

## Supporting information

### Metal ion exchange in Prussian blue analogues: Cu(II)-exchanged Zn-Co PBAs as highly selective catalysts for A<sup>3</sup> coupling

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## Synthesis of $\text{Cu}_x\text{Zn}_{1-x}\text{-Co}$ PBAs by co-precipitation

$\text{Cu}_x\text{Zn}_{1-x}\text{-Co}$  PBAs were synthesized following previously reported procedures.<sup>1</sup> In short, a solution of  $\text{K}_3[\text{Co}(\text{CN})_6]$  (0.1 M, 15 ml) was mixed with a solution (150 ml) containing specific amounts of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{ZnCl}_2$  (15 mmol in total). After stirring for 3 h, the precipitate was recovered by centrifugation, washed three times with distilled water and dried at 60°C overnight.

## Preparation of Cu(II) based catalysts

Silica gel (Sigma-Aldrich, high purity grade, pore size 150 Å, 200–425 mesh), commercial Beta zeolite (CP811BL25, Si/Al = 12.5) and MCM-41 (synthesized following the procedure reported by Grün et al.<sup>2</sup>) were dispersed (5 g/L) in 50 mM aqueous solutions of  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ . The final solution was stirred for 16 h at room temperature. The solids were then centrifuged, washed 3 times with distilled water and dried at 60°C overnight to obtain the samples: Cu(II)/MCM-41 (Cu wt.% = 19.4), Cu(II)/BEA (Cu wt.% = 23.6) and Cu(II)/ $\text{SiO}_2$  (Cu wt.% = 19.8).

Cu(II)-BTC was purchased from Sigma-Aldrich (Basolite® C 300, produced by BASF. Cu wt.% = 26.2).

## Nitroaldol (Henry) reaction

To test the basic character of selected PBAs, the nitroaldol (Henry) reaction was carried out. To this end, 20 mg of pre-activated catalyst, 1 mmol of benzaldehyde and 5 mmol of nitromethane were added to a crimp cap glass reactor and placed in a pre-heated aluminum block. The reaction was carried out at 90°C, collecting liquid samples of the product mixture after 48 and 96 h reaction time. The products were 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).

Table S1. Elemental analysis of Zn(II) exchanged samples and the remaining supernatant after the ion exchange process

PBA	Zn(II) salt	Concentration (mM)	Time (h)	Cu (wt.%)	Zn (wt.%)	Co (wt.%)	Cu <sub>loss</sub> <sup>a</sup> (wt.%)	IED <sub>Zn</sub> <sup>b</sup> (%)
CuCl <sub>2</sub> -Co		-	-	35.8	-	17.6	-	-
Cu(OAc) <sub>2</sub> -Co		-	-	38.0	-	17.0	-	-
[Zn(OAc) <sub>2</sub> ] <sub>0.01</sub> @Cu <sub>0.99</sub> -Co	Zn(OAc) <sub>2</sub>	50	16	33.6	0.254	18.1	1.05	6.15
[Zn(OAc) <sub>2</sub> ] <sub>0.09</sub> @Cu <sub>0.91</sub> -Co	Zn(OAc) <sub>2</sub>	100	16	31.1	3.01	18.0	3.05	13.1
[Zn(OAc) <sub>2</sub> ] <sub>0.12</sub> @Cu <sub>0.88</sub> -Co <sup>c</sup>	Zn(OAc) <sub>2</sub>	100	16	29.6	4.09	18.1	5.02	17.3
[Zn(OAc) <sub>2</sub> ] <sub>0.77</sub> @Cu <sub>0.23</sub> -Co <sup>d</sup>	Zn(OAc) <sub>2</sub>	100	16	8.03	27.0	17.6	25.6	77.6
[Zn(OAc) <sub>2</sub> ] <sub>0.78</sub> @Cu <sub>0.22</sub> -Co <sup>e</sup>	Zn(OAc) <sub>2</sub>	100	16	7.60	26.8	17.8	27.5	78.8
[ZnCl <sub>2</sub> ] <sub>0.30</sub> @Cu <sub>0.70</sub> -Co	ZnCl <sub>2</sub>	50	16	24.1	10.5	17.8	10.1	32.7
[ZnCl <sub>2</sub> ] <sub>0.46</sub> @Cu <sub>0.54</sub> -Co	ZnCl <sub>2</sub>	100	16	18.9	16.2	17.7	16.5	47.2
[ZnCl <sub>2</sub> ] <sub>0.62</sub> @Cu <sub>0.38</sub> -Co <sup>e</sup>	ZnCl <sub>2</sub>	100	16	12.8	22.1	17.7	22.1	64.2
[ZnCl <sub>2</sub> ] <sub>0.63</sub> @Cu <sub>0.37</sub> -Co <sup>d</sup>	ZnCl <sub>2</sub>	100	16	13.2	21.8	17.7	22.2	63.1
Zn-Co	-	-	-	-	32.0	18.7	-	-

Starting material: CuCl<sub>2</sub>-Co PBA. <sup>a</sup> Cu wt.% loss of the sample, based on the concentration of Cu released into solution during the exchange process. <sup>b</sup> Atomic ion exchange efficiency defined as atoms of Cu exchanged per atoms of Cu present in CuCl<sub>2</sub>-Co PBA. <sup>c</sup> The ion exchange process was carried out at 40 °C. <sup>d</sup> The ion exchange process was carried out at 60 °C. <sup>e</sup> The ion exchange process was carried out at 80 °C.

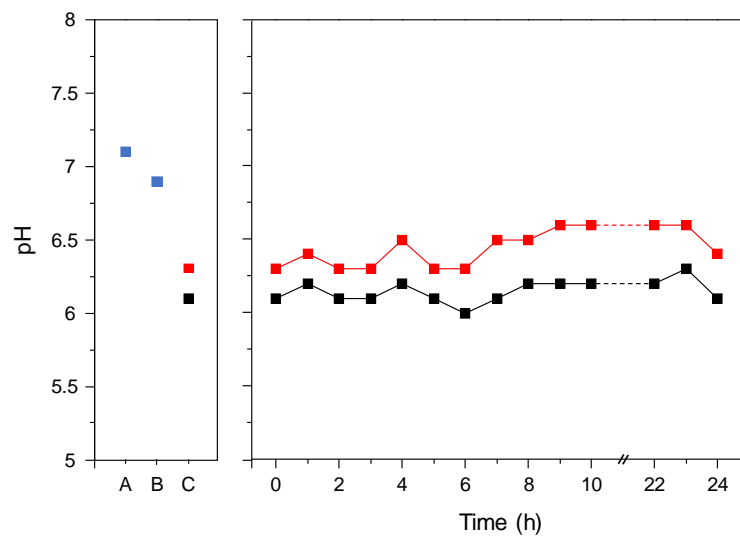


Figure S1. Solution pH during the Cu(II) exchange process with  $\text{Cu}(\text{ClO}_4)_2$  (red) and  $\text{Cu}(\text{OAc})_2$  (black). A: pH of water. B: pH of water + Zn-Co PBA (1 g/L). C: pH of a 1g/L solution of  $\text{Cu}(\text{OCl}_4)_2$  (red) and  $\text{Cu}(\text{OAc})_2$  (black).

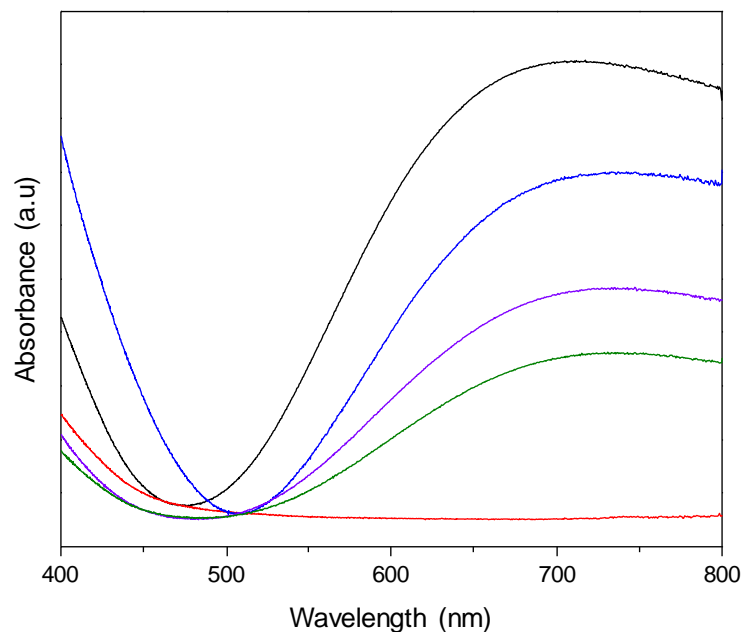


Figure S2. UV/vis spectra of Zn-Co (red),  $[\text{Cu}(\text{OAc})_2]_{0.20}@\text{Zn}_{0.80}\text{-Co}$  (green),  $[\text{Cu}(\text{OAc})_2]_{0.45}@\text{Zn}_{0.55}\text{-Co}$  (violet),  $[\text{Cu}(\text{OAc})_2]_{0.90}@\text{Zn}_{0.10}\text{-Co}$  (blue) and  $\text{CuCl}_2\text{-Co PBA}$  (black).

No band corresponding to the presence of  $\text{Co}(\text{II})$  – expected around 500 nm – was observed in the spectra of any of the studied samples, which exhibit only one broad band, assigned to the d-d transitions of  $\text{Cu}(\text{II})$ .<sup>3-5</sup> This not only indicates the presence of  $\text{Cu}(\text{II})$  in the PBA structure after ion exchange, but also that the  $[\text{Co}(\text{CN})_6]^{3-}$  do not undergo a redox process. This confirms that a mechanism similar to that observed in electrochemical insertions is not the main pathway of the  $\text{Cu}(\text{II})$  exchange.

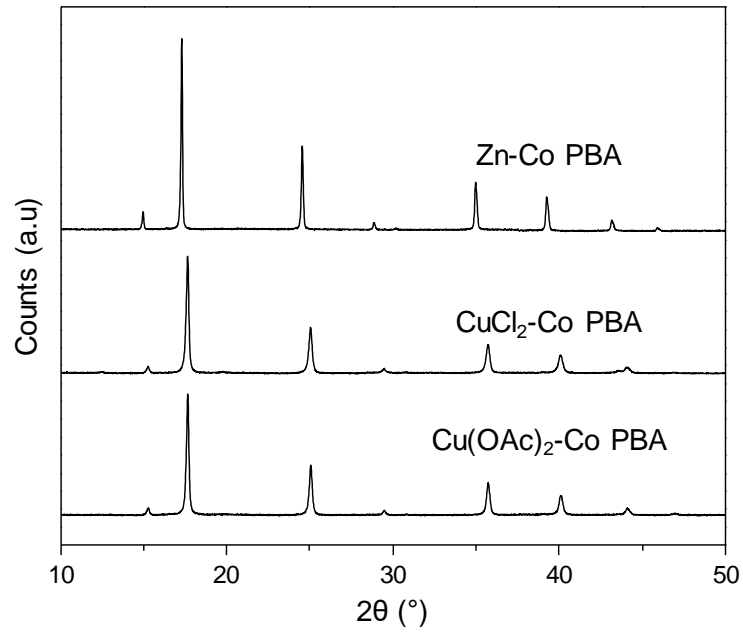


Figure S3. XRD patterns of Zn-Co, CuCl<sub>2</sub>-Co and Cu(OAc)<sub>2</sub>-Co PBA.

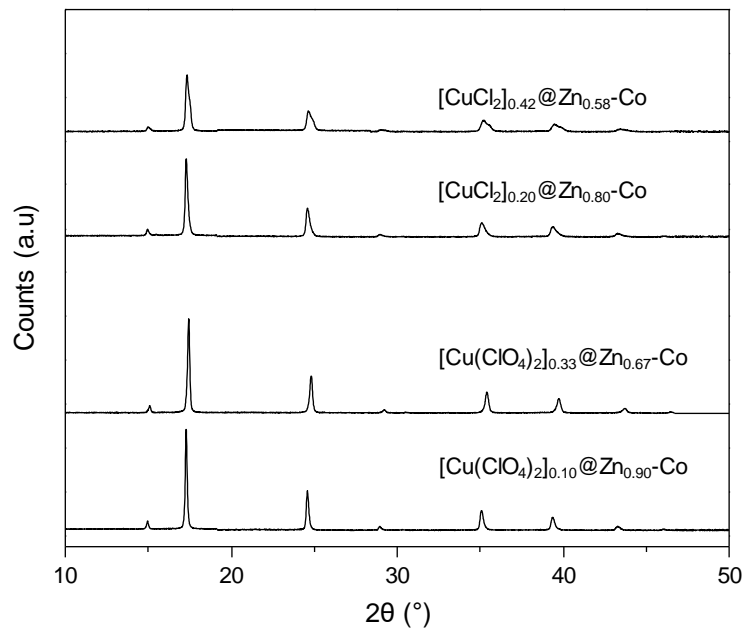


Figure S4. XRD patterns of the [CuCl<sub>2</sub>]<sub>x</sub>@Zn<sub>1-x</sub>-Co and [Cu(ClO<sub>4</sub>)<sub>2</sub>]<sub>x</sub>@Zn<sub>1-x</sub>-Co PBAs.

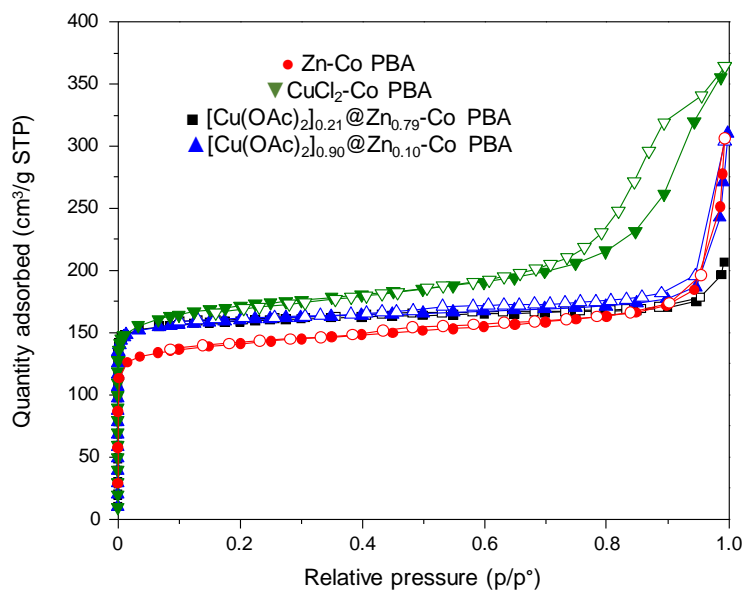


Figure S5. Nitrogen physisorption isotherms of selected PBA samples. Filled symbols denote adsorption and open symbols denote desorption.

Table S2. Textural properties of selected PBA samples determined from N<sub>2</sub> physisorption at -196.15 °C.

PBA	$S_{\text{BET}}$ (m <sup>2</sup> /g)	$V_{\text{micro}}$ (cm <sup>3</sup> /g)	$S_{\text{ext}}$ (m <sup>2</sup> /g)
Zn-Co	453	0.172	106
CuCl <sub>2</sub> -Co	540	0.221	145
[Cu(OAc) <sub>2</sub> ] <sub>0.21</sub> @Zn <sub>0.79</sub> -Co	479	0.202	60
[Cu(OAc) <sub>2</sub> ] <sub>0.90</sub> @Zn <sub>0.10</sub> -Co	482	0.217	72

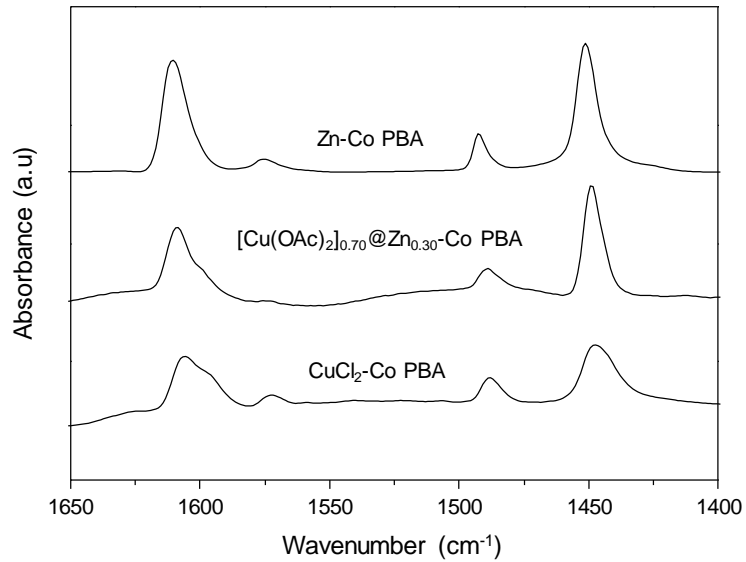


Figure S6. Difference IR spectra of adsorbed pyridine (normalized to 10 mg of PBA/cm<sup>2</sup>) for selected PBA samples.

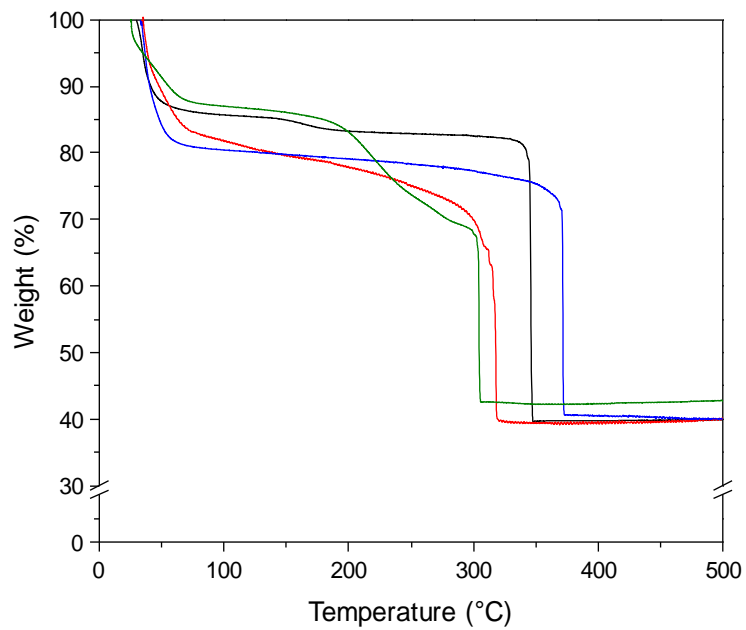


Figure S7. TGA profiles for Zn-Co PBA (black), CuCl<sub>2</sub>-Co PBA (blue), [Cu(OAc)<sub>2</sub>]<sub>0.21</sub>@Zn<sub>0.79</sub>-Co PBA (red) and [Cu(OAc)<sub>2</sub>]<sub>0.90</sub>@Zn<sub>0.10</sub>-Co PBA (green).



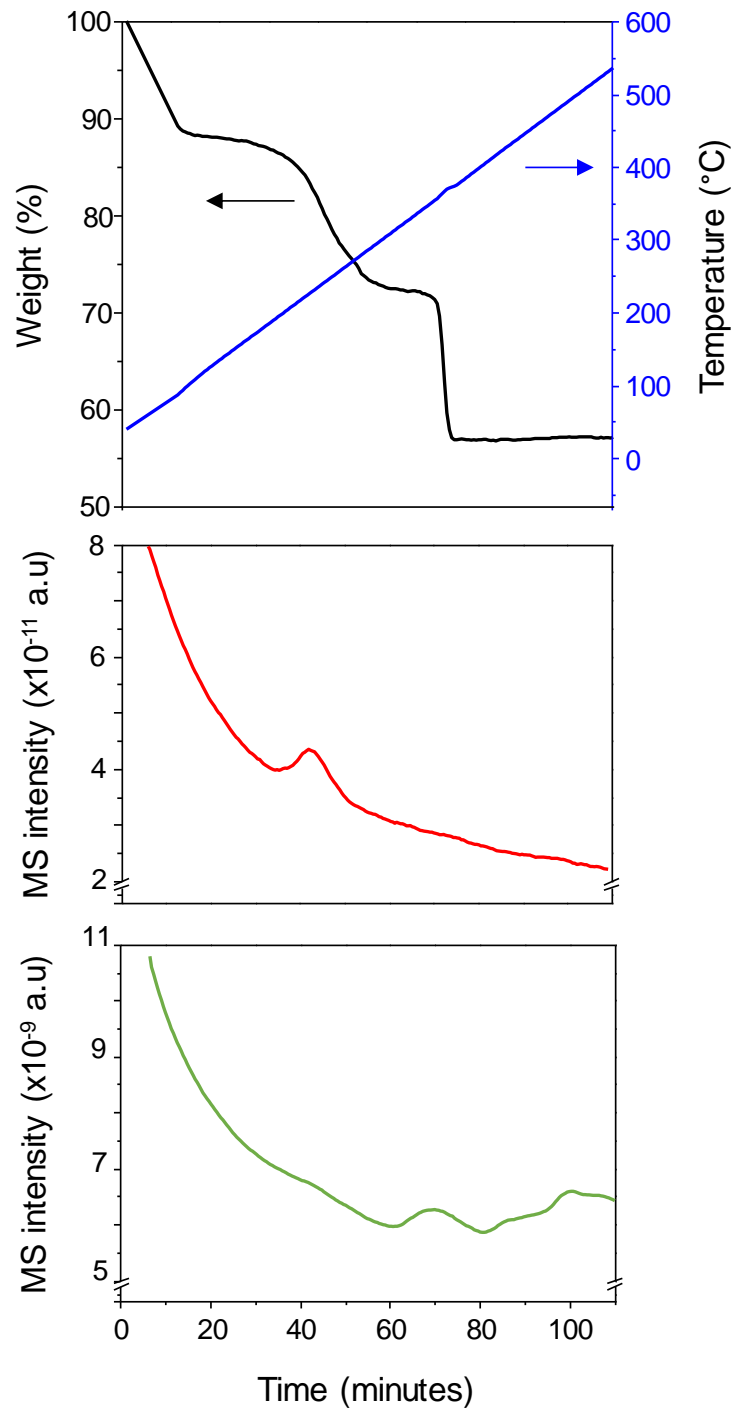


Figure S8. Thermal decomposition of  $[\text{Cu}(\text{OAc})_2]_{0.90}@\text{Zn}_{0.10}\text{-Co PBA}$  investigated by monitoring the  $m/z$  values: 44 (corresponding to  $\text{CO}_2$ , green line) and 60 (corresponding to  $\text{CH}_3\text{COOH}$ , red line).

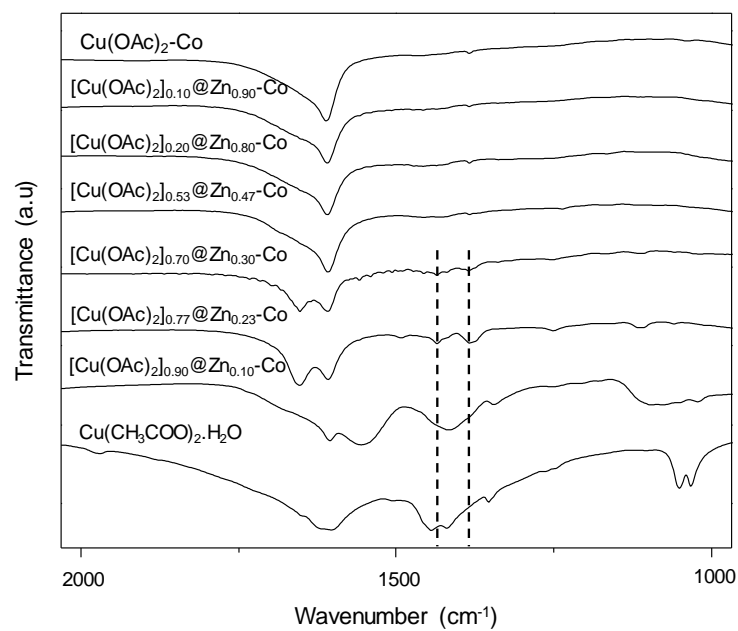
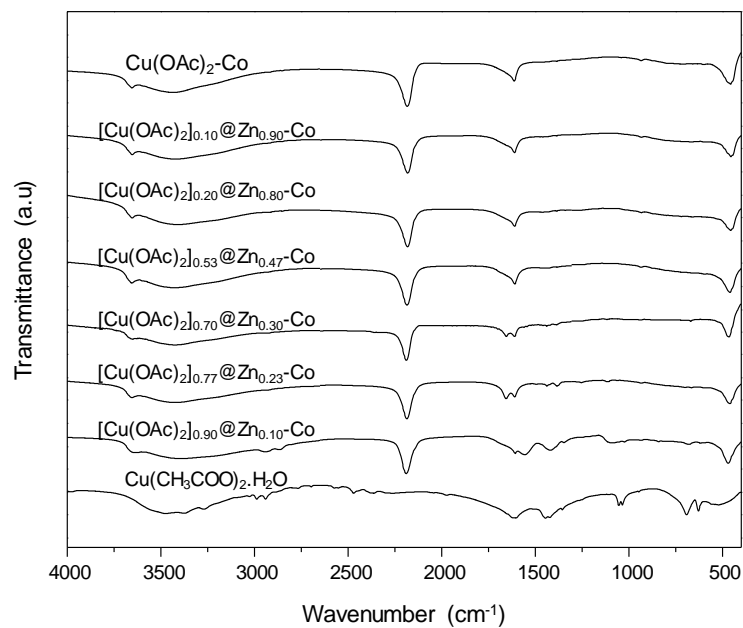


Figure S9. Top: FTIR spectra of selected PBA samples. Bottom: focus on the -COO- stretching region.

Table S3. Catalytic activity of the prepared PBAs for the A<sup>3</sup> coupling reaction of phenylacetylene, piperidine and benzaldehyde.

PBA	X (%) <sup>a</sup>	S (%) <sup>b</sup>	Y (%)
Zn-Co	4	>99	4
[Cu(ClO <sub>4</sub> ) <sub>2</sub> ] <sub>0.10</sub> @Zn <sub>0.90</sub> -Co	5	>99	5
[Cu(ClO <sub>4</sub> ) <sub>2</sub> ] <sub>0.33</sub> @Zn <sub>0.67</sub> -Co	25	95 <sup>c</sup>	24
[Cu(OAc) <sub>2</sub> ] <sub>0.11</sub> @Zn <sub>0.89</sub> -Co	12	>99	12
[Cu(OAc) <sub>2</sub> ] <sub>0.12</sub> @Zn <sub>0.88</sub> -Co	13	>99	13
[Cu(OAc) <sub>2</sub> ] <sub>0.15</sub> @Zn <sub>0.85</sub> -Co	19	98 <sup>c</sup>	19
[Cu(OAc) <sub>2</sub> ] <sub>0.19</sub> @Zn <sub>0.81</sub> -Co	22	>99	22
[Cu(OAc) <sub>2</sub> ] <sub>0.20</sub> @Zn <sub>0.80</sub> -Co	26	>99	26
[Cu(OAc) <sub>2</sub> ] <sub>0.21</sub> @Zn <sub>0.79</sub> -Co	27	>99	27
[Cu(OAc) <sub>2</sub> ] <sub>0.45</sub> @Zn <sub>0.55</sub> -Co	55	96 <sup>c</sup>	53
[Cu(OAc) <sub>2</sub> ] <sub>0.53</sub> @Zn <sub>0.47</sub> -Co	62	87 <sup>c</sup>	54
[Cu(OAc) <sub>2</sub> ] <sub>0.67</sub> @Zn <sub>0.33</sub> -Co	65	90 <sup>c</sup>	59
[Cu(OAc) <sub>2</sub> ] <sub>0.70</sub> @Zn <sub>0.30</sub> -Co	82	90 <sup>c</sup>	74
[Cu(OAc) <sub>2</sub> ] <sub>0.77</sub> @Zn <sub>0.23</sub> -Co	>99	98 <sup>c</sup>	98
[Cu(OAc) <sub>2</sub> ] <sub>0.90</sub> @Zn <sub>0.10</sub> -Co	96	98 <sup>c</sup>	94
[CuCl <sub>2</sub> ] <sub>0.20</sub> @Zn <sub>0.80</sub> -Co	18	88 <sup>c</sup>	16
[CuCl <sub>2</sub> ] <sub>0.42</sub> @Zn <sub>0.58</sub> -Co	53	98 <sup>c</sup>	52
[CuCl <sub>2</sub> ] <sub>0.55</sub> @Zn <sub>0.45</sub> -Co	55	95 <sup>c</sup>	52
[CuCl <sub>2</sub> ] <sub>0.83</sub> @Zn <sub>0.17</sub> -Co	61	97 <sup>c</sup>	59
CuCl <sub>2</sub> -Co <sup>b</sup>	28	60 <sup>c</sup>	17
Cu(OAc) <sub>2</sub> -Co <sup>c</sup>	36	66 <sup>c</sup>	24
Cu <sub>0.14</sub> Zn <sub>0.86</sub> -Co	7	95 <sup>c</sup>	7
Cu <sub>0.26</sub> Zn <sub>0.74</sub> -Co	11	96 <sup>c</sup>	11
Cu <sub>0.41</sub> Zn <sub>0.59</sub> -Co	51	>99	51
Cu <sub>0.67</sub> Zn <sub>0.33</sub> -Co	53	>99	53
Cu <sub>0.86</sub> Zn <sub>0.14</sub> -Co	60	93 <sup>c</sup>	56
Cu <sub>0.96</sub> Zn <sub>0.04</sub> -Co	54	94 <sup>c</sup>	51

<sup>a</sup> Conversion of phenylacetylene. <sup>b</sup> Selectivity to the A<sup>3</sup> product based on phenylacetylene. <sup>c</sup> Acetophenone was the only phenylacetylene-derived side-product detected. Reaction conditions: phenylacetylene (0.05 mmol), piperidine (0.1 mmol) and benzaldehyde (0.1 mmol). 110°C. 10 mg of PBA. 6 h reaction time.

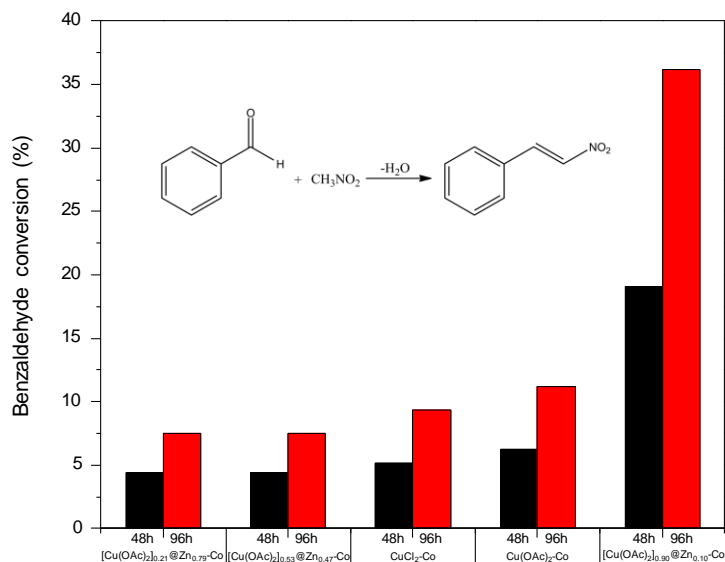


Figure S10. Benzaldehyde conversion in the nitroaldol (Henry) reaction of nitromethane (5 mmol) and benzaldehyde (1 mmol) at 90°C over selected PBA samples (20 mg).

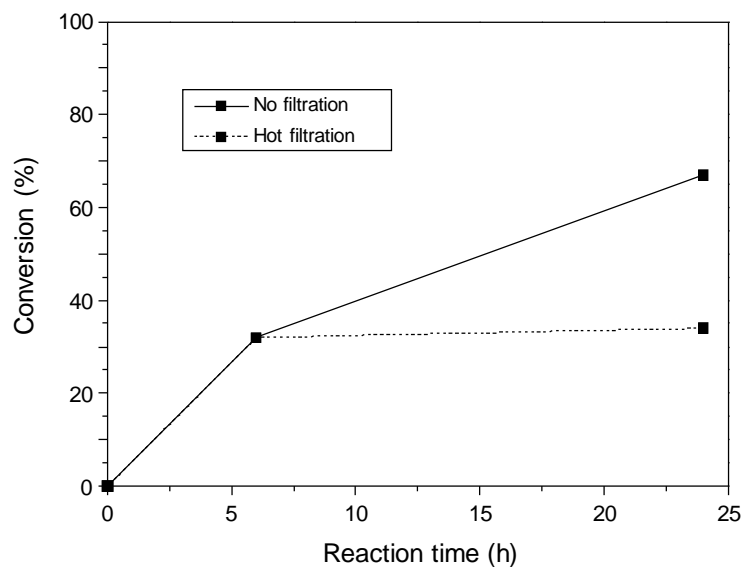


Figure S11. Conversion of phenylacetylene in the A<sup>3</sup> coupling of phenylacetylene (0.05 mmol), piperidine (0.1 mmol) and benzaldehyde (0.1 mmol) at 110°C over 1 mg of [Cu(OAc)<sub>2</sub>]<sub>0.90</sub>@Zn<sub>0.10</sub>-Co. Dashed lines represent the conversion after removal of the catalyst in the hot filtration test.

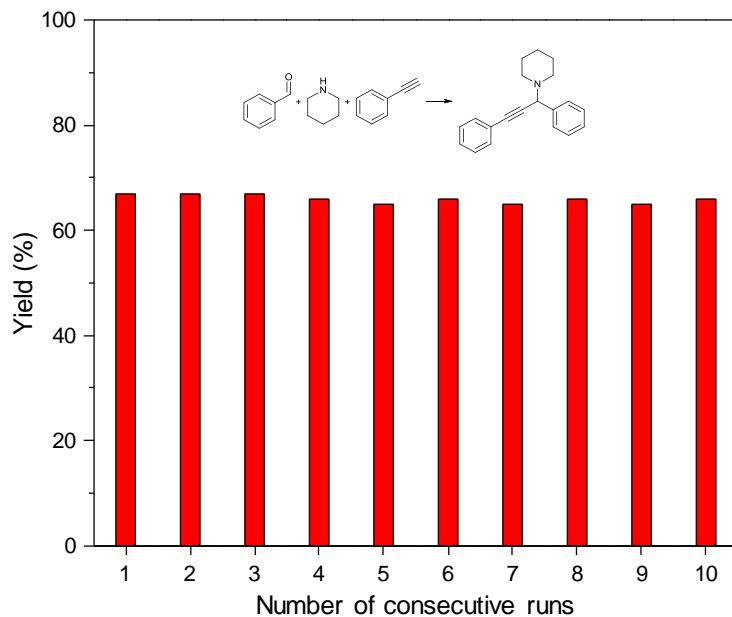


Figure S12. Recycling tests for the A<sup>3</sup> coupling of phenylacetylene (0.05 mmol), piperidine (0.1 mmol) and benzaldehyde (0.1 mmol) at 110°C over 1 mg of [Cu(OAc)<sub>2</sub>]<sub>0.90</sub>@Zn<sub>0.10</sub>-Co. Yield of A<sup>3</sup> product after 24 h reaction time.

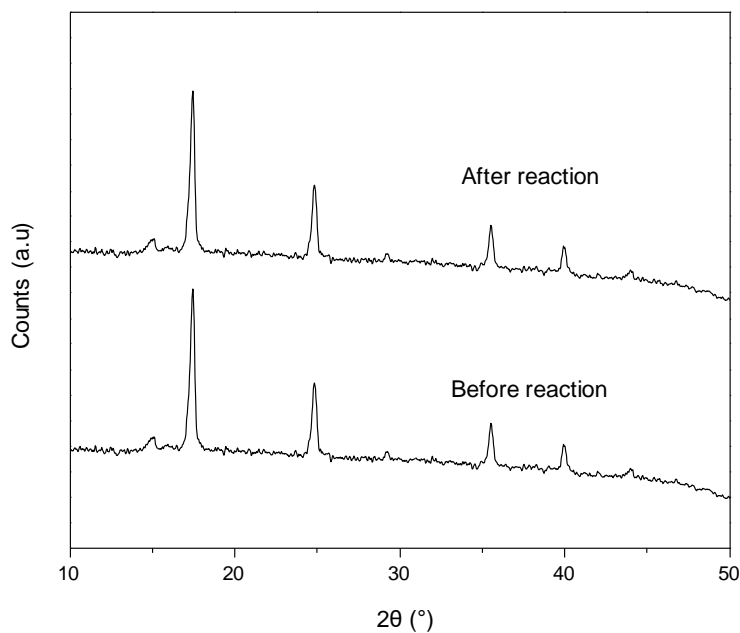


Figure S13. XRD pattern of [Cu(OAc)<sub>2</sub>]<sub>0.90</sub>@Zn<sub>0.10</sub>-Co PBA before and after the A<sup>3</sup> coupling reaction. Reaction conditions: phenylacetylene (0.05 mmol), piperidine (0.1 mmol) and benzaldehyde (0.1 mmol). 110°C. 10 mg of catalyst. 24 h reaction time.

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