

### Supporting Information for

## **Micro-Cu<sub>4</sub>I<sub>4</sub>-MOF: reversible iodine adsorption and catalytic properties for tandem reaction of Friedel–Crafts alkylation of indoles with acetals**

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- 1. Materials and instrumentation**
- 2. Synthesis and characterization of 1 and 2**
- 3. Catalytic properties of 2**
- 4. References**

### **1. Materials and instrumentation**

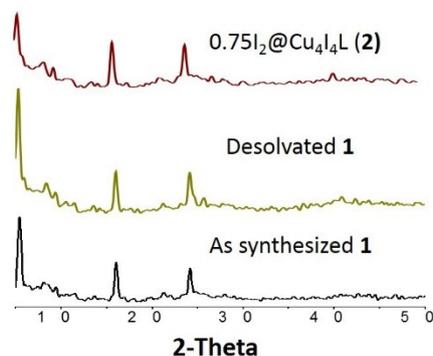
4-fluoro benzaldehyde dimethyl acetal, 4-methyl benzaldehyde dimethyl acetal, 4-nitro benzaldehyde dimethyl acetal, 1-pyrene formaldehyde dimethyl acetal were synthesized according to literature.<sup>1</sup> All others were obtained from commercial sources (Acros) and used without further purification. <sup>1</sup>H NMR data were collected on a Bruker Avance-300 spectrometer. Chemical shifts are reported in  $\delta$  relative to TMS. All fluorescence measurements were carried out on a Cary Eclipse spectrofluorimeter (Varian, Australia) equipped with a xenon lamp and quartz carrier at room temperature. Thermogravimetric analyses were carried out on a TA Instrument Q5 simultaneous TGA under flowing nitrogen at a heating rate of 10°C/min. XRD pattern was obtained on D8. ADVANCE X-ray powder diffractometer (XRPD) with Cu K $\alpha$  radiation ( $\lambda = 1.5405 \text{ \AA}$ ). The scanning electron microscopy (SEM) micrographs were recorded on a Gemini Zeiss Supra TM scanning electron microscope equipped with energy-dispersive X-ray detector (EDS). MS spectra were obtained by Bruker maxis ultra-high resolution-TOF MS system. XPS were conducted on the ESCALAB 250. Column chromatography was carried out on silica gel (Wakogel S1

C-200).

## 2. Synthesis and characterization of 1 and 2

**Synthesis of Cu<sub>4</sub>I<sub>4</sub>-MOF (1).**<sup>2</sup> An acetonitrile solution (3 mL) of CuI (40 mg, 0.1 mmol) was quickly added to a hot acetonitrile (2 mL) solution of L (30 mg, 0.05 mmol). The mixture was stirred and refluxed for 1 h to provide the yellow micro-sized crystals. The product was collected by centrifugation. The obtained micro-Cu<sub>4</sub>I<sub>4</sub>-MOF was washed by MeOH (3 times), and was heated at 90°C for 1 h to generate the desolvated sample.

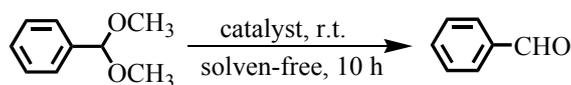
**Synthesis of I<sub>2</sub>@Cu<sub>4</sub>I<sub>4</sub>-MOF (2).**<sup>2</sup> When desolvated micro-crystals of **1** were placed in I<sub>2</sub> (*p*(I<sub>2</sub>) is ca. 0.3 mm Hg) atmosphere for 30 min., dark crystals of **2** (0.75I<sub>2</sub>@Cu<sub>4</sub>I<sub>4</sub>-MOF) was obtained in quantitative yield. The loading amount of molecular iodine (12.5 wt %) in **2** is determined by TGA trace.



**Fig. S1** XRPD patterns of as-synthesized **1**, desolvated **1** and iodine-loaded **2**.

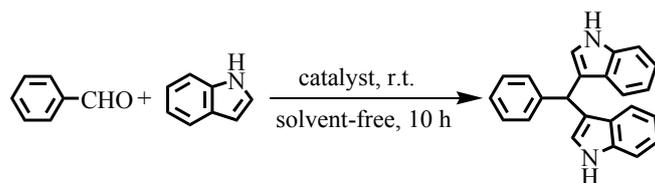
## 3. Catalytic properties of 2

**General catalytic procedure for aldehyde acetal deprotection.**

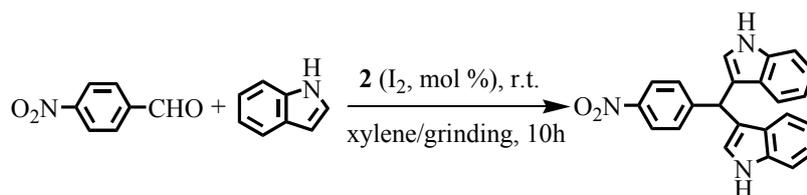


A mixture of aldehyde acetal (152.2 mg, 1 mmol) and 0.75I<sub>2</sub>@CuI-MOF (**2**, 12.4mg, 1 mol % I<sub>2</sub>) was stirred at room temperature for 10 h (monitored by TLC). After addition of CDCl<sub>3</sub> (1 mL), the catalyst of **2** was recovered by centrifugation. The solution was characterized by <sup>1</sup>H NMR, yield > 99 %. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 10.04 (s, 1H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.61 (d t, *J* = 14.8, 7.8 Hz, 3H).

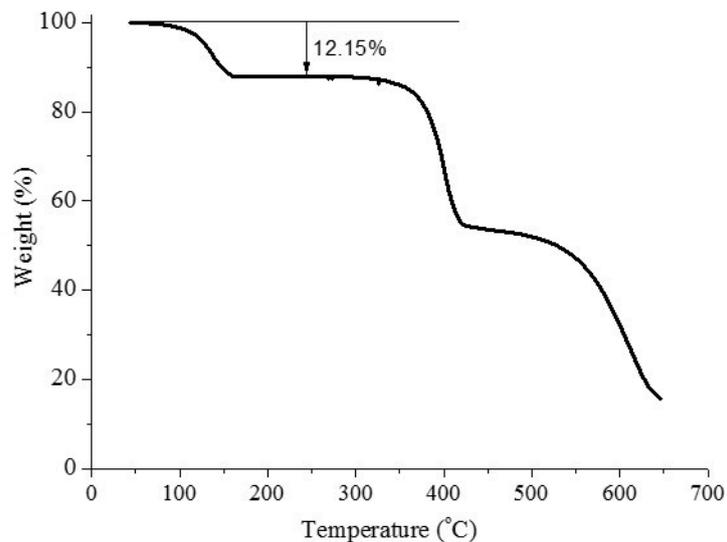
**General catalytic procedure for Friedel–Crafts alkylation of indole.**



A mixture of benzaldehyde (106.1 mg, 1 mmol) and indole (234.3 mg, 2 mmol) in the presence of 0.75I<sub>2</sub>@CuI-MOF (**2**, 12.4 mg, 1 mmol % I<sub>2</sub>) was stirred at room temperature for 10 h (monitored by TLC). After addition of ethyl acetate (2 mL), the catalyst was recovered by centrifugation. The product of bis(indolyl)methane was purified by column chromatography on silica gel (CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether = 1 : 3) to provide target product as a white solid (yield, 93 %). <sup>1</sup>H NMR (300 MHz, DMSO): δ = 10.79 (s, 2H), 7.34 (t, *J* = 6.8 Hz, 4H), 7.25 (dd, *J* = 7.7, 6.7 Hz, 4H), 7.20 – 7.11 (m, 1H), 7.02 (t, *J* = 7.5 Hz, 2H), 6.83 (dd, *J* = 13.7, 5.1 Hz, 4H), 5.81 (s, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ = 144.13, 136.71, 128.82, 128.34, 127.13, 126.26, 123.75, 122.00, 120.01, 119.65, 119.32, 111.20, 40.26. MS-EI, *m/z*, Anal. Calcd: 321.14, Exp: 321.13 (M<sup>+</sup>).

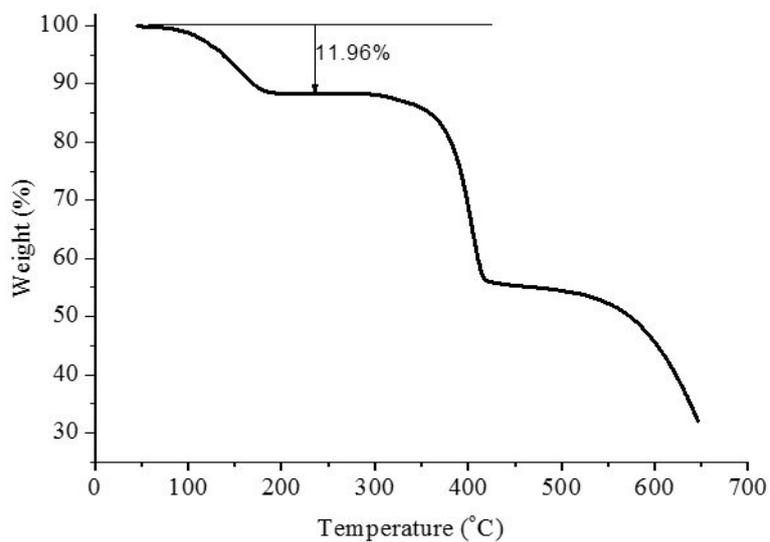


A mixture of 4-nitrobenzaldehyde (151.1 mg, 1 mmol), indole (234.3 mg, 2 mmol) and **2** (12.4 mg, 1 mol % I<sub>2</sub>) was ground 10 min at room temperature for every other 2 h (5 times). After addition of ethyl acetate (2 mL), the catalyst was recovered by centrifugation. The product was purified by column chromatography on silica gel (CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether = 2 : 1) to provide target product as a white solid (yield, 89 %). The molecular iodine loss is 2.8 % after the reaction, which is confirmed by the TGA analysis (Fig. S2).



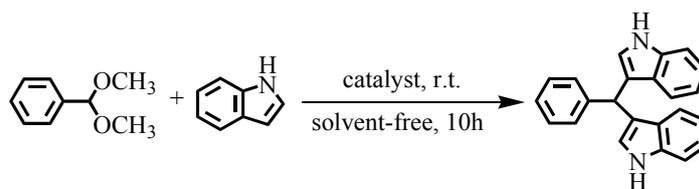
**Fig. S2** The TGA trace of **2** after solid phase grading. The iodine content in as-synthesized **2** is 12.5 %.

In addition, the reaction can be carried out in xylene in the presence of **2** at room temperature. A xylene (1 mL) solution of 4-nitrobenzaldehyde (151.1 mg, 1 mmol), indole (234.3 mg, 2 mmol) and **2** (12.4 mg, 1 mol % I<sub>2</sub>) was stirred at room temperature for 10 h (monitored by TLC) to afford the product in 90 % yield. The iodine loss was confirmed to be 4.3 %, see Fig. S3.



**Fig. S3** The TGA trace of **2** after alkylation in xylene. The iodine content in as-synthesized **2** is 12.5 %.

**General catalytic procedure for Friedel–Crafts alkylation of indole with benzaldehyde acetal.**



A mixture of benzaldehyde acetal (152.2 mg, 1 mmol) and indole (234.3 mg, 2 mmol) in the presence of 0.75I<sub>2</sub>@CuI-MOF (**2**, 12.4mg, 1 mmol % I<sub>2</sub>) was stirred at room temperature for 10 h (monitored by TLC). After addition of ethyl acetate (2mL), the catalyst was recovered by centrifugation. The product of bis(indolyl)methane was purified by column chromatography on silica gel (CH<sub>2</sub>Cl<sub>2</sub>/petroleum = 1 : 3) to provide the product as white solid (Yield, 93 %). <sup>1</sup>H NMR (300 MHz, DMSO): δ = 10.79 (s, 2H), 7.34 (t, *J* = 6.8 Hz, 4H), 7.25 (dd, *J* = 7.7, 6.7 Hz, 4H), 7.20 – 7.11 (m, 1H), 7.02 (t, *J* = 7.5 Hz, 2H), 6.83 (dd, *J* = 13.7, 5.1 Hz, 4H), 5.81 (s, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ = 144.13, 136.71, 128.82, 128.34, 127.13, 126.26, 123.75, 122.00, 120.01, 119.65, 119.32, 111.20, 40.26. MS-EI, *m/z*, Anal. Calcd: 321.14, Exp: 321.13 (M<sup>+</sup>). After washed with ethyl acetate and dried in air, the regenerated catalyst was directly used for next catalytic run.

**Table S1.** Yields of **2**-catalysed Friedel–Crafts alkylation of indole with benzaldehyde acetal

Recycle number	1	2	3	4	5
Yield (%) <sup>a</sup>	93	90	89	89	86

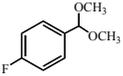
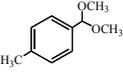
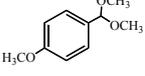
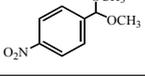
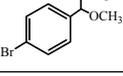
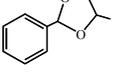
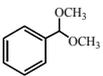
<sup>a</sup> Isolated yield.

**General catalytic procedure for expanded Friedel–Crafts alkylation of indole with different benzaldehyde acetals.**

The experimental procedure is the same as shown above except the substituted benzaldehyde acetals and iodines were used instead of benzaldehyde acetal and indole to perform the reactions. The results were summarized in Table 2.

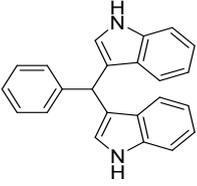
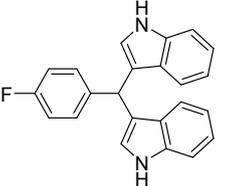
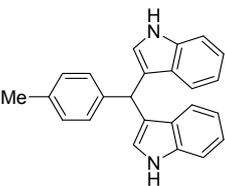
**Table S2.** **2**-catalysed Friedel–Crafts alkylation of indole and substituted indole with aromatic and aliphatic acetals

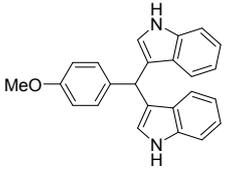
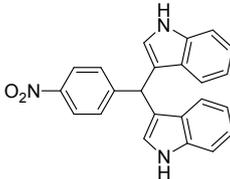
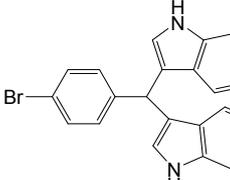
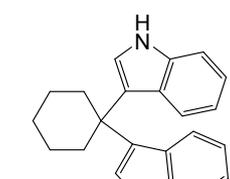
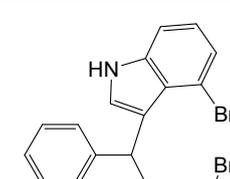
Entry	aromatic aldehydes	indoles	Yield (%) <sup>a</sup>
1			93

2			90
3			88
4			87
5			89
6			90
7			85
8			89
9			86

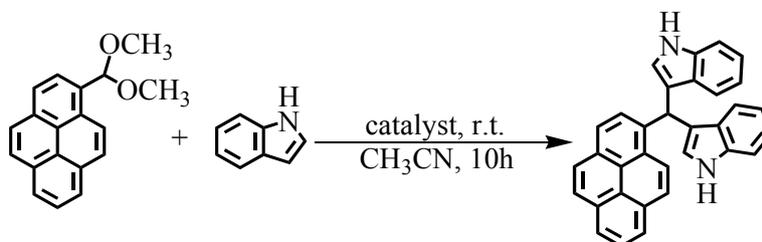
<sup>a</sup> Isolated yield.

**Table S3.** Bis(indolyl)methanes characterization

Compound	Characterization data
	<sup>1</sup> H NMR (300 MHz, DMSO): $\delta$ = 10.79 (s, 2H), 7.34 (t, $J$ = 6.8 Hz, 4H), 7.25 (d d, $J$ = 7.7, 6.7 Hz, 4H), 7.20 – 7.11 (m, 1H), 7.02 (t, $J$ = 7.5 Hz, 2H), 6.83 (dd, $J$ = 13.7, 5.1 Hz, 4H), 5.81 (s, 1H). <sup>13</sup> C NMR (101 MHz, CDCl <sub>3</sub> ): $\delta$ = 144.13, 136.71, 128.82, 128.34, 127.13, 126.26, 123.75, 122.00, 120.01, 119.65, 119.32, 111.20, 40.26.
	<sup>1</sup> H NMR (400 MHz, DMSO) $\delta$ = 10.83 (s, 2H), 7.35 (d, $J$ = 8.0 Hz, 4H), 7.26 (d, $J$ = 7.6 Hz, 2H), 7.09 (d, $J$ = 8.6 Hz, 2H), 7.06 – 6.96 (m, 2H), 6.86 (t, $J$ = 7.3 Hz, 2H), 6.82 (s, 2H), 5.85 (s, 1H). <sup>13</sup> C NMR (101 MHz, DMSO) $\delta$ = 159.86, 141.58, 137.22, 130.53, 127.11, 124.11, 121.46, 119.6, 118.77, 115.26, 115.05, 112.01, 39.50.
	<sup>1</sup> H NMR (300 MHz, DMSO) $\delta$ = 10.77 (s, 2H), 7.33 (d, $J$ = 8.1 Hz, 2H), 7.29 – 7.15 (m, 4H), 7.03 (d d, $J$ = 15.3, 7.8 Hz, 4H), 6.93 – 6.74 (m, 4H), 5.76 (s, 1H), 2.24 (s, 3H). <sup>13</sup> C NMR (101 MHz, CDCl <sub>3</sub> ) $\delta$ = 141.15, 136.74, 135.61, 129.06, 128.69, 127.19, 123.70, 121.96, 120.05, 119.96, 119.29, 111.20, 39.87, 21.18.

	$^1\text{H NMR}$ (400 MHz, DMSO) $\delta$ = 10.79 (s, 2H), 7.35 (d, $J$ = 7.0 Hz, 2H), 7.27 (t, $J$ = 6.8 Hz, 4H), 7.03 (t, $J$ = 6.2 Hz, 2H), 6.84 (d d, $J$ = 15.9, 8.6 Hz, 6H), 5.78 (s, 1H), 3.69 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, DMSO) $\delta$ = 157.79, 137.43, 137.10, 129.68, 127.11, 123.92, 121.31, 119.65, 118.92, 118.60, 113.86, 111.90, 55.37, 39.33.
	$^1\text{H NMR}$ (400 MHz, DMSO) $\delta$ = 10.93 (s, 2H), 8.15 (d, $J$ = 8.0 Hz, 2H), 7.61 (d, $J$ = 8.0 Hz, 2H), 7.36 (d, $J$ = 7.9 Hz, 2H), 7.29 (d, $J$ = 7.5 Hz, 2H), 7.05 (t, $J$ = 7.1 Hz, 2H), 6.88 (d, $J$ = 13.8 Hz, 4H), 6.03 (s, 1H). $^{13}\text{C NMR}$ (101 MHz, DMSO): $\delta$ = 153.61, 146.25, 137.10, 129.93, 126.86, 124.35, 123.88, 121.59, 119.40, 118.91, 117.17, 112.07, 39.98.
	$^1\text{H NMR}$ (400 MHz, DMSO): $\delta$ = 10.85 (s, 2H), 7.45 (d, $J$ = 8.4 Hz, 2H), 7.34 (d, $J$ = 8.1 Hz, 2H), 7.27 (dd, $J$ = 17.3, 12.5 Hz, 4H), 7.04 (t, $J$ = 7.3 Hz, 2H), 6.87 (d, $J$ = 7.4 Hz, 2H), 6.83 (d, $J$ = 1.9 Hz, 2H), 5.83 (s, 1H). $^{13}\text{C NMR}$ (101 MHz, DMSO): $\delta$ = 145.00, 136.98, 131.26, 131.01, 126.80, 124.02, 121.22, 119.22, 118.73, 117.90, 111.97, 60.14.
	$^1\text{H NMR}$ (400 MHz, DMSO): $\delta$ = 10.73 (s, 2H), 7.40 – 7.27 (m, 4H), 7.24 (d, $J$ = 8.0 Hz, 2H), 6.88 (d, $J$ = 14.6 Hz, 2H), 6.68 (s, 2H), 2.43 (s, 4H), 1.58 (s, 4H), 1.50 (s, 2H). $^{13}\text{C NMR}$ (101 MHz, DMSO): $\delta$ = 137.19, 126.05, 122.08, 121.03, 120.63, 117.88, 111.46, 38.78, 36.83, 26.56, 22.94.
	$^1\text{H NMR}$ (400 MHz, DMSO): $\delta$ = 11.14 (s, 2H), 7.38 (d, $J$ = 8.0 Hz, 2H), 7.26 (t, $J$ = 7.4 Hz, 2H), 7.17 (t, $J$ = 7.8 Hz, 2H), 7.08 (d, $J$ = 6.0 Hz, 3H), 6.96 (s, 2H), 6.53 (s, 2H), 5.79 (s, 1H). $^{13}\text{C NMR}$ (101 MHz, DMSO): $\delta$ = 146.09, 138.69, 129.26, 128.29, 127.01, 126.09, 124.07, 123.32, 122.39, 119.96, 113.68, 111.64, 60.14.

#### Catalytic procedure for Friedel–Crafts alkylation of indole with 1-formylpyrene acetal.



A mixture of 1-formylpyrene acetal (276.3 mg, 1 mmol), indole (234.3 mg, 2 mmol) and **2** (12.4 mg, 1 mol %) in  $\text{CH}_3\text{CN}$  (1 mL) was stirred at room temperature for 10 h (monitored by TLC). After addition of ethyl acetate (2 mL), the catalyst was isolated by centrifugation. The product

was purified by column on silica gel (CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether = 1 : 3) to provide white solid (Yield, 28 %). <sup>1</sup>H NMR (400 MHz, DMSO): δ = 10.84 (s, 2H), 8.61 (d, *J* = 9.4 Hz, 1H), 8.32 – 8.18 (m, 2H), 8.13 (d, *J* = 11.7 Hz, 3H), 8.05 (t, *J* = 7.6 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 7.9 Hz, 2H), 7.03 (t, *J* = 7.6 Hz, 2H), 6.96 (s, 1H), 6.82 (t, *J* = 7.5 Hz, 2H), 6.77 (s, 2H), 5.75 (s, 1H). <sup>13</sup>C NMR (101 MHz, DMSO): δ = 139.22, 137.12, 131.38, 130.80, 129.74, 128.47, 127.88, 127.69, 127.08, 126.96, 126.56, 125.49, 125.28, 125.08, 124.82, 124.63, 124.07, 121.41, 119.40, 118.76, 118.48, 112.02, 63.52. MS-EI, *m/z*, Anal.Calcd :445.17, Exp: 445.16 (M-).

#### 4. References

1. M. Zhang, Y. Wang, Y. Yang and X. Hu, *Advanced Synthesis & Catalysis*, 2012, **354**, 981-985.
2. C.-W. Zhao, J.-P. Ma, Q.-K. Liu, X.-R. Wang, Y. Liu, J. Yang, J.-S. Yang and Y.-B. Dong, *Chem. Commun.*, 2016, **52**, 5238 – 5241.