Supporting Information

for

Mechanochromic MOF Nanoplates: Spatial Molecular Isolation of Light-Emitting Guests in a Sodalite Framework Structure

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1 Synthesis procedure of Perylene@ZIF-8 nanoplates and monoliths

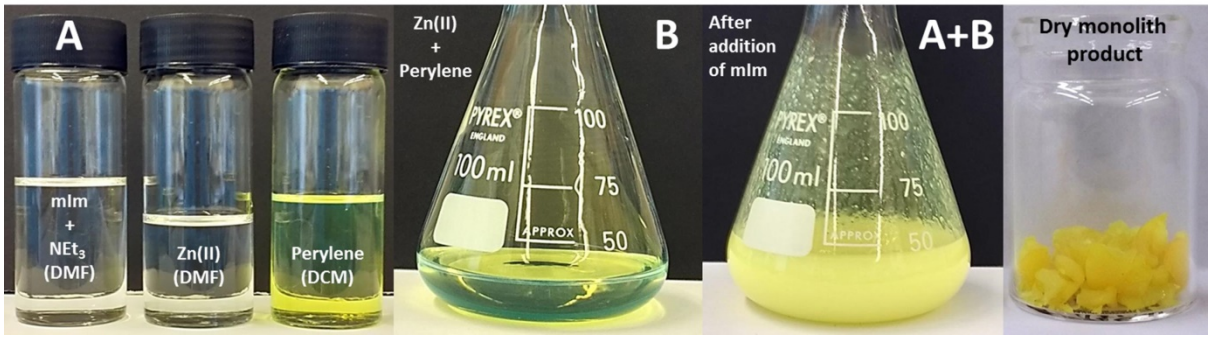

Figure S1. Photographs depicting the synthesis protocol of the Perylene@ZIF-8 compound. Upon mixing the clear solutions A and B, we observed a rapid reaction leading to the formation of a light-yellow coloured product.

Three clear solutions were prepared in three different glass vials namely: 1) 6.0 mmol of $Zn(NO_3)_2$ solution in 15 ml of *N*, *N*-Dimethylformamide (DMF), 2) 0.2 mmol of Perylene in 18 ml of Dichloromethane (DCM), and, 3) 15 ml DMF solution of 24.0 mmol of 2-methylimidazole (mIm) deprotonated using 24.0 mmol of Triethylamine (NEt_3) (named as solution A). Zn^{2+} solution and Perylene solutions were mixed together (to form solution B), which was then combined with solution A. Sudden product formation was observed upon the mixing of solutions A and B, yielding a light-yellow coloured compound (see figure S1). 50 ml of DCM was added into the Erlenmeyer flask containing the product and sonicated for 10 minutes, then the product was separated by centrifugation at 8000 rpm for 5 minutes. To make sure that the obtained product (i.e. Perylene@ZIF-8) was free from any surface adhered Perylene, the centrifuged product was further washed twice with 50 ml of DCM, each time accompanied by vigorous sonication (10 min) during the washing steps. After washing the sample with DCM, it was further washed with 50 ml of methanol (to make sure product is free from unreacted 2-methylimidazole) and then finally with 50 ml of acetone, accompanied by a 10-min vigorous sonication at each washing stage. The washed sample isolated by centrifuge was dried at 90°C under vacuum for 6 hours. Drying of sample yields a darker-yellow coloured monolithic material containing Perylene@ZIF-8 (see Figure S1).

2 Materials characterization

To prepare the nanoplates for atomic force microscopy (AFM) and transmission electron microscopy (TEM) imaging, as-synthesized wet samples of Perylene@ZIF-8 were first being sonicated for 15 minutes in a diluted acetone solution to reduce aggregation. For AFM study, the nanoplate sample was drop casted onto a small glass substrate and dried, then imaged using the Veeco Dimension 3100 instrument equipped with a silicon probe under the tapping mode. For TEM study, the diluted nanoplate sample was deposited onto a holey carbon copper grid and left to dry. TEM images were collected on the JEOL JEM-2100 LaB6 at 200 keV. Diffuse reflectance spectra were collected on the 2600 UV-Vis spectrophotometer under ambient conditions. Steady-state photoluminescence data was recorded using the UPRtek MK350N Plus spectrophotometer. X-ray diffraction (XRD) data was collected using the Rigaku MiniFlex equipped with a Cu Kα source (1.541 Å), from 2θ angle of 2° to 30° with 0.01° step size and a scan speed of 1° min^{-1}. Thermogravimetric analysis (TGA) was conducted on the TA Instrument Q50 at a heating rate of 20 °C min^{-1} from 30-700 °C under constant nitrogen flow. The powder pellets were prepared in a Ø13 mm die using a laboratory grade hydrostatic press.

3 Transmission electron microscopy (TEM)

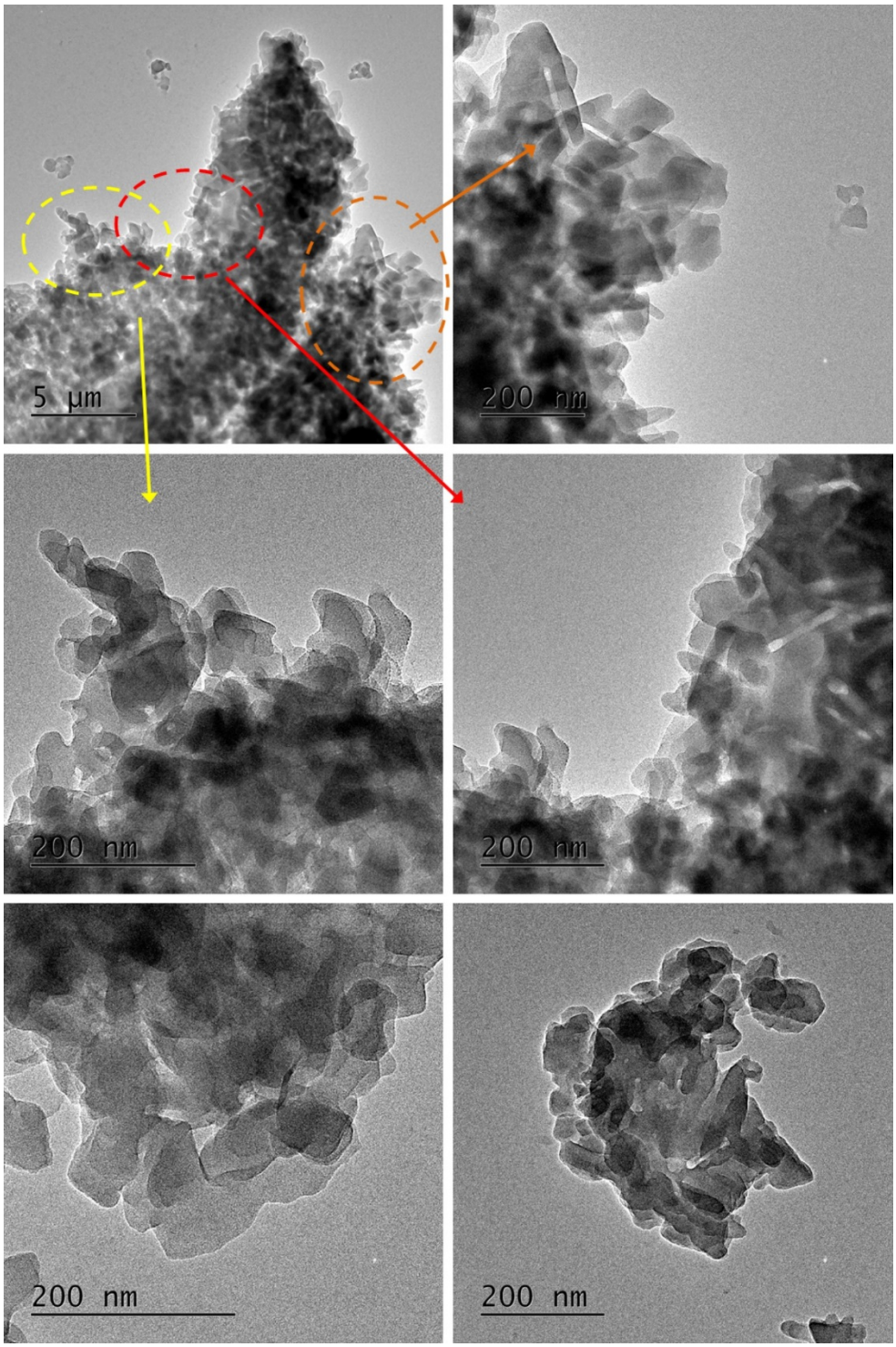

Figure S2. TEM micrographs of Perylene@ZIF-8 nanoplates revealing their thin 2-D morphologies and the intertwined aggregated assembly. The fine-scale nanoplates explained in the manuscript can be seen at the edges of the aggregated nanoplates.

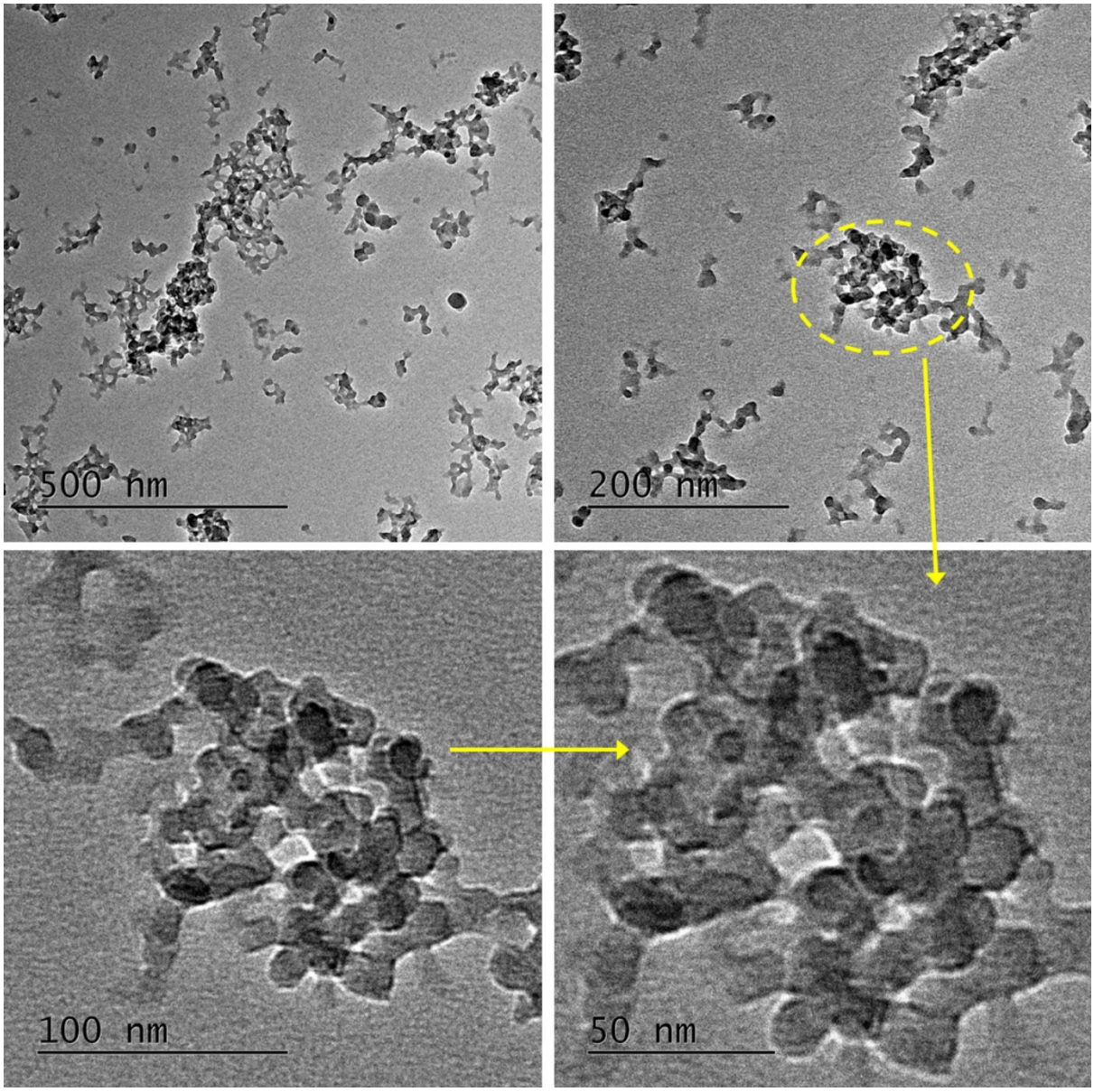

Figure S3. TEM micrographs showing very fine scale nanoplates of Perylene@ZIF-8, where the aggregate consisted of uniformly sized nanoplates of ~10 nm.

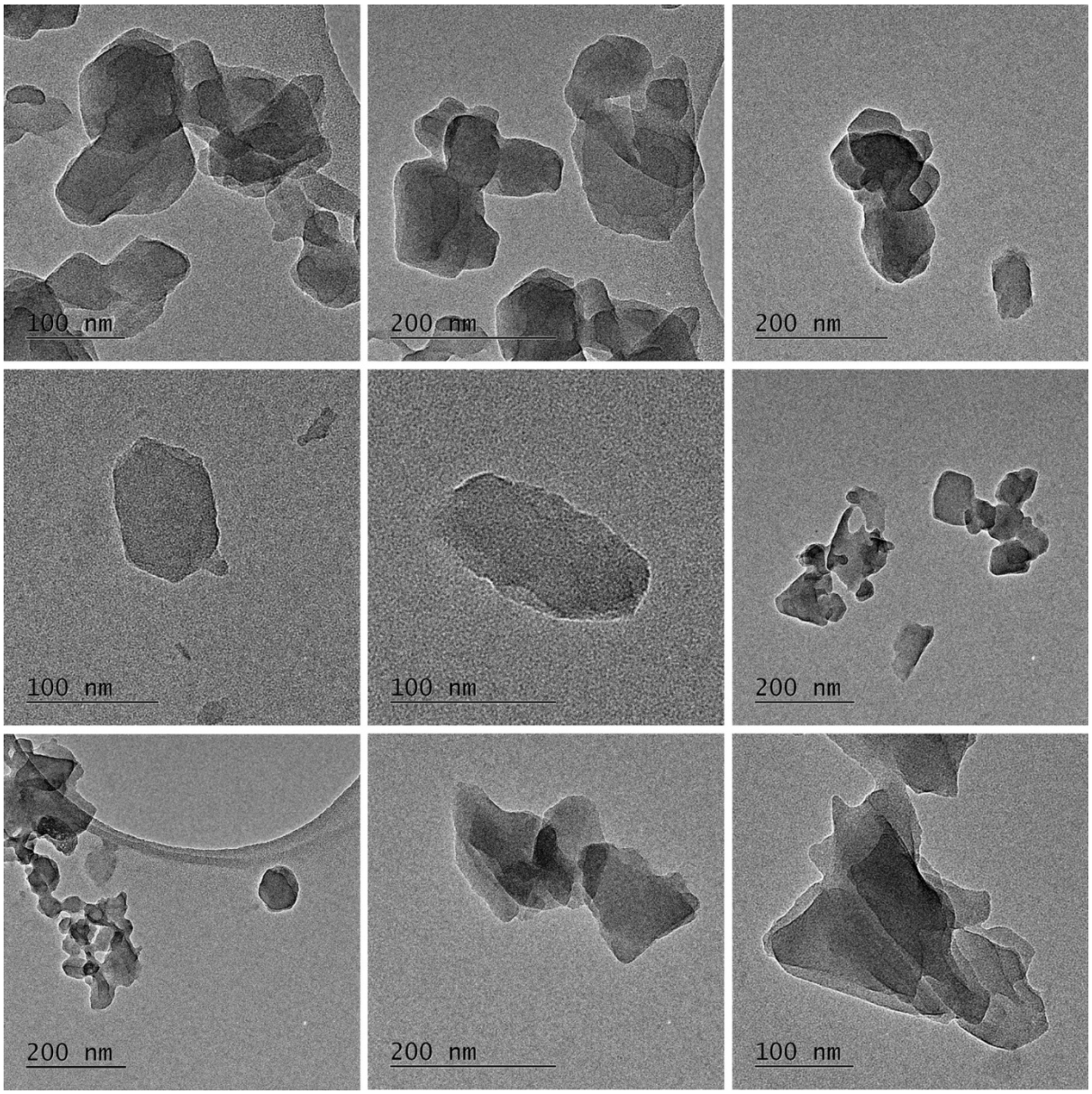

Figure S4. TEM micrographs showing the ability of some of the nanoplates to separate from one another. However, some of the intertwined nanoplates cannot be isolated even with prolonged sonication of sample containing aggregated nanoplates, due to their synthesis from highly concentrated reactants.

4 Photoluminescent emission spectra with different palletization pressures

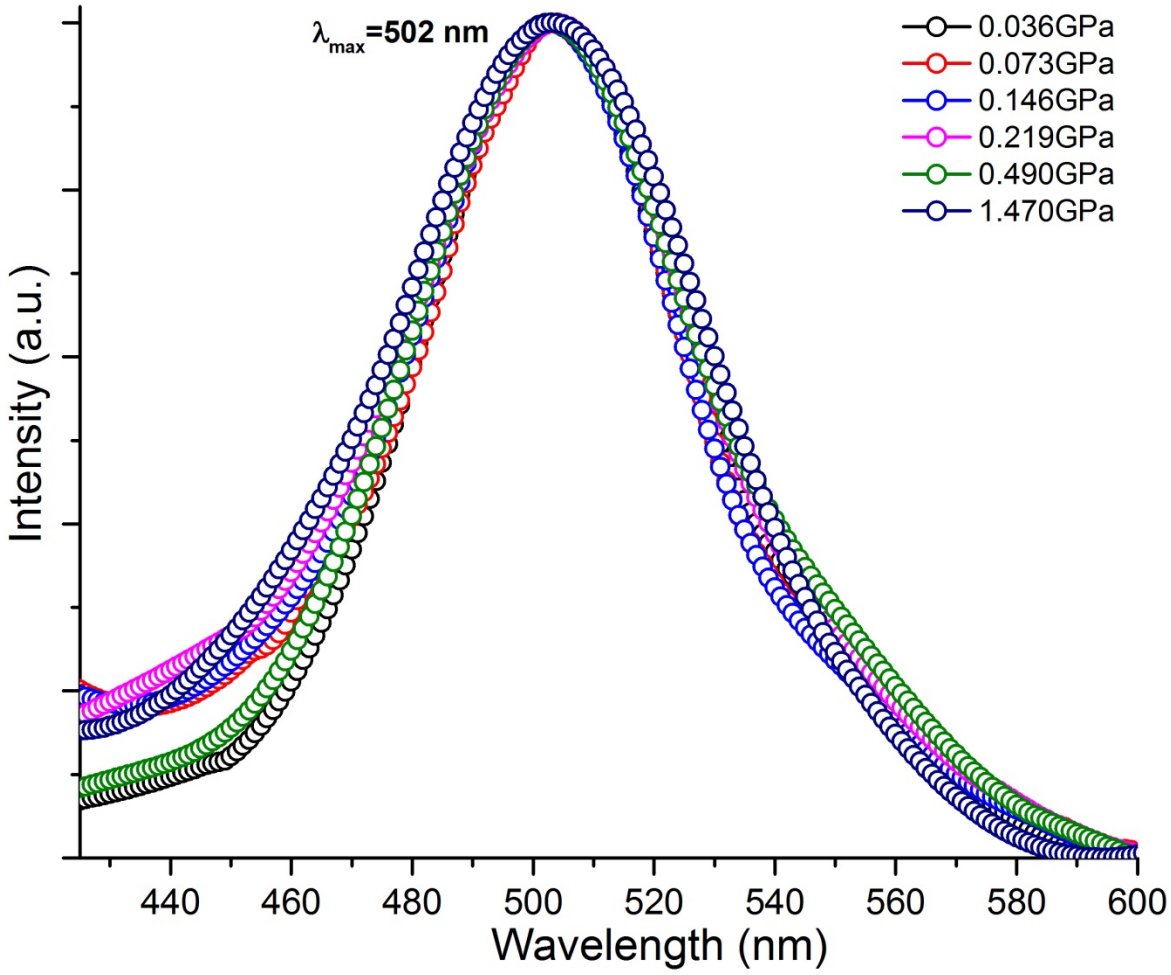

Figure S5. Emission spectra of pressed pellets of Perylene@ZIF-8 powder systematically obtained at a range of pressures, from *ca*. 0.04 to 1.5 GPa. The λ_{max} was found to be constant for all samples regardless of their pelletizing pressures.

5 Band gap theoretical calculation

Band gap values were calculated using the DMol3 module implemented in the Material Studio package. A 1×1×1 unit cell was considered for calculating the energy levels of the (vacant) ZIF-8 framework and the isolated Perylene molecule. To model the guest@host assembly containing a confined Perylene guest molecule, the Perylene molecule was docked into the void of the ZIF-8 (host) framework and geometrically optimized using the Forcite module. The band gap of the optimized guest@host structure was then calculated using DMol3.

Perylene@ZIF-8

Task parameters	
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Scf_spin_mixing	5.000000e-001
Scf_diis	6 pulay
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Pseudopotential	none
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Kpoints	off
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Plot	lumo
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ZIF-8 & distorted ZIF-8

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Perylene

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6 Determination of X-ray structure from Pawley refinement

Table S1. Changes in the unit cell parameters of the pristine ZIF-8 versus distorted ZIF-8 structure, the latter due to high concentration reaction and encapsulation of the Perylene guest within the ZIF-8 pore.

Compound	ZIF-8 reported by Yaghi et *al*.[1]	Nanoplates of ZIF-8 (Distorted cell)
Crystal System	Cubic	Triclinic
Space Group	I-4 3 m	P1
X-ray Source	MoKα	CuKα
λ [Å]	0.71073	1.5418
Refinement Range of 2θ [°]	-	5 to 30
a [Å]	16.9910(12)	17.339
b (Å]	16.9910(12)	17.127
c [Å]	16.9910(12)	17.072
α [°]	90	87.073
β [°]	90	90.321
γ [°]	90	84.677
Volume [Å^3]	4905.2	5041.48
Peak Profile	-	Pseudo-Voigt
R factor	0.0314 (R1)	0.0818 (R_{wp})
Structure Solution Method	Single Crystal	Powder Refinement
Software	SHELXTL' 97	Reflex (Material Studio)

7 Thermogravimetric analysis (TGA)

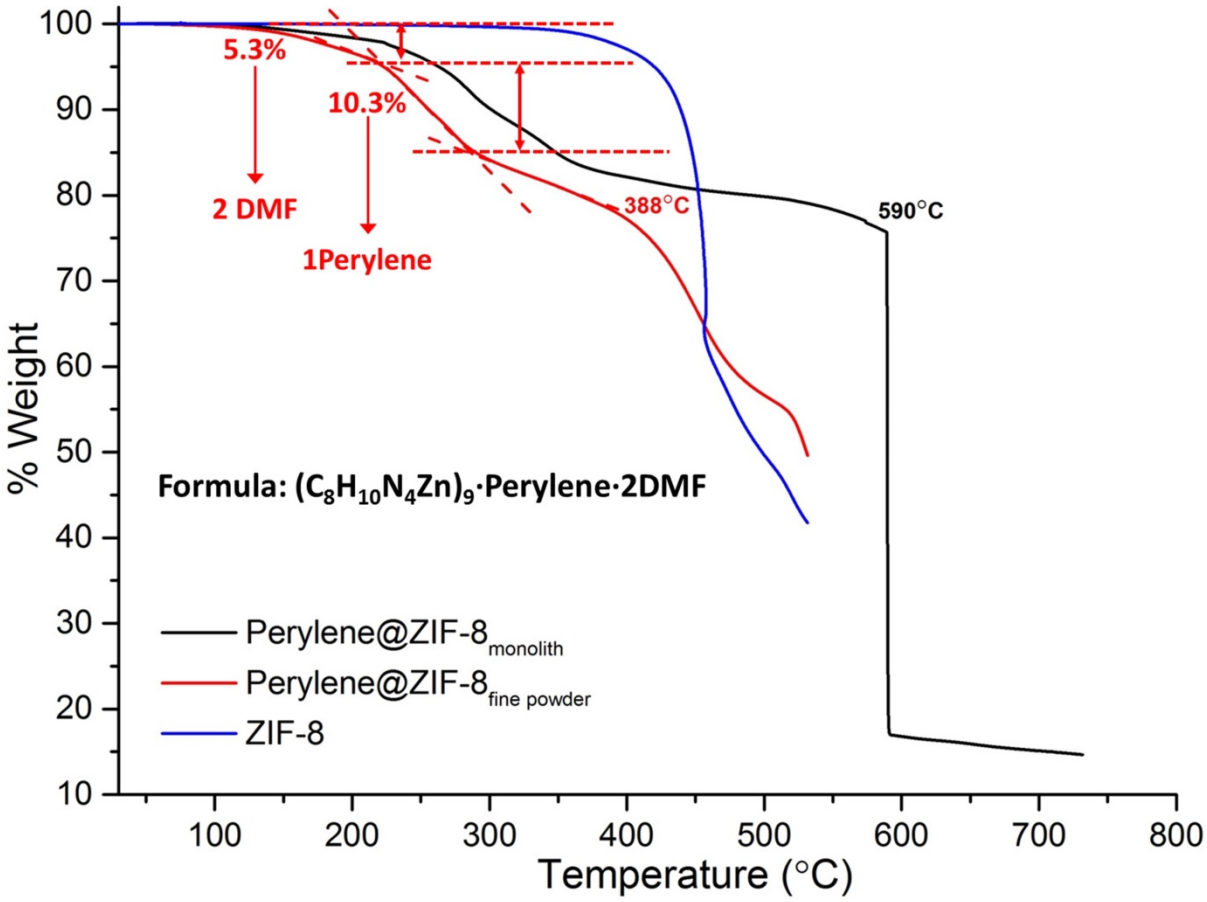

Figure S6. TGA of Perylene@ZIF-8 compound revealing its probable formula. Higher thermal stability of monolithic Perylene@ZIF-8 can be seen from the figure compared to the pristine ZIF-8 or powdered Perylene@ZIF-8 compound. Sharp decomposition at 590°C of the monolithic compound and higher thermal stability suggest dense packing of nanoplates of Perylene@ZIF-8 could enhance thermomechanical stability compared with the pristine ZIF-8 host.

8 References

1. Park, K. S.; Ni, Z.; Cote, A. P.; Choi, J. Y.; Huang, R.; Uribe-Romo, F. J.; Chae, H. K.; O'Keeffe, M.; Yaghi, O. M., Exceptional chemical and thermal stability of zeolitic imidazolate frameworks. *Proc Natl Acad Sci USA* **2006,** *103* (27), 10186-91.