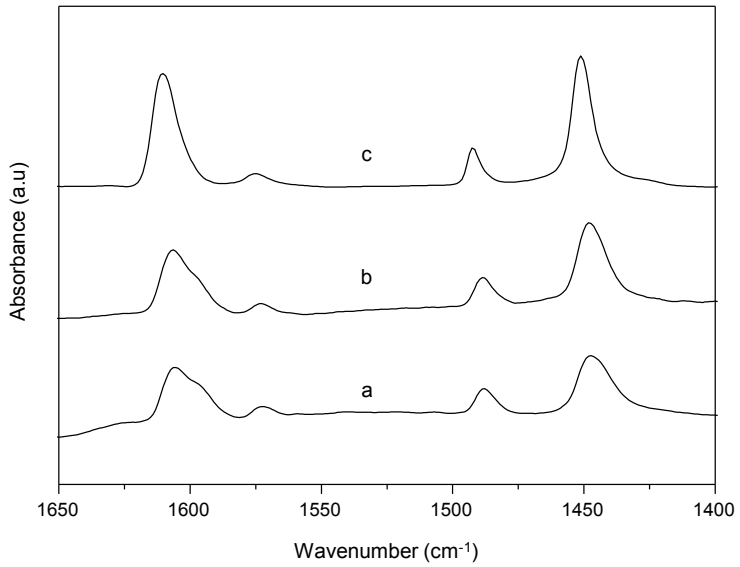

Figure S4. Difference IR spectra of adsorbed pyridine (normalized to 10 mg of PBA/cm^2) for: a) Cu-Co PBA b) $Cu_{0.86}Zn_{0.14}$-Co PBA and c) Zn-Co PBA.

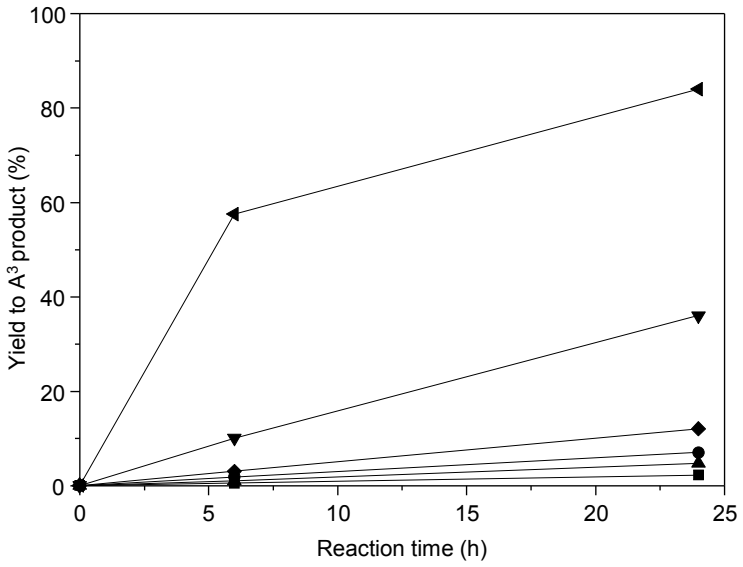

Fig. S5. Yield to the A^3 product in the coupling of phenylacetylene (0.05 mmol), piperidine (0.1 mmol) and benzaldehyde (0.1 mmol) at 383 K over PBAs: Fe-Co (■), Co-Co (●), Ni-Co (▲), Cu-Co (▼), Zn-Co (♦), $Cu_{0.86}Zn_{0.14}$-Co (◄).

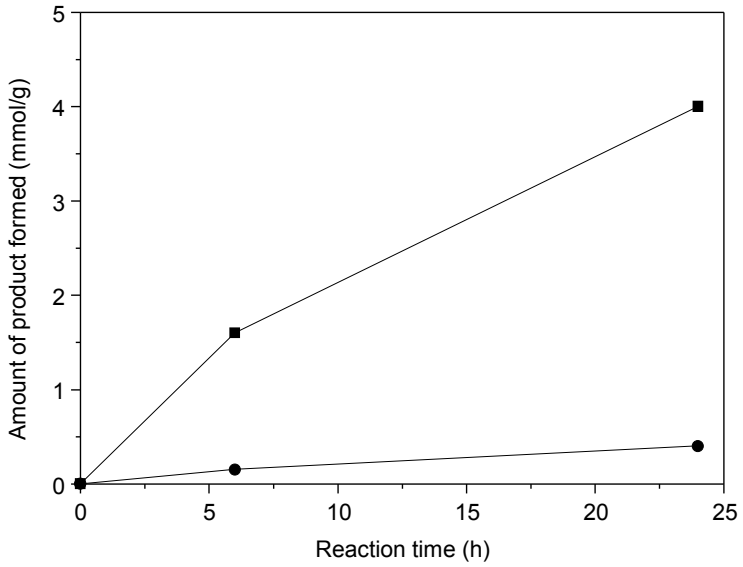

Fig S6. Productivity for the A^3 coupling (●) and MPV reduction (■) reaction expressed as mmol of product (A^3 product and benzyl alcohol, respectively) formed per g of Fe-Co PBA.

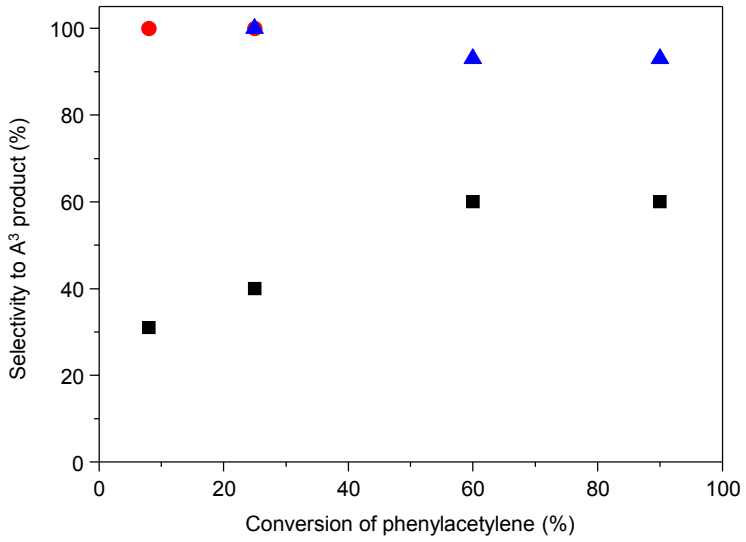

Fig. S7. Selectivity to the A^3 product at different phenylacetylene conversions with Cu-Co PBA (■), Zn-Co PBA (●) and $Cu_{0.86}Zn_{0.14}$-Co PBA (▲).

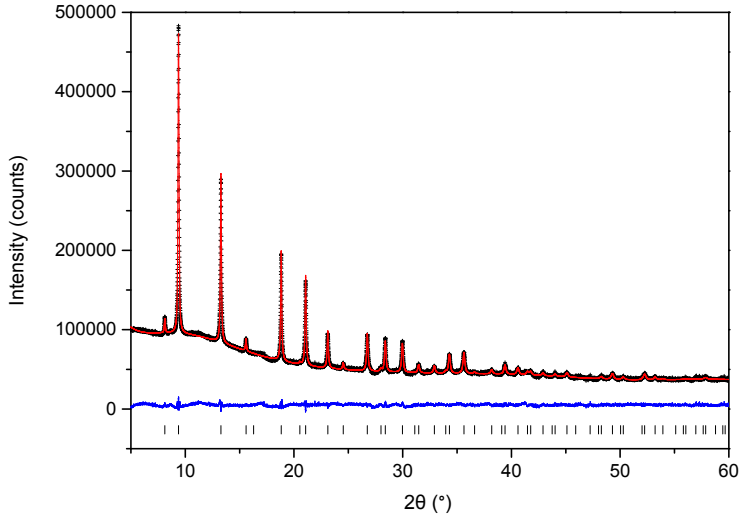

Fig. S8. Pawley refinement of $Cu_{0.86}Zn_{0.14}$-Co PBA: observed pattern (+), calculated pattern (red line), difference (blue line) and expected peak positions (|).

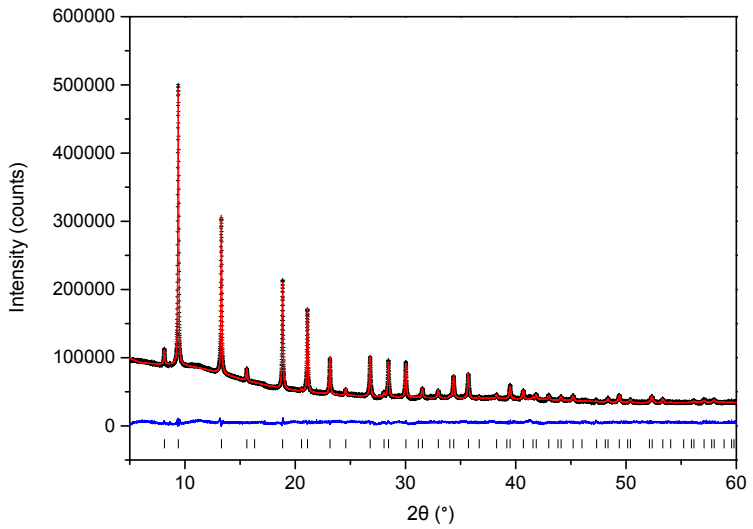

Fig. S9. Pawley refinement of Cu-Co PBA: observed pattern (+), calculated pattern (red line), difference (blue line) and expected peak positions (|).

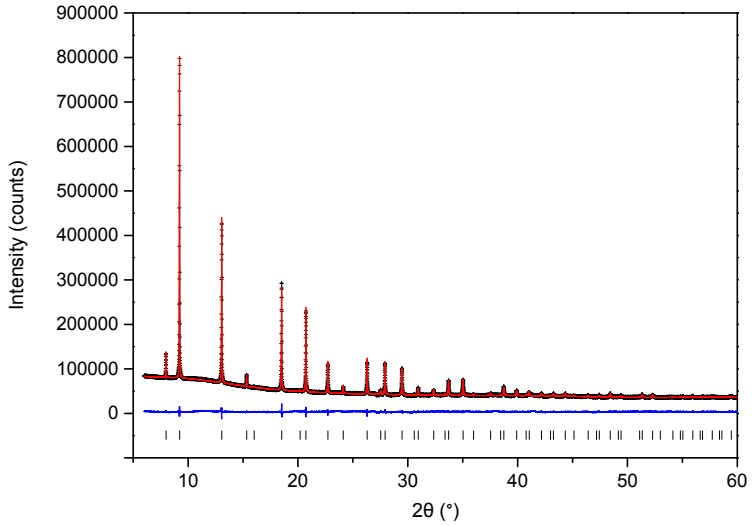

Fig. S10. Pawley refinement of Zn-Co PBA: observed pattern (+), calculated pattern (red line), difference (blue line) and expected peak positions (|).

Table S3. Summary of the crystallographic parameters obtained from the Pawley refinement of selected PBA samples.

	Cu-Co	Zn-Co	$Cu_{0.86}Zn_{0.14}$-Co
Wavelength (Å)	0.82522	0.82538	0.82522
Space group	*Fm*-3*m*	*Fm*-3*m*	*Fm*-3*m*
a (Å)	10.07163 (18)	10.26025 (17)	10.0908 (3)
R_{wp} (%)	3.05	2.98	3.10
χ^2	32.1	25.3	37.2

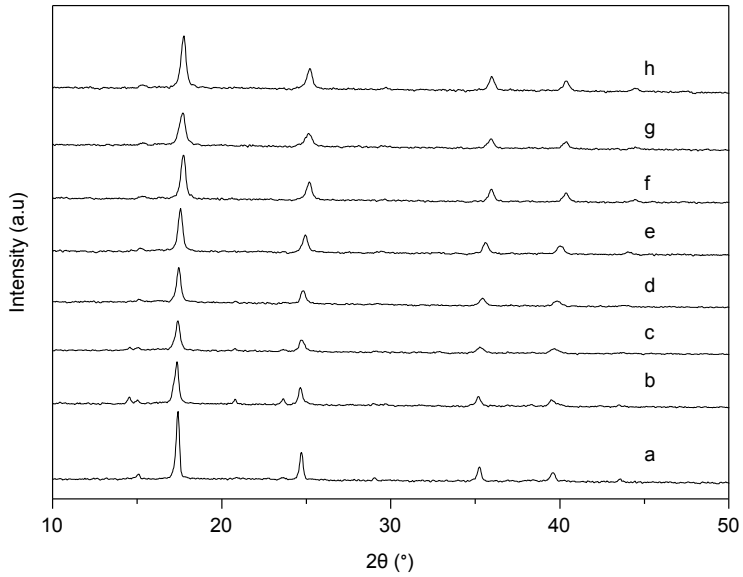

Fig. S11. PXRD patterns for PBA samples: a) Zn-Co, b) $Cu_{0.14}Zn_{0.86}$-Co, c) $Cu_{0.26}Zn_{0.74}$-Co, d) $Cu_{0.41}Zn_{0.59}$-Co, e) $Cu_{0.67}Zn_{0.33}$-Co, f) $Cu_{0.86}Zn_{0.14}$-Co, g) $Cu_{0.96}Zn_{0.04}$-Co and h) Cu-Co.

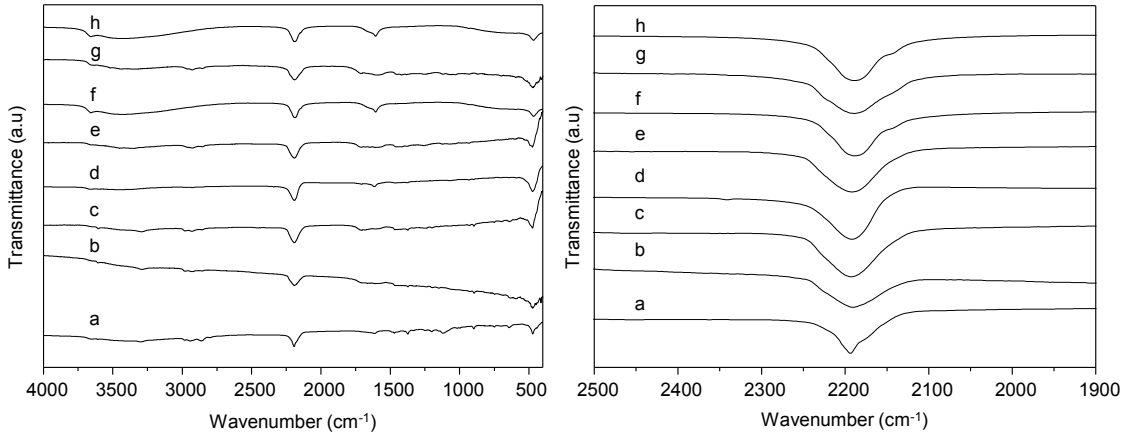

Fig. S12. FTIR spectra (left) and C≡N stretching region of the FTIR spectra (right) of: a) Zn-Co, b) $Cu_{0.14}Zn_{0.86}$-Co, c) $Cu_{0.26}Zn_{0.74}$-Co, d) $Cu_{0.41}Zn_{0.59}$-Co, e) $Cu_{0.67}Zn_{0.33}$-Co, f) $Cu_{0.86}Zn_{0.14}$-Co, g) $Cu_{0.96}Zn_{0.04}$-Co and h) Cu-Co.

Table S4. Comparison of PBAs with homogenous catalysts and heterogeneous catalyst from literature.

	6 h		24 h	
Catalyst	X (%)[a]	Y A^3 (%)[b]	X (%)[a]	Y A^3 (%)[b]
Zn-Co PBA	3	3	12	12
Cu-Co PBA	25	10[c]	60	36[c]
$Cu_{0.86}Zn_{0.14}$-Co PBA	60	56[c]	90	85[c]
$Cu(OAc)_2$	97	4[d]	>99	5[d]
$Cu(ClO_4)_2$	69	<1[d]	90	<1[d]
$CuCl_2$	94	<1[d]	>99	<1[d]
$ZnCl_2$	35	33[c]	70	66[c]
[Cu(2-pymo)$_2$]	-	-	-	71[e]
CuNPs/G	-	-	-	96[f]

[a] Conversion of phenylacetylene. [b] Yield of the A^3 product based on phenylacetylene. [c] Acetophenone was the only side-product detected. [d] 1,4-diphenylbuta-1,3-diyne (from the homocoupling of phenylacetylene) was the only side-product detected. [e] Yield after 21 h. Reaction conditions: 1 mmol phenylacetylene, 1.1 mmol benzaldehyde, 1.1 mmol piperdine, 1 mL dioxane, 10%mol Cu, 373 K (N_2 atmosphere) [7]. [f] Yield after 24 h. Reaction conditions: 1 mmol of phenylacetylene, 1.2 mmol of benzaldehyde, 1.2 mmol of piperidine, 3 ml of toluene, 1 mol% Cu/G (2.6 wt%), 373 K (N_2 atmosphere) [8].

Table S5. Yield (%) of the A^3 coupling product at 383 K over $Cu_{0.86}Zn_{0.14}$-Co PBA using different solvents.

Reaction time (h)	Solvent			
	2-Butanol	Dioxane	Toluene	DMSO
6	54	5	3	4
24	85	14	6	10

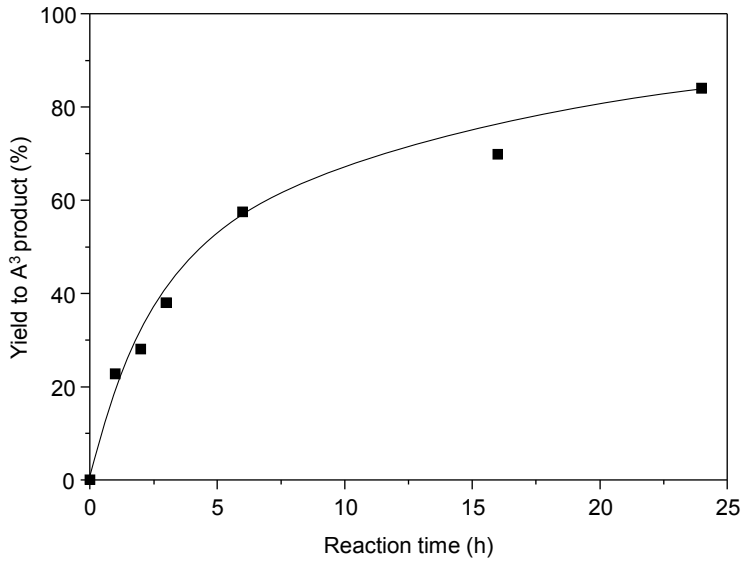

Fig. S13. Yield to A^3 product vs. time plot for the coupling of phenylacetylene (0.05 mmol), piperidine (0.1 mmol) and benzaldehyde (0.1 mmol) at 383 K over $Cu_{0.86}Zn_{0.14}$-Co PBA.

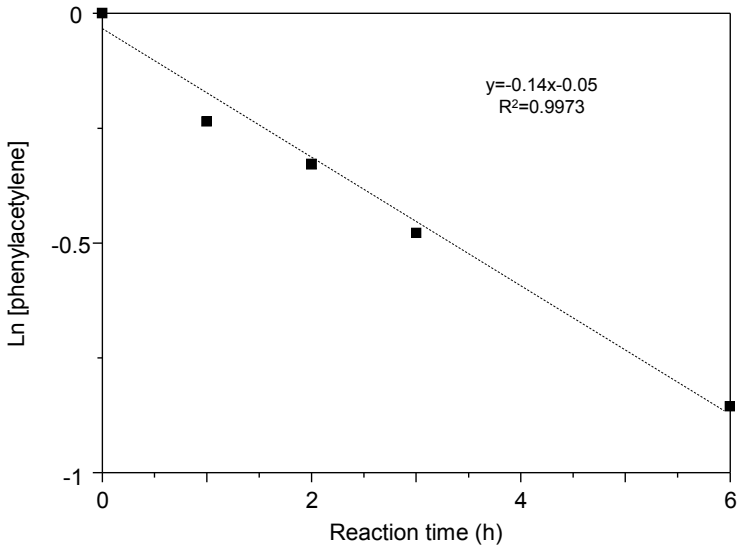

Fig. S14. Linear relation between the natural logarithm of the concentration of phenylacetylene and time. Reaction conditions: phenylacetylene (0.05 mmol), piperidine (0.1 mmol) and benzaldehyde (0.1 mmol) at 383 K over $Cu_{0.86}Zn_{0.14}$-Co PBA.

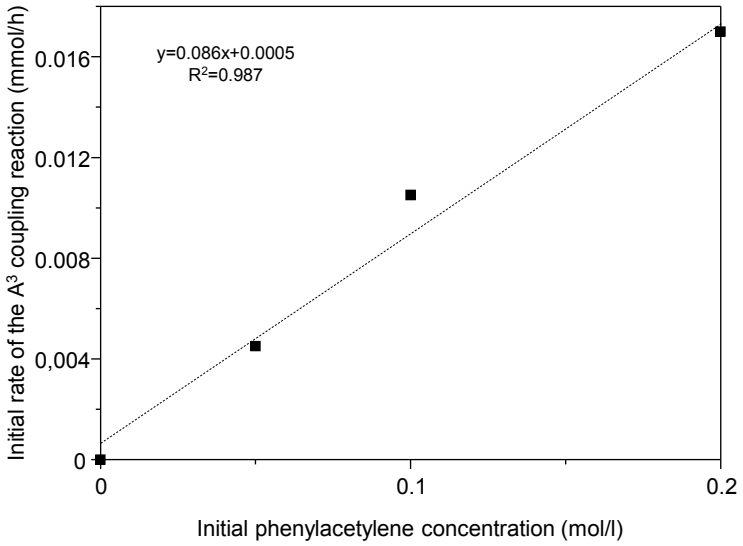

Fig. S15. Variation of the reaction rate with respect to the concentration of phenylacetylene. Reactions were carried out with 0.1 mmol of piperidine and 0.1 mmol of benzaldehyde at 383 K for 1 h over $Cu_{0.86}Zn_{0.14}$-Co PBA.

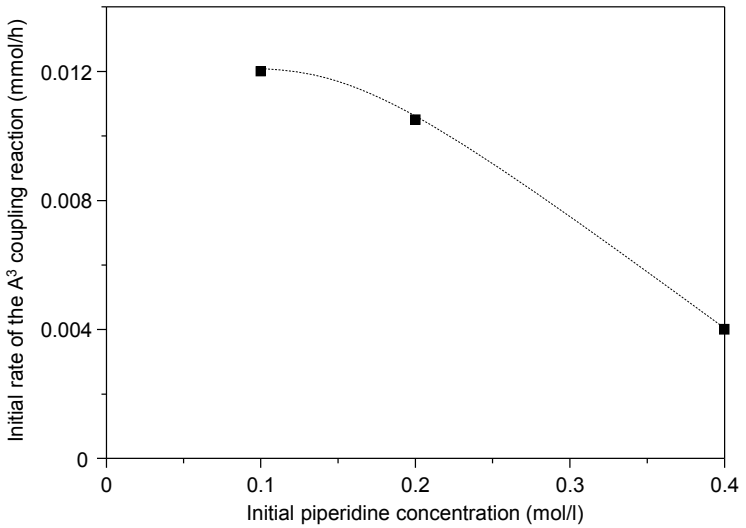

Fig. S16. Variation of the reaction rate with respect to the concentration of piperidine. Reactions were carried out with 0.05 mmol of phenylacetylene and 0.1 mmol of benzaldehyde at 383 K for 1 h over $Cu_{0.86}Zn_{0.14}$-Co PBA.

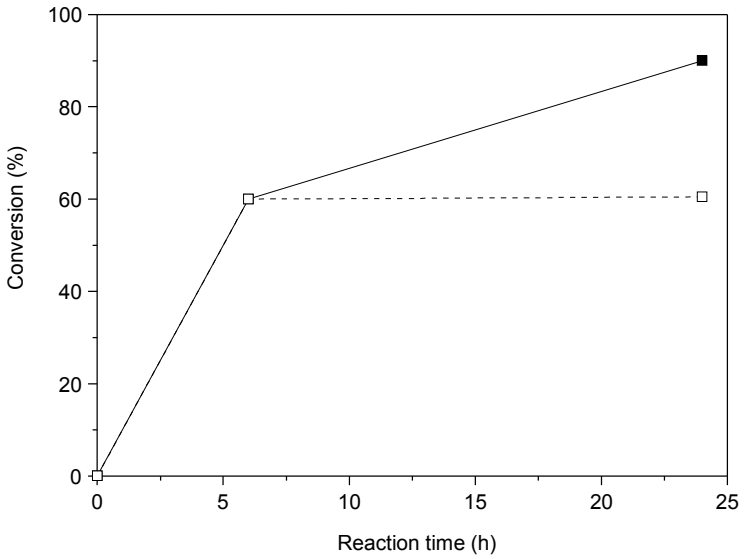

Fig. S17. Conversion of phenylacetylene in the A^3 coupling of phenylacetylene (0.05 mmol), piperidine (0.1 mmol) and benzaldehyde (0.1 mmol) at 383 K over $Cu_{0.86}Zn_{0.14}$-Co PBA. Dashed lines represent the conversion after removal of the catalyst in the hot filtration test.

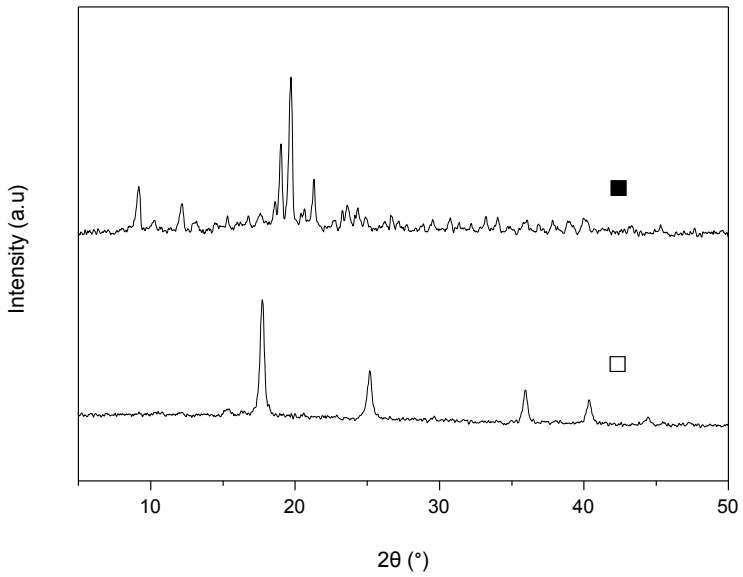

Fig. S14. XRD pattern of $Cu_{0.86}Zn_{0.14}$-Co PBA before (□) and after (■) the A^3 coupling reaction. Reaction conditions: phenylacetylene (0.05 mmol), piperidine (0.1 mmol) and benzaldehyde (0.1 mmol). 24 h at 383 K.

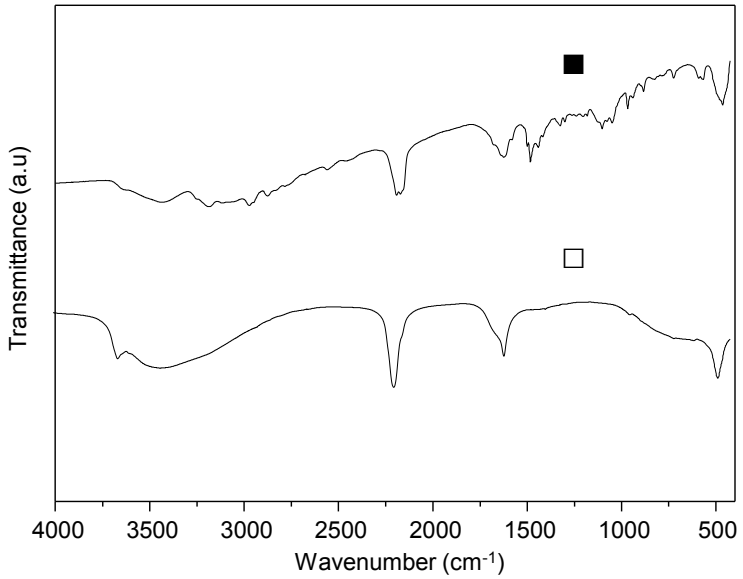

Fig. S15. FTIR spectrum of $Cu_{0.86}Zn_{0.14}$-Co PBA before (□) and after (■) the A^3 coupling reaction. Reaction conditions: phenylacetylene (0.05 mmol), piperidine (0.1 mmol) and benzaldehyde (0.1 mmol). 24 h at 383 K.

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