Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Defect engineering: an effective tool for enhancing the catalytic performance of copper-MOFs for the click reaction and the A^3 coupling

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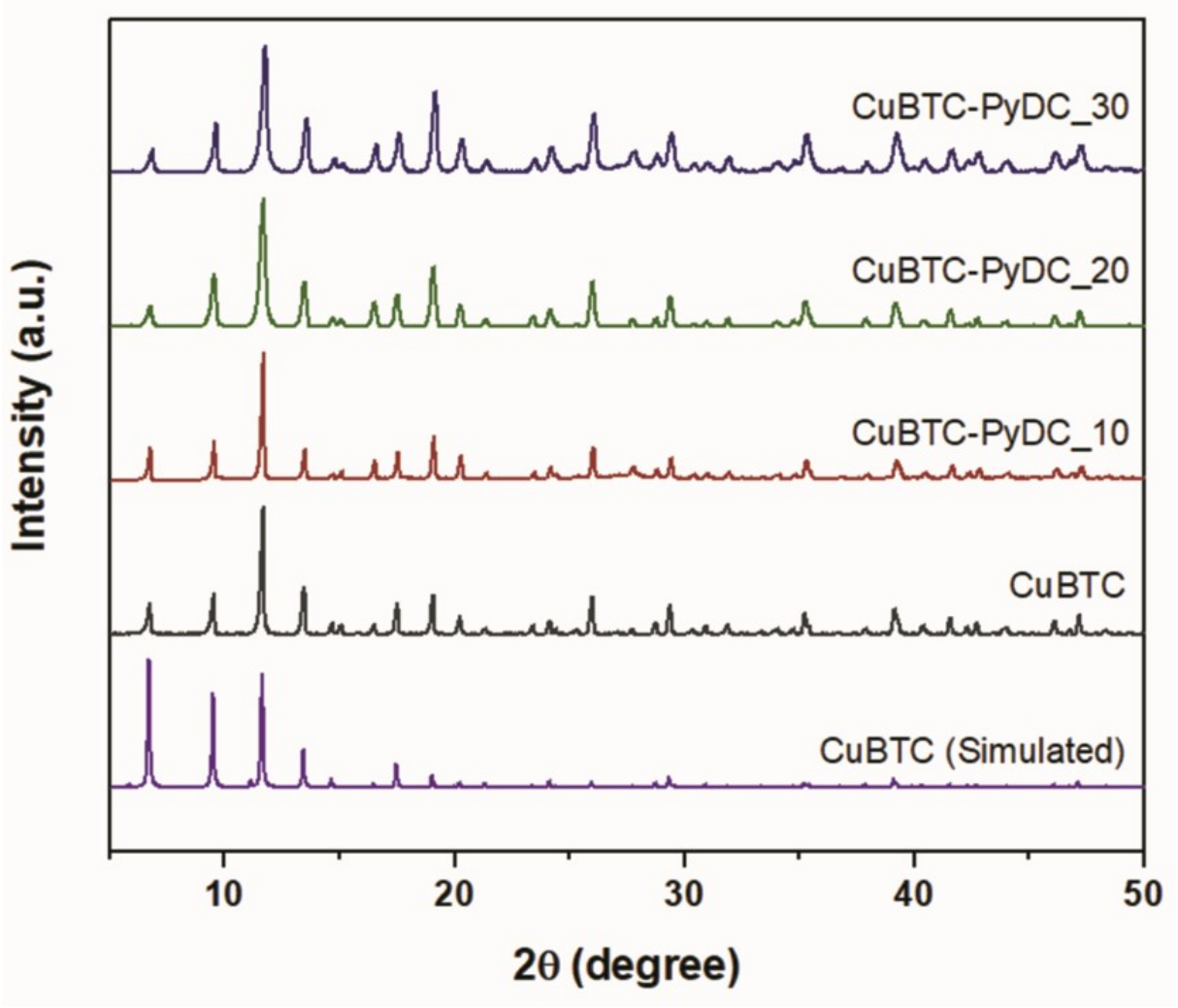

Fig. S1 PXRD patterns of CuBTC and DE-CuBTC MOFs.

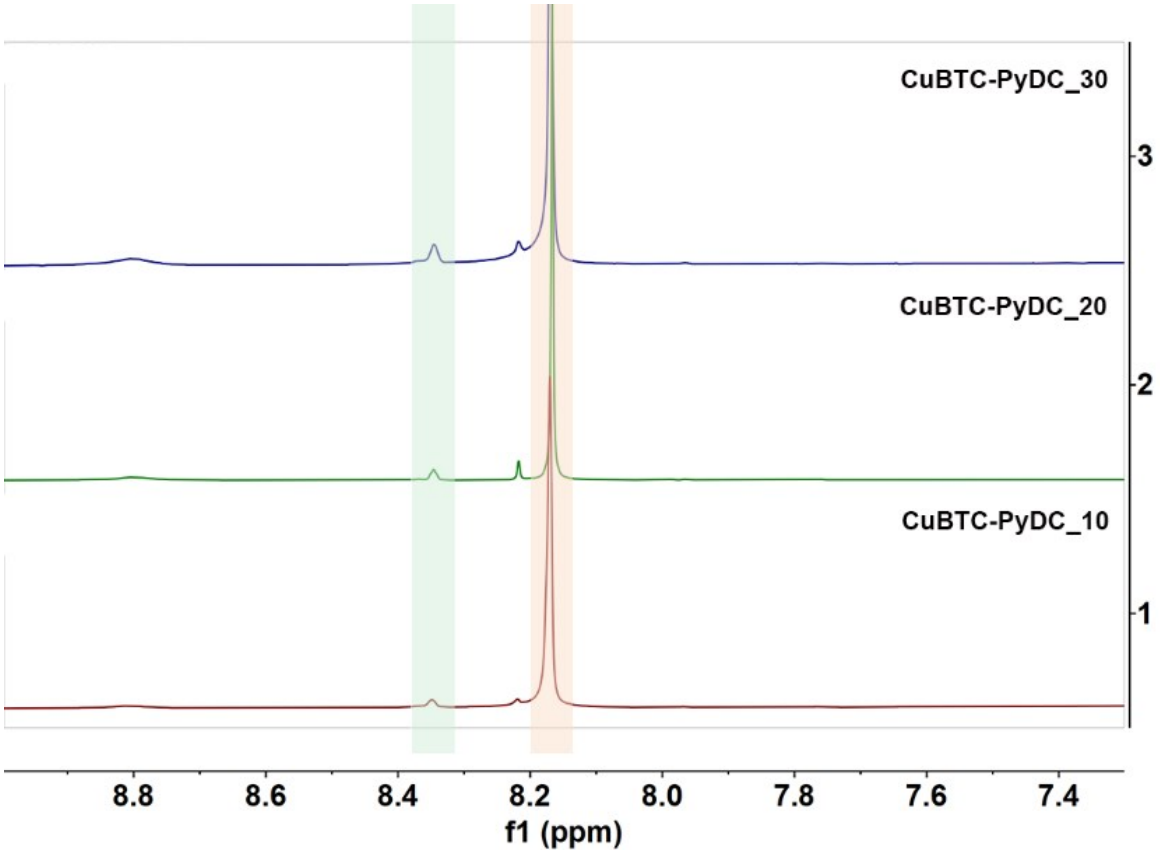

Fig. S2 ^{1}H NMR spectra of base-digested, activated CuBTC and DE-CuBTC MOFs.

The ^{1}H NMR results were achieved by following our previously report.[S1] The activated samples were digested in NaOD/D_2O and the mixtures were heated. During this process, the Cu contents were transformed into a black solid which could be filtered off, and the organic linkers (BTC) in the frameworks were dissolved. Therefore, the shielding effect of the paramagnetic Cu ions on NMR is excluded. As shown in Figure S2, the peak at around 8.17 ppm (orange region) corresponds to the three protons on the benzene ring of BTC. The peak at around 8.35 ppm (green region) is assigned to one of the protons of PyDC. The calculation is shown below:

$$\text{Doping ratio (PyDC)} = I_{green} / [(I_{orange}/3)+I_{green}] \times 100\%$$

Table S1. The integration of peaks labelled by coloured regions and doping ratios of the amount of PyDC to that of total linkers of the obtained DE-CuBTC MOFs.

Sample	I_{green}	I_{orange}	Doping Ratio of PyDC to BTC (%)	
			Feeding	Obtained
CuBTC-PyDC_10	1	31.13	10	8.8
CuBTC-PyDC_20	1	14.38	20	17.2
CuBTC-PyDC_30	1	8.16	30	26.8

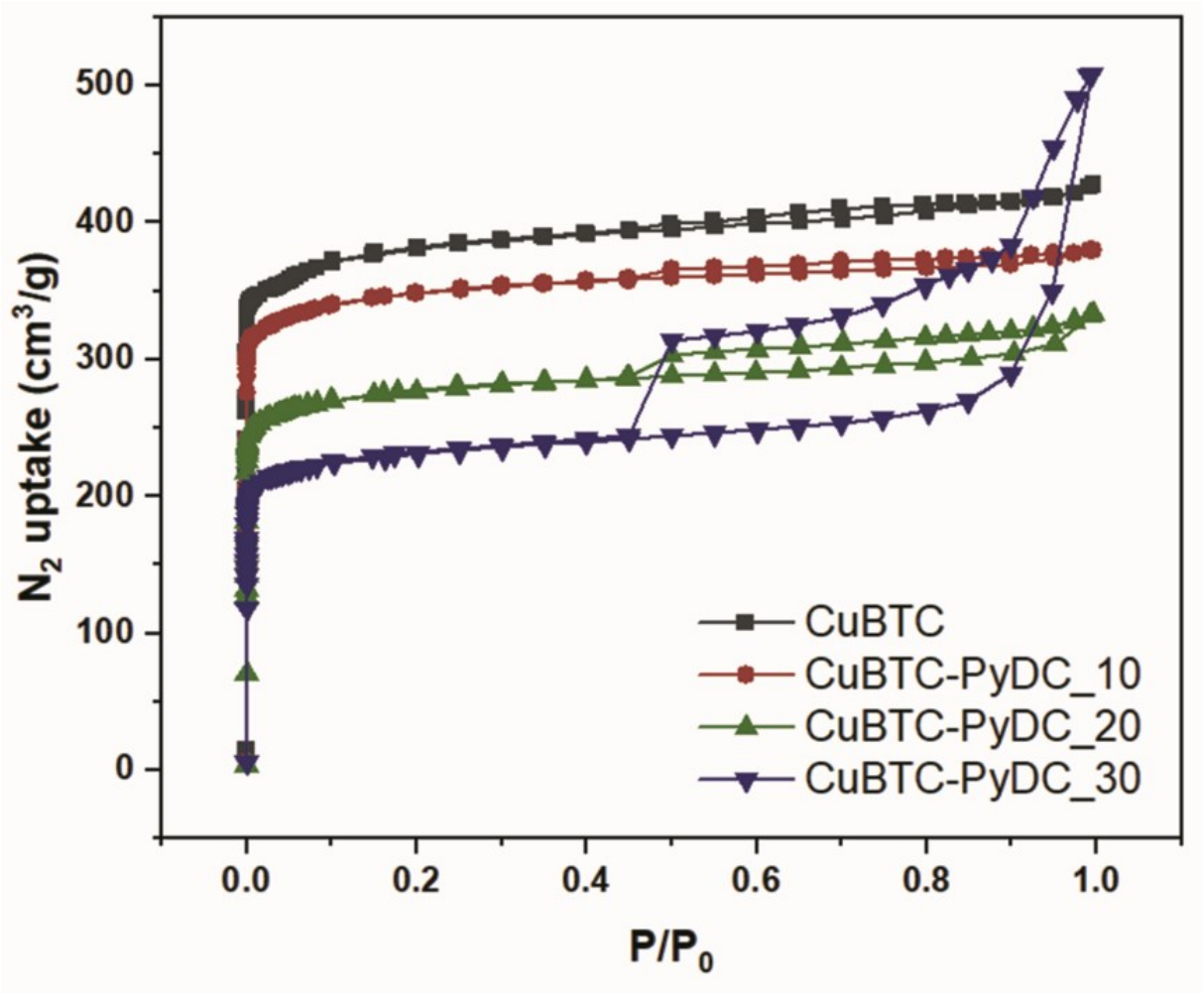

Fig. S3 N_2 adsorption isotherms of CuBTC and DE-CuBTC MOFs.

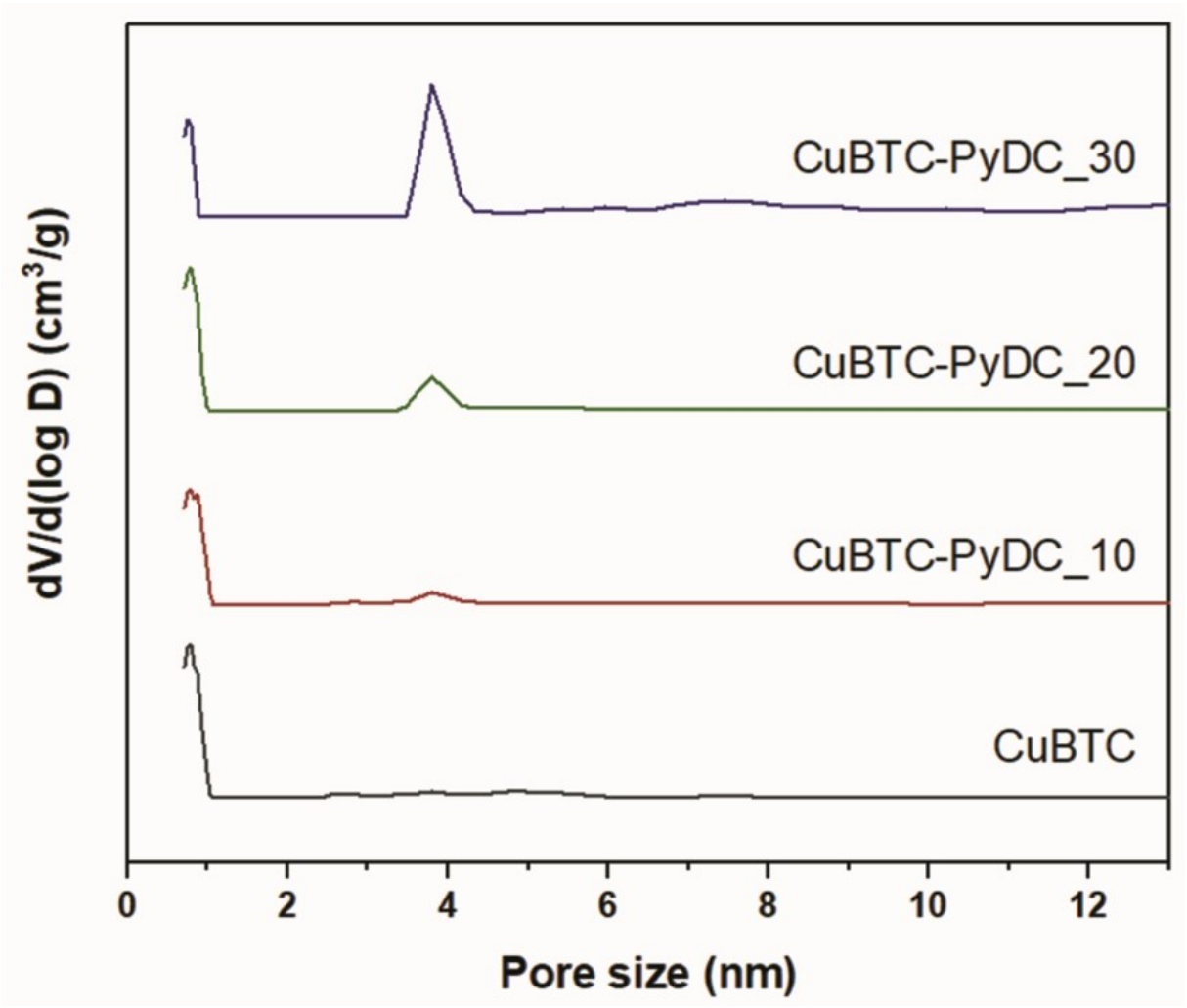

Fig. S4 The density functional theory (DFT) pore size distribution curves of CuBTC and DE-CuBTC MOFs.

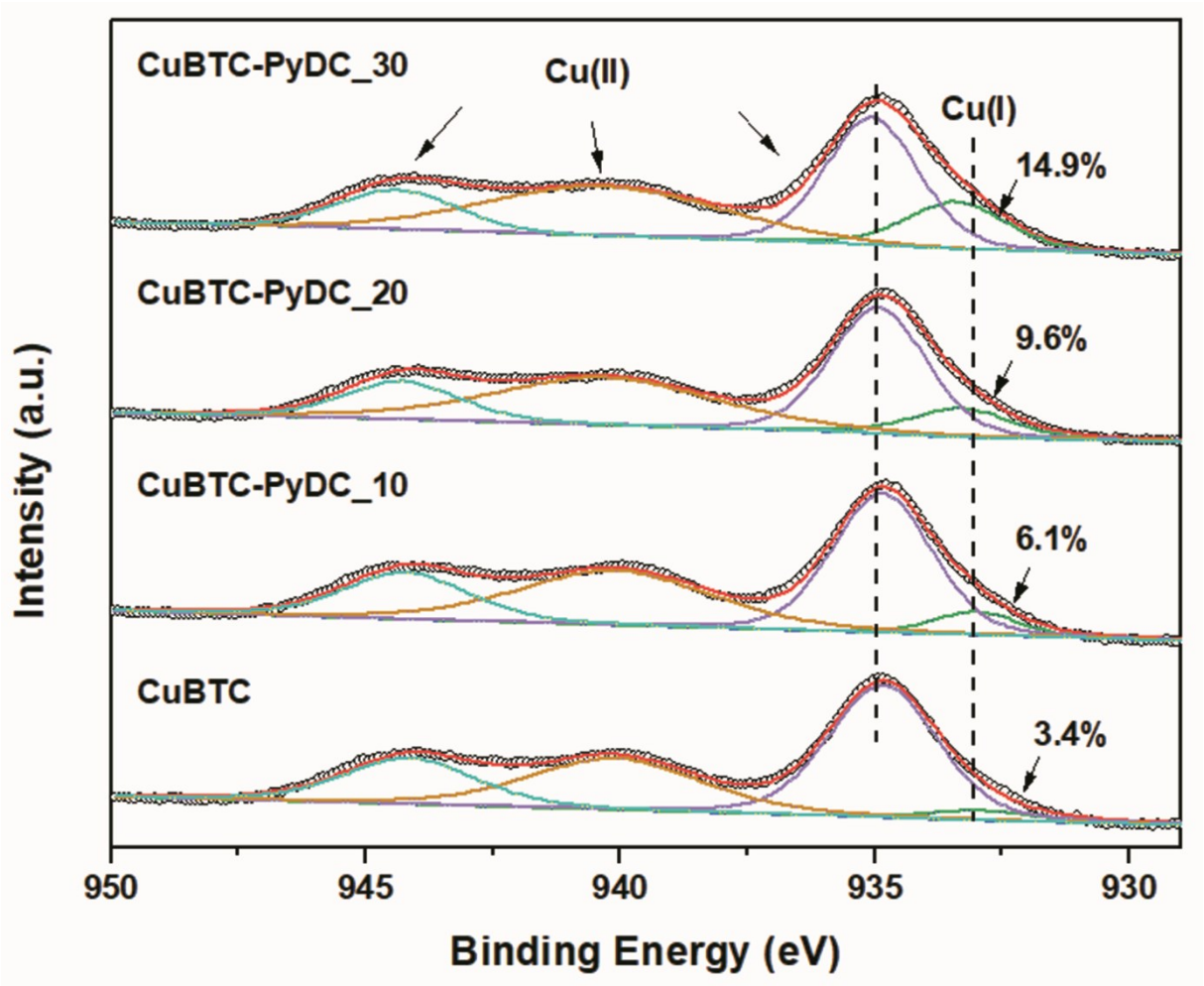

Fig. S5 Deconvoluted XP spectra in the Cu 2p 3/2 region of CuBTC and DE-CuBTC MOFs.

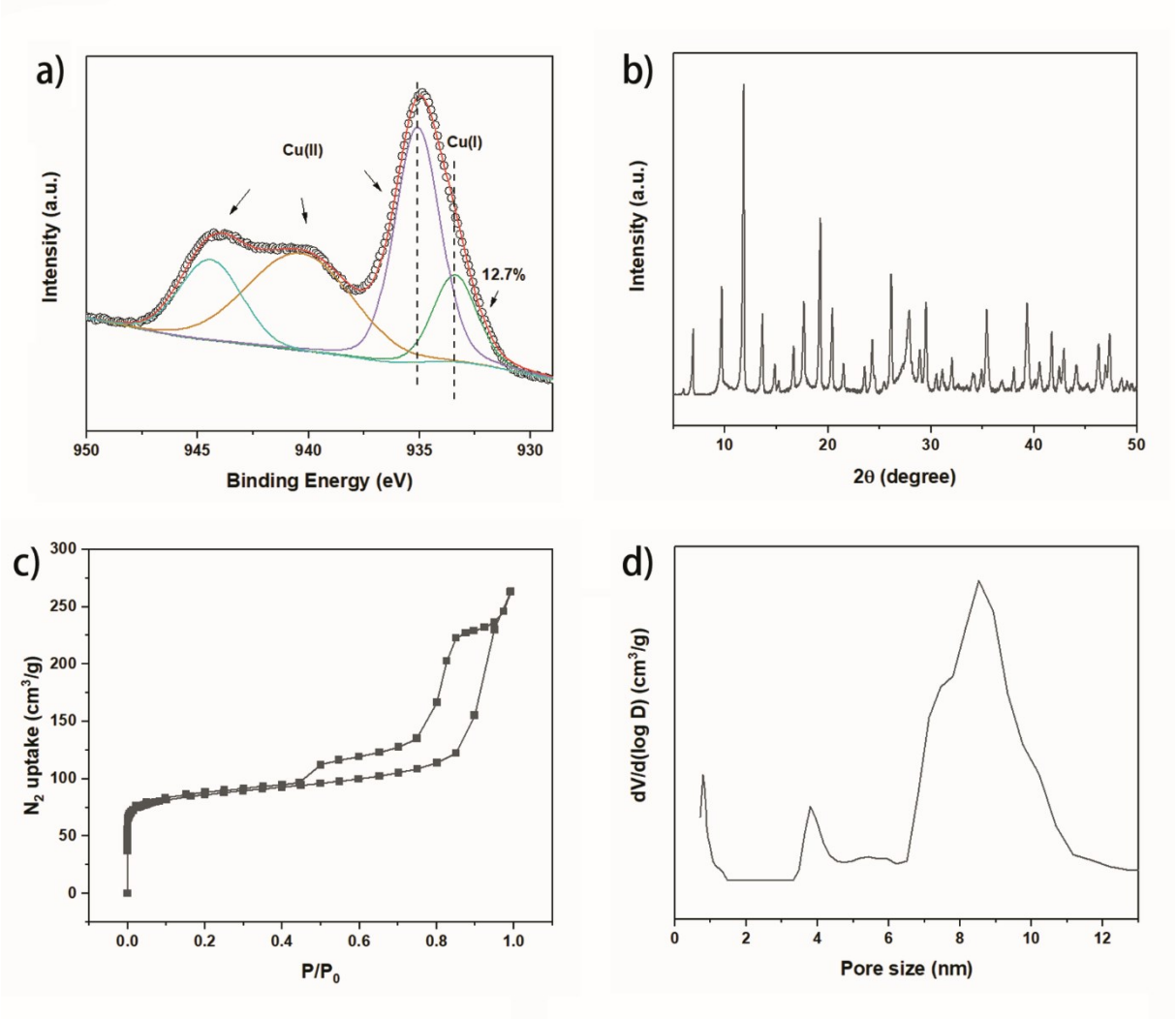

Fig. S6 a) deconvoluted XP spectra in the Cu 2p 3/2 region, b) PXRD pattern, c) N_2 adsorption isotherm, d) pore size distribution curve of CuBTC-PyDC_40.

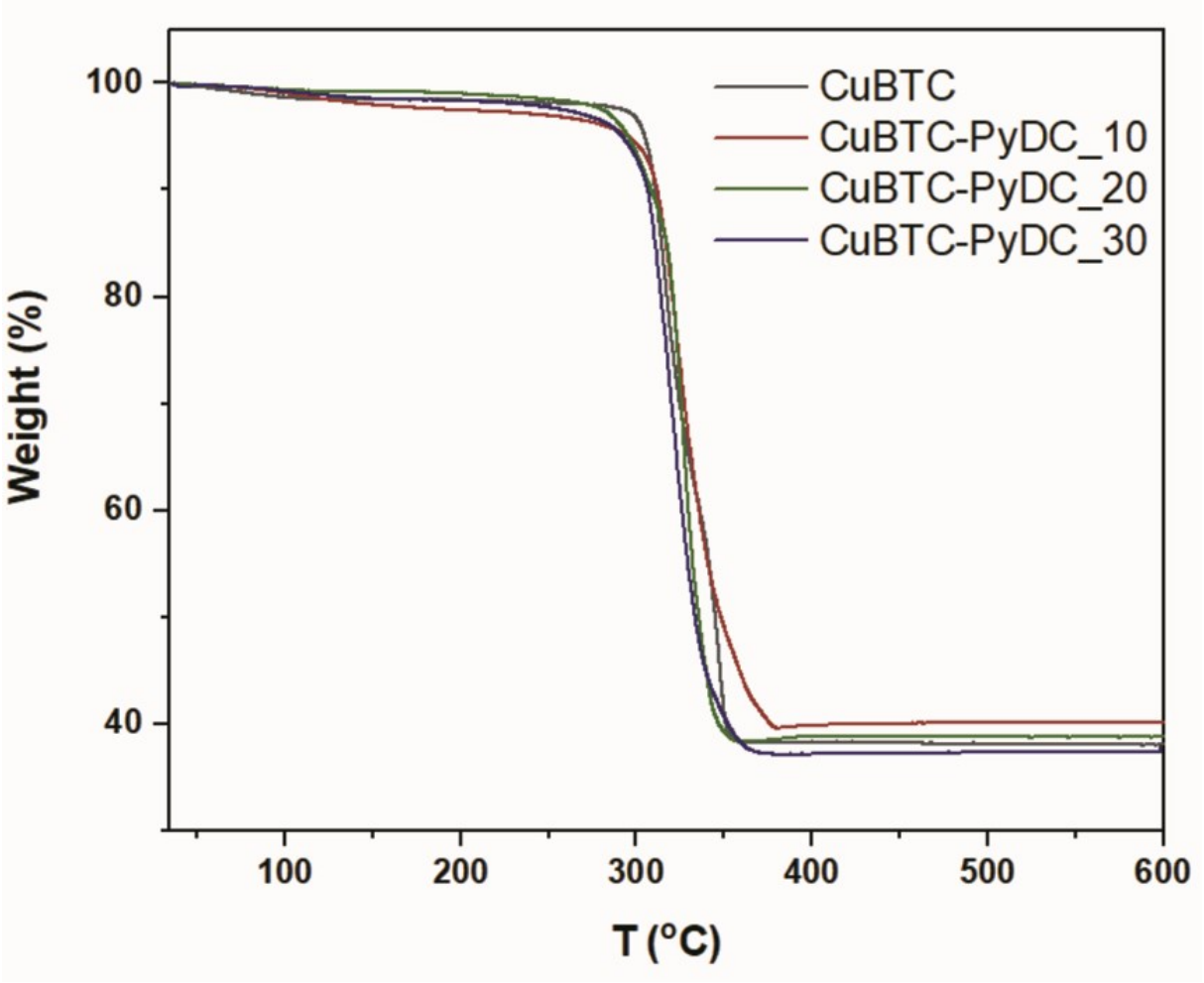

Fig. S7 TG curves of the prepared DE-CuBTC MOFs in comparison with the pristine CuBTC.

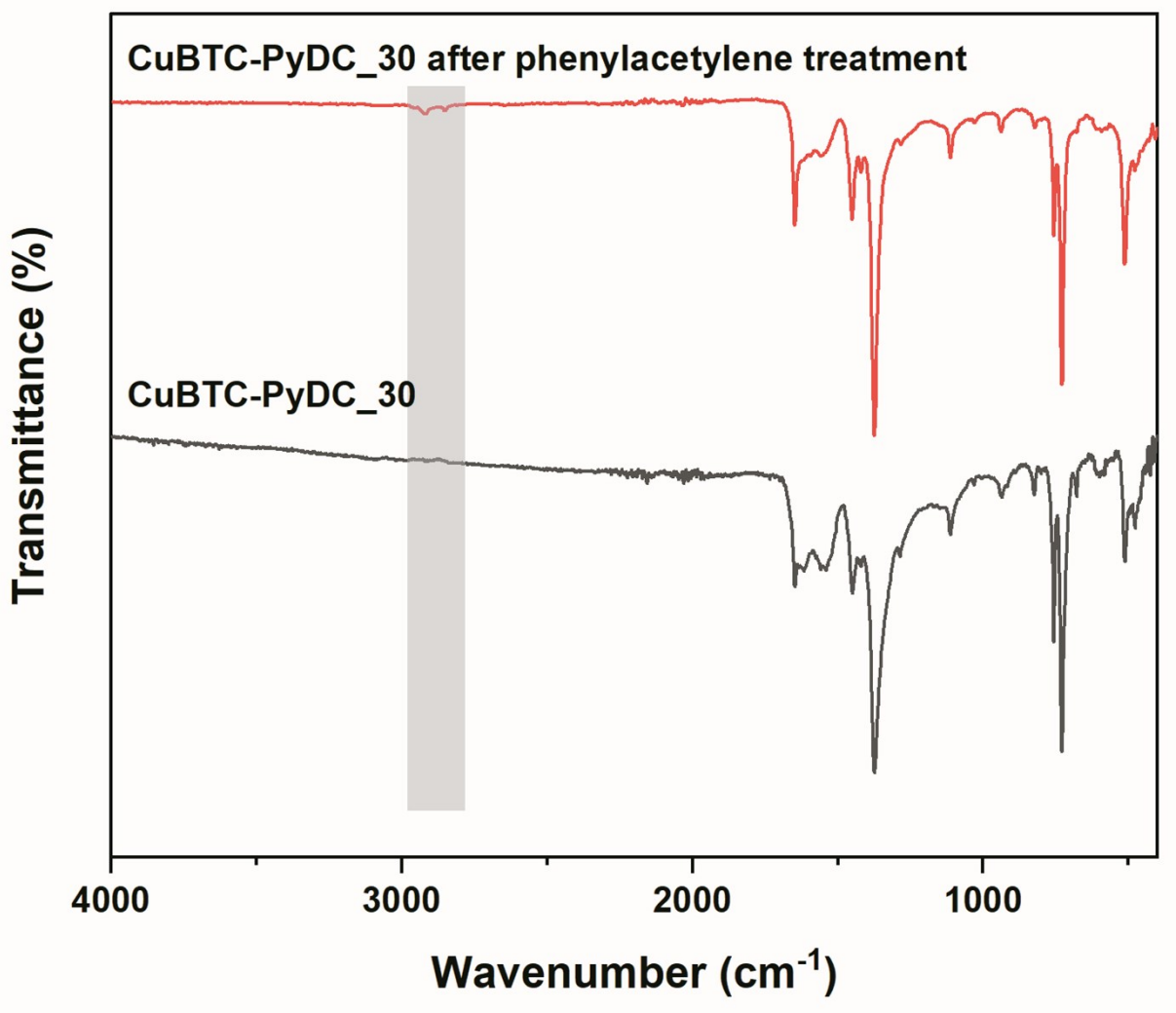

Fig. S8 FTIR spectra of CuBTC-PyDC_30 before and after phenylacetylene treatment.

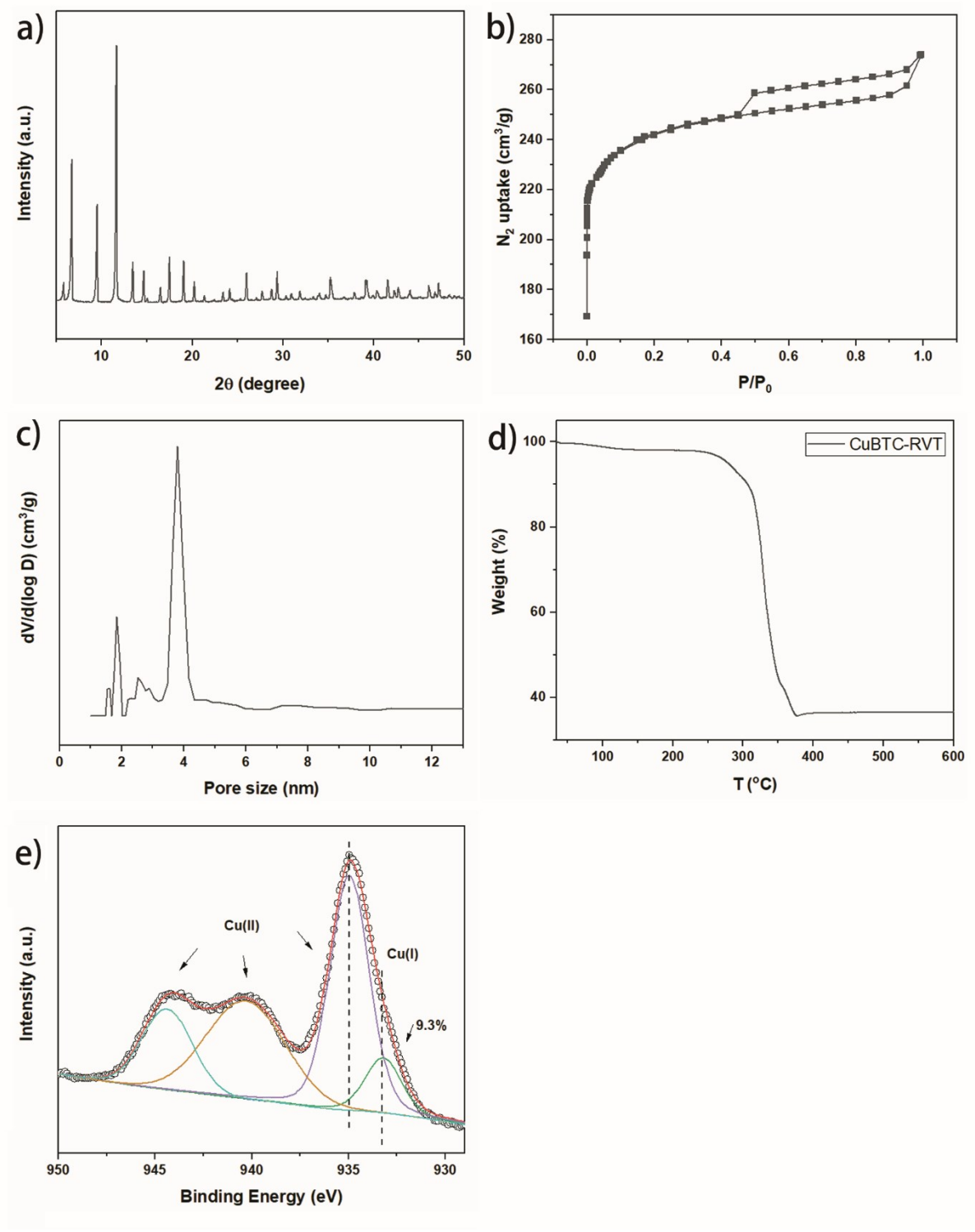

Fig. S9 a) PXRD pattern, b) N_2 adsorption isotherm, c) pore size distribution curve, d) TG curve, and e) deconvoluted XP spectra in the Cu 2p 3/2 region of CuBTC-RVT.

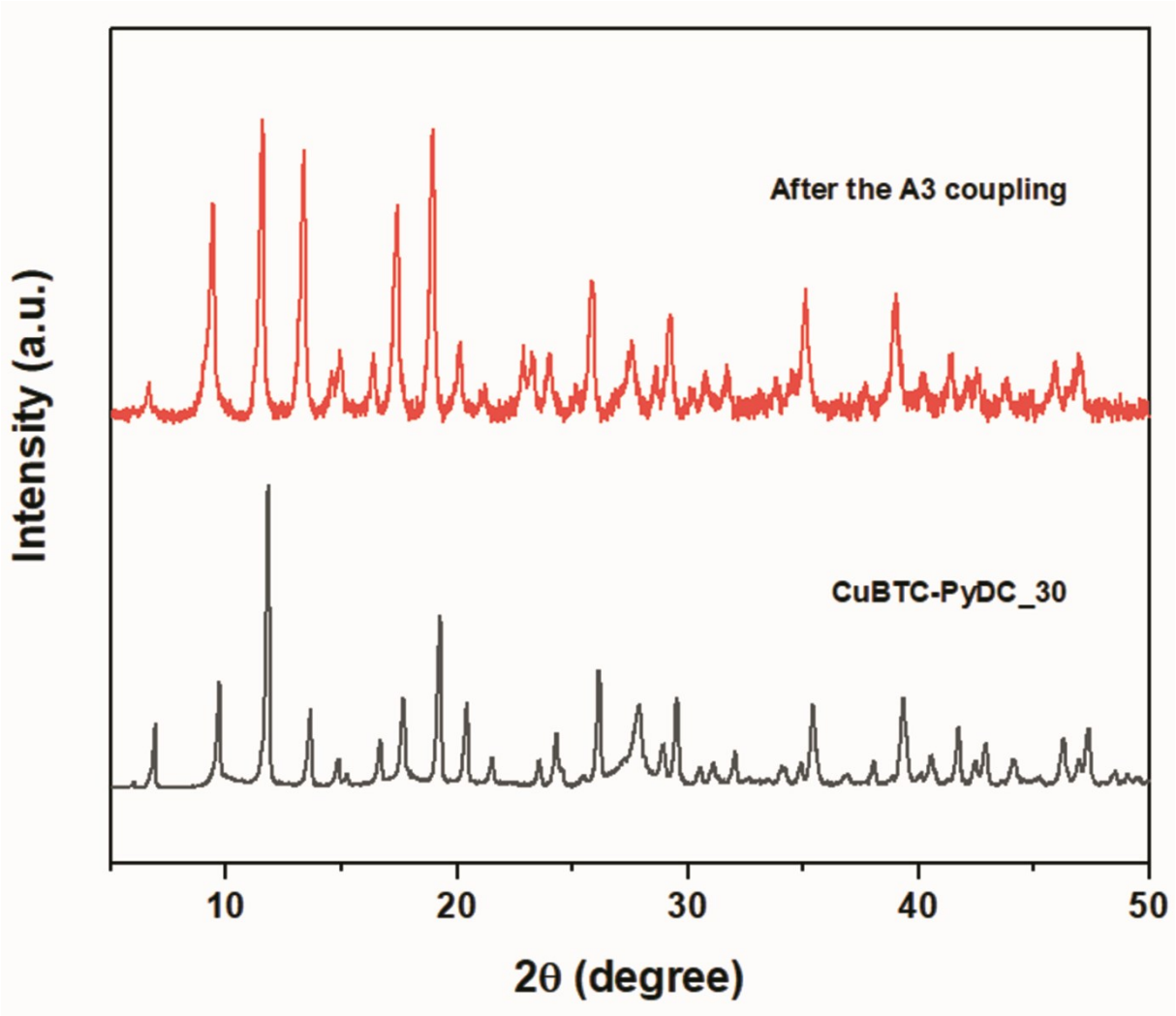

Fig. S10 PXRD patterns of CuBTC-PyDC_30 before and after A^3 coupling reaction.

References

S1 Z. Fan, J. Wang, W. Wang, S. Burger, Z. Wang, Y. Wang, C. Wöll, M. Cokoja and R. A. Fischer, *ACS Applied Materials & Interfaces*, 2020. DOI: 10.1021/acsami.0c07249