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Fabrication of novel hybrid nanoflowers from boron nitride nanosheets and metal-organic frameworks: A solid acid catalyst with enhanced catalytic performance

Peng Wang,^a Hao Li,^b Qiang Gao,^a Pei-Zhou Li,^a Xin Yao,^a Linyi Bai,^a Kim Truc Nguyen,^a Ruqiang Zou ^{*cd} and Yanli Zhao^{*ade}

^a Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, 21 Nanyang Link, Singapore 637371, Singapore. E-mail: zhaoyanli@ntu.edu.sg.

^b Department of Chemistry, University of Texas at Austin, Austin, Texas, USA.

^c Department of Materials Science and Engineering, College of Engineering, Peking University, Beijing 100871, China. E-mail: rzou@pku.edu.cn.

^d Singapore Peking University Research Centre for a Sustainable Low-Carbon Future, 1 Create Way, Singapore 138602, Singapore.

^e School of Materials Science and Engineering, Nanyang Technological University, Singapore 639798, Singapore.

Experimental Section

Materials: Benzaldehyde (ReagentPlus, ≥99%), hexagonal boron nitride (BN, 98%, 1 μm powders), and terephthalic acid (BDC, 98%) were purchased from Sigma-Aldrich. Aluminum chloride hexahydrate (99%) and methanol (HPLC grade) were supplied with Alfa-Aesar. All the chemicals were used as received without further purification.

Measurements: Powder X-ray diffraction (PXRD) measurements were performed on a Bruker Powder D8 Advance diffractometer at 40 kV and 30 mA using Cu Kα radiation ($\lambda = 1.5418 \text{ \AA}$). FT-IR spectra were recorded as KBr pellets on a SHIMADZU IRPrestige-21 spectrometer. UV-vis spectra were recorded with Shimadzu UV-3600 UV-Vis-NIR spectrophotometer at 298 K. The gas adsorption/desorption isotherms were measured on an autosorp-IQ instrument from Quantachrome Instruments Corporation. Before the measurements, all the samples were pretreated by evacuating at 180 °C for 10 h. SEM images were obtained on a JSM 6340 scanning electron microscope (0.5–30 kV) equipped with Cold cathode FEG as electron source. Zeta potential measurements were carried out with a Zetasizer Nano ZS instrument from Malvern Instruments Ltd. at 298 K using a 633 nm ‘red’ laser. The contents of boron were determined by ICP-MS (Agilent 7700). Thermogravimetric

analysis (TGA) was carried out on a TGA-Q500 thermoanalyzer with a heating rate of 10 °C/min under nitrogen atmosphere.

Exfoliation of BN to obtain BNNSs: BN powder (1.0 g) was added into a 250 mL flask, and DMF (200 mL) was added as dispersion solvent. The sealed flask was sonicated for 1 day, and then the dispersion was centrifuged at 4 000 rpm for 30 min to remove aggregates. The centrifugation operation was repeated for three cycles.

Replacement DMF with water to re-disperse BNNSs: DMF solution (10 mL) of BNNSs was centrifuged at 10 000 rpm for 30 min to precipitate residual BNNSs. The white solid was added with deionized water (10mL) and sonicated for another 4 h. To further improve the dispersion of BNNSs in water, 10 vessels of above mixture were combined together, and then treated with an ultrasonic probe at 250 W for 1h followed by stewing for over two days. The resulted supernatant was a light-blue solution, and the boron contents were determined as 0.037mg/mL via ICP-MS.

Zeta potential measurements: A diluted solution of BNNSs (2 mL original solution, added with 6 mL deionized water) was added with $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (10 mg), which was sonicated for 30 min. The aluminum decorated BNNSs were centrifuged at 10 000 rpm, washed with water and re-dispersed in equivalent water. The zeta potentials of diluted BNNSs solution and aluminum coordinated BNNSs solution were measured with a Zetasizer Nano ZS instrument.

Synthesis of BNNSs/MOFs and related materials: Different amounts of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (24mg, 48mg, 96mg) were added into BNNSs aqueous solution (20 mL), which was sonicated for 3 h. After adding $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (96mg), BNNSs precipitated immediately. For the 24 mg and 48 mg samples, they were transferred into 25 mL Teflon-lined steel autoclave containing equivalent BDC in molar to $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$. The autoclave was kept at 150 °C under static conditions for 24 h. After cooling down to room temperature, the white solid product was isolated by centrifugation. Then, all these samples were activated in boiling DMF for 8 h (200 mg samples in 300 mL DMF) in order to remove the remaining water or unreacted ligands trapped in the pores. Finally, all the products were isolated by repeated centrifugation and washed with methanol to remove DMF in the pores. The resulting white solids were dried in a vacuum oven at 150 °C overnight before further analysis and utilization. The sample with $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (24 mg) was denoted as **BNNSs/MOF-1**, and the 48 mg one was denoted as **BNNSs/MOF-2**. The sample without BNNSs was also synthesized using $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (48mg) and BDC (34mg) in deionized water (20 mL), which was denoted as **MIL-53-com**.

For comparison, previously reported MIL-53 bulky crystals were prepared using a procedure with a slight modification: $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (960mg)

and BDC (680mg) were mixed with deionized water (5mL), and the other steps were same to the preparation of BNNSs/MOFs. The obtained sample was denoted as **MIL-53-bulk**.

MIL-53 with BN powders was also synthesized instead of using BNNSs. The detailed process was: $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (960 mg), BDC (680mg) and BN powder (200 mg) were mixed with deionized water (5mL), and the other steps were same to the preparation of BNNSs/MOFs. The obtained sample was denoted as **BN Powder/MOF**.

Adsorption of FITC in ethanol: A stock solution of FITC (125 mg L^{-1}) was prepared by dissolving FITC in HPLC grade ethanol. The FITC solution was used for adsorption directly. BNNSs/MOF-2 and MIL-53-bulk were tested in the kinetic adsorption studies. Before adsorption, the samples were dried in a vacuum oven at $150 \text{ }^\circ\text{C}$ for 6 h. The adsorbent (10.0 mg) was added to the FITC ethanol solution (12 mL). For a kinetic study, the supernatant was collected at different time intervals for the determination of unabsorbed FITC at 298K. After adsorption, the solution was centrifuged at 10 000 rpm for 2 min and then analyzed for the concentration of residual FITC using a UV spectrophotometer at the calibrated maximum wavelength of 457 nm.

Acetalization of benzaldehyde with methanol: A 25-mL round-bottomed flask was charged with the catalyst (60 mg) in methanol (6 mL) and benzaldehyde (100 μL). The reaction mixture was stirred for the required time at room temperature. To make the reaction time profiles, the mixture (100 μL) was taken out at different time intervals. The obtained liquid solution was diluted by ethyl acetate, centrifuged at 10 000 rpm for 2 min, and analyzed by GC (Thermo gas chromatograph equipped with a flame ionization detector and an HP-5 capillary column) to determine the conversion of benzaldehyde. Nitrobenzene (50 μL) was used as internal standard, and a little byproduct (such as benzoic acid) was detected. Solids were subjected to thermal dehydration at $150 \text{ }^\circ\text{C}$ for 6 h before their use.

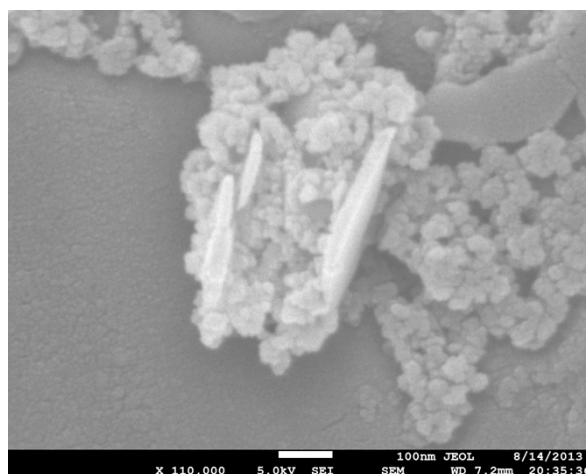


Figure S1. SEM image of BNNSs/MOF

synthesized in DMF.

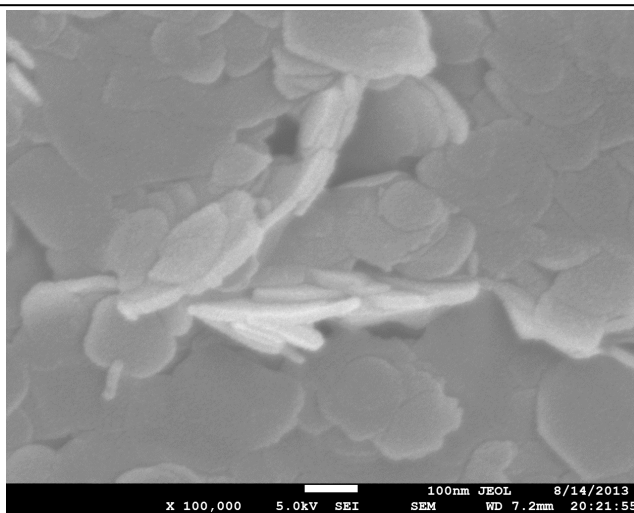


Figure S2. SEM image of BN powders.

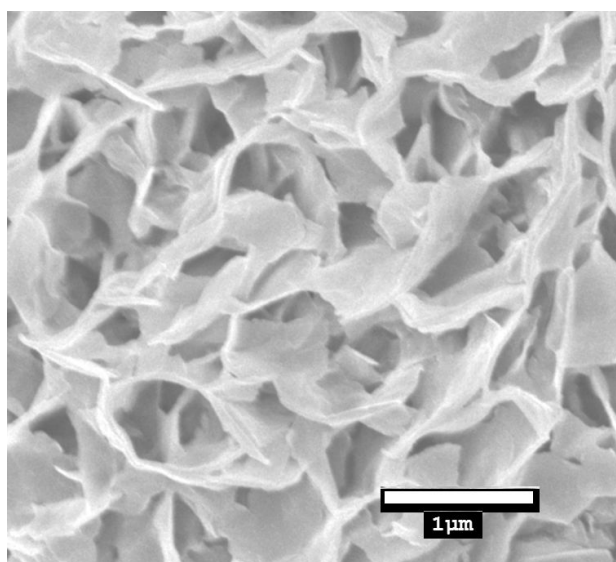


Figure S3. SEM image of BNNs/MOF-1.

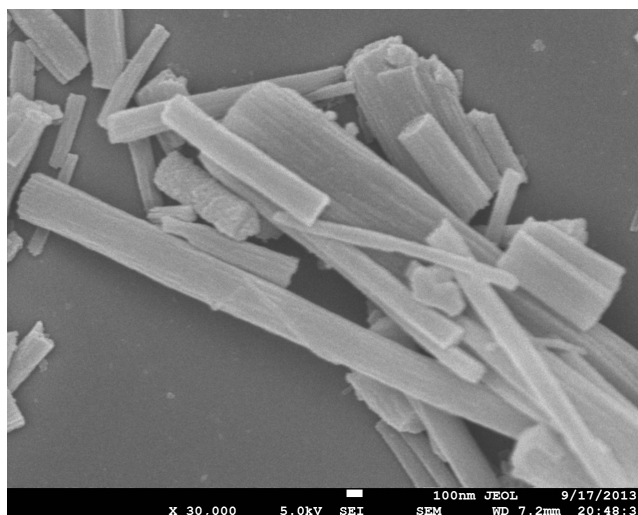


Figure S4. SEM image of MIL-53-com.

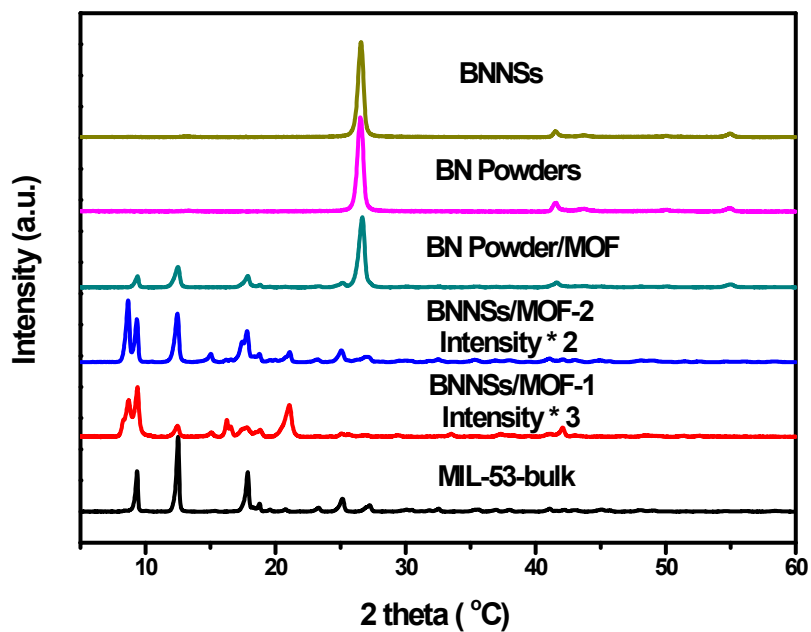


Figure S5. Powder XRD patterns of MIL-53-bulk, BNNs/MOF-1, BNNs/MOF-2, BN Powder/MOF, BN powders and BNNs (from bottom to up).

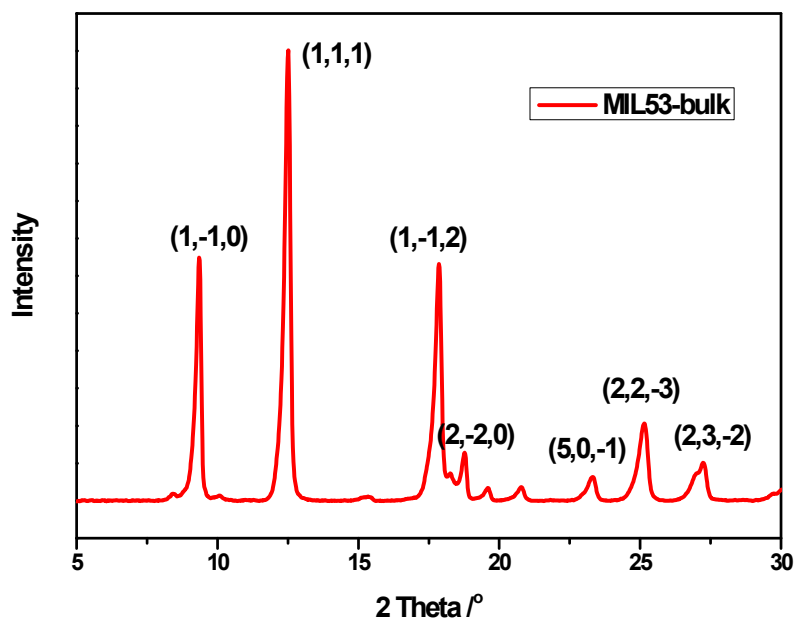


Figure S6. Detailed powder XRD pattern of MIL-53-bulk.

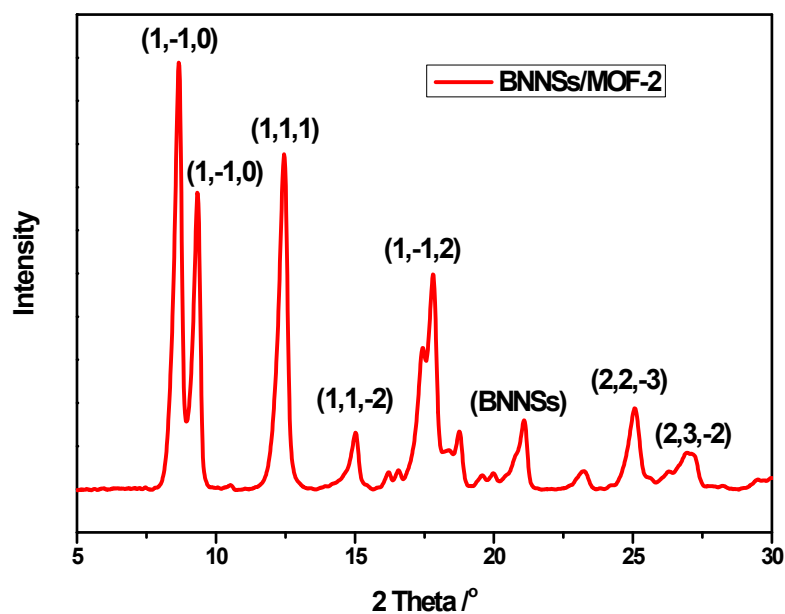


Figure S7. Detailed powder XRD pattern of BNNs/MOF-2.

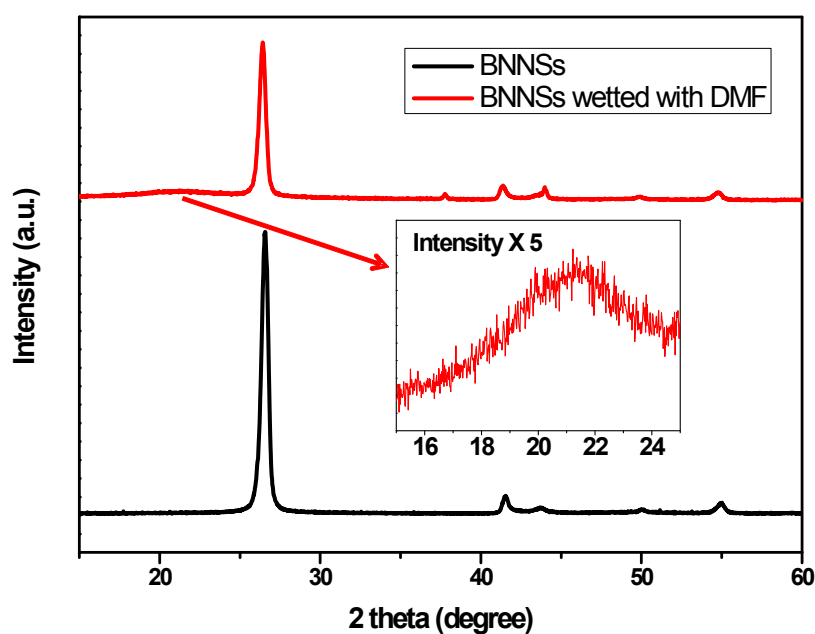


Figure S8. Powder XRD patterns of BNNs and DMF-wetted BNNs.

We wetted the exfoliated BNNs with DMF, and the obtained powder showed a bit different XRD pattern from the dry sample. Firstly, the intensity of the primary d(002) peak decreased after wetted with DMF. Secondly, a new broad peak appeared around 21° , although its intensity was weak. It proves that the expansion of d(002) space can be realized with the dispersion of BNNs with other matrix, such as DMF.

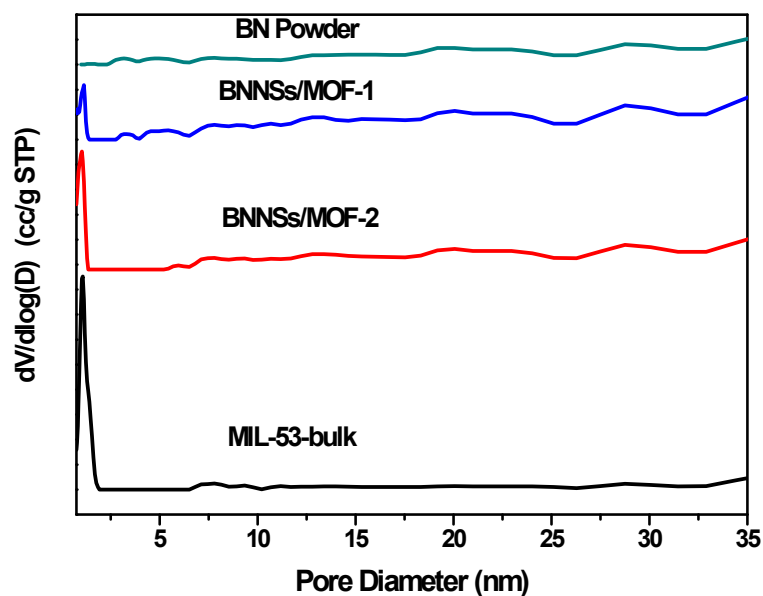


Figure S9. Pore size distributions for the parent and hybrid materials.

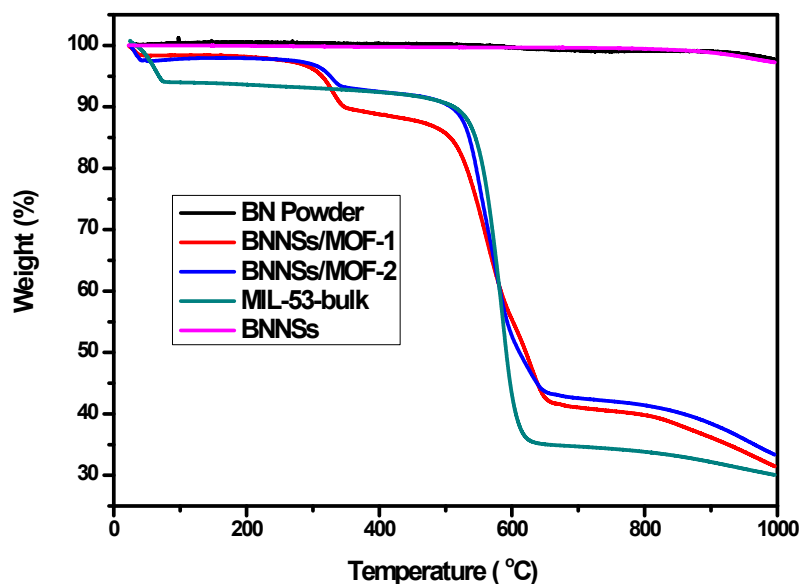


Figure S10. Thermogravimetric analysis for the parent and hybrid materials.

The decomposition of free 1,4-benzenedicarboxylic acid occurs in the range of 275-420 °C. For BNNSs/MOF hybrid, some 1,4-benzenedicarboxylate molecules may be adsorbed on the BNNSs surface due to the π - π interaction, which showed the weight loss at around 300°C. These molecules cannot be completely removed under the refluxing in DMF and methanol.

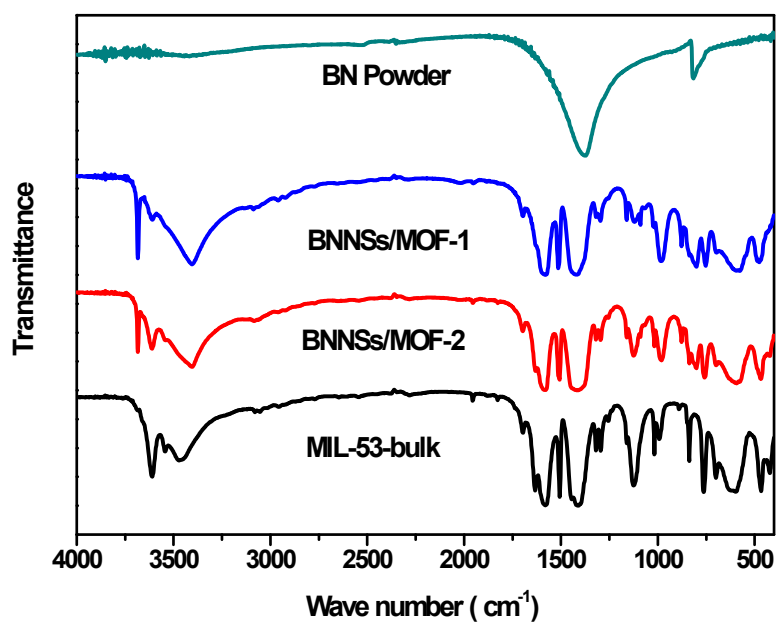


Figure S11. FT-IR spectra for the parent and hybrid materials.

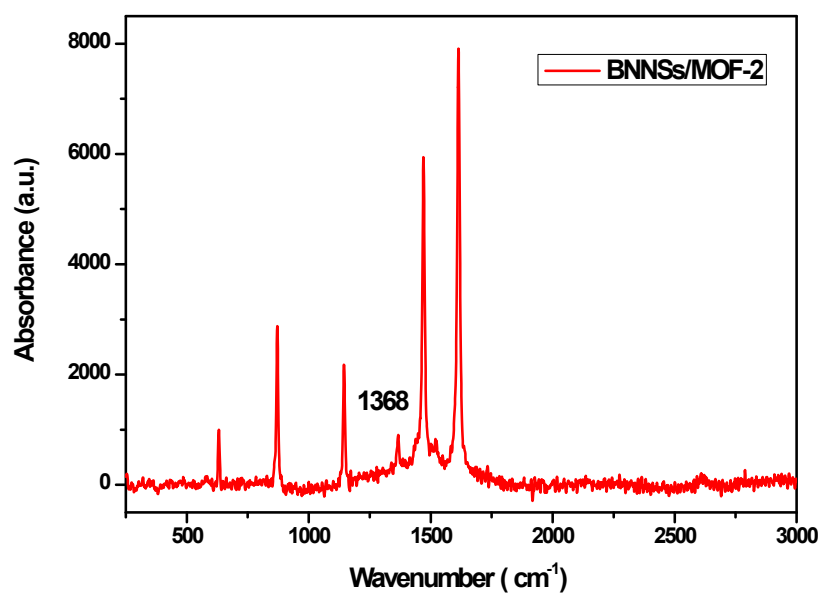


Figure S12. Raman spectrum of BNNs/MOF-2.

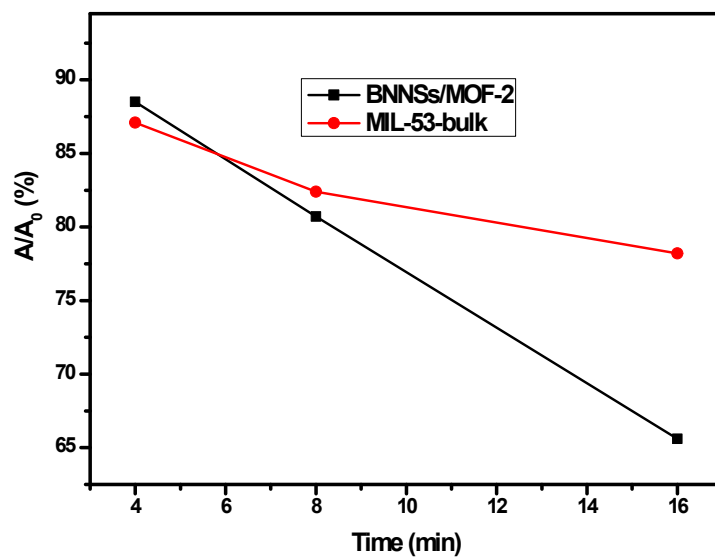


Figure S13. Adsorption of FITC by MIL-53-bulk and BNNs/MOF-2 upon time.

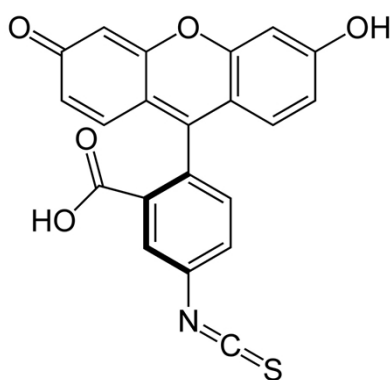


Figure S14. Chemical structure of FITC.

Table S1. Zeta potentials of BNNs aqueous solution before and after the coordination with aluminum ions.

Samples	BNNs in water	Al ³⁺ coordinated BNNs
Zeta potentials (mV)	+0.60	+16.52

Table S2. Textural parameters and components for the parent and hybrid materials.

Samples	Boron content in weight (%)	S_{BET} (m^2/g)	V_{t} (cm^3/g)	V_{mic}^a (cm^3/g)	$V_{\text{mes+mac}}$ (cm^3/g)
BN Powders	43.6	29	0.14	0	0.14
MIL-53	-	1042	0.55	0.46	0.09
BNNSs/MOF-1	1.6 (3.7) ^b	306	0.36	0.11	0.25
BNNSs/MOF-2	0.7 (1.6) ^b	699	0.48	0.30	0.18

^aMicropore volume, V_{mic} , was calculated from the t -plot method. ^bThe contents in parentheses were weight contents of BN.