Highly Photostable and Fluorescent Microporous Solids Prepared via Solid-state Entrapment of BODIPY Dyes in a Nascent Metal-Organic Framework

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3. References

1. Experimental Details

1.1. Materials

Zinc oxide was calcinated overnight at 400°C in a Thermolyne furnace prior to use. Zinc oxide (>99.0%), 2-methylimidazole (HMeIm, 99%), and Basolite Z1200® (produced by BASF) were purchased from Sigma Aldrich. Ammonium nitrate (Certified ACS) was purchased from Fisher. Pyrromethene 605 (PM605), Pyrromethene 546 (PM546) and Pyrromethene 650 (PM650) were obtained from Exciton. BODIPY fluorophore HClBOH was prepared as described in Krumova *et al.*¹ MeOH, EtOH, acetonitrile (ACN), and dichloromethane (DCM) were purchased from Fisher. Caffeinium hydrogensulfate ((Hcaf)(HSO4)) was prepared as described previously.²

1.2. Synthesis of PM605@ZIF-8 samples

1.2.1. Ion- and Liquid-Assisted Grinding (ILAG)

All ILAG reactions were performed at 1 mmol scale, by placing a mixture of solid reactants ZnO (1 mmol, 81.4 mg), HMeIm (2 mmol, 164.2 mg), NH₄NO₃ (10 mg), and different amounts of PM605 (or other BODIPY fluorophore) into a 10 mL stainless steel jar with 75 μ L EtOH. For low loading PM605@ZIF-8_{ILAG} samples (wt% 0.05 and 0.5) the PM605 was added to the jar from a known concentration stock in dichloromethane and the solvent was evaporated under the N₂ stream prior to adding the solid reactants. Two 7 mm diameter stainless steel balls were added to the reaction mixture, and the mixture was milled using a Retch MM400 ball mill for 30 minutes at 29.5 Hz.

1.2.2. Accelerated aging (AA)

All AA reactions were performed at 2 mmol scale, by placing 2 mmol of ZnO (163 mg), HMeIm (328.4 mg), (Hcaf)(HSO₄) (23.4 mg), and different amounts of PM605 into a 10 mL stainless steel milling jar along one stainless steel ball of 7 mm diameter. For low loading PM605@ZIF-8_{ILAG} samples (wt% 0.05 and 0.5) the PM605 was added to the jar from a known concentration stock in dichloromethane and the solvent was evaporated under the N₂ stream prior to adding the solid reactants. The mixtures were briefly milled using Retch MM400 ball mill for 5 min at 29.5 Hz to. The samples were then left to age in a Secador controlled humidity chamber at nominal 100% RH (using water) which was situated in an incubator set at 45 °C for 2 days.

Both, PM605@ZIF-8_{ILAG} and PM605@ZIF-8_{AA}, samples were washed by stirring the powders overnight in MeOH and then rinsing 3 times with dichloromethane to remove the trace amounts of catalyst, organic ligand and surface absorbed PM605. After washing the samples were evacuated in a vacuum oven at 80 °C overnight. Samples were characterized using PXRD immediately after the synthesis as well as after the washing and evacuation.

1.3. Powder X-ray Diffraction

Powder X-ray diffraction (PXRD) patterns were collected using a Bruker D2 powder diffractometer equipped with a Cu-K α (λ =1.54060 Å) source and Lynxeye detector set at a discriminant range of 0.110 V to 0.250 V. The patterns were collected in the range of 3° to 40°. Analysis of PXRD patterns was conducted using Panalytical X'Pert Highscore Plus software. Experimental PXRD patterns of PM605@ZIF-8 powders were compared to simulated PXRD pattern of ZIF-8 (CSD code VELVOY) calculated from published crystal structures using Mercury crystal structure viewing software. Crystallographic Information File containing the published crystal structure was obtained from the Cambridge Structural Database (CSD).

1.4. Steady-State Fluorescence Measurements

Fluorescence emission spectra of PM605@ZIF-8 solids were measured on a Biotek Synergy 2 multi-mode microplate reader using clear polystyrene 96-well microplates. The wells were filled with ~20 mg of the sample, and the powders were pressed with a specially designed plastic plunger containing a flat bottom. This treatment allowed for a flat surface and helped to obtain reproducible fluorescence measurements from the bottom of the microplate. The fluorescence spectra were recorded from 540-700 nm upon exciting at 520 nm. The excitation spectra were recorded from 300-580 nm when monitoring the fluorescence emission at 600 nm.

1.5. UV-Vis Absorption Spectroscopy

The UV-Vis absorption spectra of PM605@ZIF-8_{ILAG} and PM605@ZIF-8_{AA} samples were collected on a Varian Cary 5000 UV-Vis-NIR spectrophotometer equipped with a Praying Mantis diffuse-reflectance accessory (Harrick Scientific Products) and recorded from 300 nm to 580 nm.

1.6. Fluorescence Quantum Yield Measurements

Fluorescence quantum yield measurements were conducted in a Quanta- ϕ integrated sphere setup from Horiba Scientific, connected to and operated from a Fluoromax 4 fluorometer also from Horiba Scientific. Samples (PM605@ZIF-8_{ILAG} solids) were placed on disposable powder cups (spectralon material) and covered with a quartz glass. Excitation was performed at 490 nm and emission integration was performed in the range of 510 nm to 795 nm. Data analysis was executed with the software included with the Quanta- ϕ integrated sphere.

1.7. Time-Resolved Fluorescence Studies

Fluorescence lifetime measurements were carried out using a Picoquant Fluotime 200 time-correlated single photon counting setup employing an LDH-P-C-470 picosecond diode laser (Picoquant) with an excitation wavelength at 466 nm as the excitation source. 488-long pass filter was used to minimize the scattered excitation light. The laser was controlled by a PDL 800 B picosecond laser driver from Picoquant. The excitation rate was 10 MHz, and the detection frequency was less than 100 kHz. A maximum count of at least 30 000 photons was

collected at the magic angle for each sample. Fluorescence lifetimes of PM605@ZIF-8 samples were monitored at 560 nm while that of PM605 in acetonitrile was obtained when monitoring at 560 nm. A home built triangular mini-cuvette was used for the solid samples. Fluorescent solid samples were tightly packed in the sample holder of the cuvette, and the cuvette was closed with a quartz slide. The fluorescence decay traces were fitted using FluoFit (Picoquant) software with a scattering correction enabled.

1.8. Photostability Studies

The photostability of PM605 inside of ZIF-8 pores was evaluated by comparing it to the photostability of free PM605 dye in acetonitrile. 40 mg of PM605@ZIF-8 powder (0.0053 wt% PM605) was dispersed in 1.5 mL of acetonitrile, and its fluorescence intensity after a given irradiation time was compared to the sample containing an equivalent amount (0.021 mg) of free PM605 in solution and 40 mg of preformed ZIF-8 powder. The samples were prepared in fluorescent quartz cuvettes and irradiated with an LED lamp (~450±25 nm) while constantly stirring.To prevent samples from warming up upon irradiation with the lamp, a glass water bath was placed over the sample cuvettes during the irradiation. Photobleaching rates of PM605 in different samples were compared to the dark control samples that were covered in aluminum foil during the irradiation periods. Fluorescence spectra of PM605 after a given irradiation time were measured in a PTI Quanta Master spectrofluorimeter. The fluorescence spectra were recorded from 510-700 nm upon exciting at 500 nm using 2 nm bandwidth excitation and emission slits. Samples were stirred during the acquisition to avoid the precipitation of a solid PM605@ZIF-8 and ZIF-8 powder.

1.9. Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was conducted on a TA Instruments Q1000 Thermogravimetric System with a Pt pan under dynamic atmosphere of air. Samples were heated to an upper temperature limit ranging from 800°C to 900°C at a rate of 20°C/min. The balance and purge flow were 40 ml/min and 60 ml/min respectively.

1.10. N₂ Sorption Measurements

The N₂ sorption isotherms of PM605@ZIF-8_{ILAG} and PM605@ZIF-8_{AA} samples were measured using a Quantachrome ASiQ automatic volumetric gas adsorption analyzer, and the surface areas calculated according to the BET model. The samples were degassed at 80 °C for 8 h prior to analysis.

2. Supplementary Tables and Figures

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Sample		Encapsulation Enciency	% of pores occupied
	PM6050.05@ZIF-8ILAG	~100 %	0.07
ILAG	PM6050.5@ZIF-8ILAG	98 %	0.72
	PM6051.5@ZIF-8ILAG	~ 100 %	2.22
	PM6055.0@ZIF-8ILAG	96 %	7.10
	PM6050.05@ZIF-8AA	93 %	0.07
AA	PM6050.5@ZIF-8AA	85 %	0.64
	PM6051.5@ZIF-8AA	77 %	1.74
	PM6055.0@ZIF-8AA	73 %	5.50

Table S1. PM605 encapsulation efficiency in PM605@ZIF-8_{ILAG} and PM605@ZIF-8_{AA} samples containing different loading of PM605.

*Determined by measuring the absorbance of PM605 obtained after overnight wash with MeOH and three consecutive washes with dichloromethane

Table S2. Quantum yields of fluorescence for PM605 inside of ZIF-8 pores. Samples evaluated consisted of PM605@ZIF-8_{ILAG} with increasing loading - in the range of 0.05 wt% to 5%wt - of PM605.

Sample	0.05 wt%	0.5 wt%	1.5 wt%	5 wt%
$\Phi_{ m f}$	67.5%	39.6%	27.8%	7.9%

Table S3. Fluorescence lifetimes of PM605 in acetonitrile and inside of ZIF-8 pores of PM6050.05@ZIF-8ILAG samples with increasing loading of PM605. Also listed are estimated emission quantum yields based on a radiative lifetime value of 10 ns for BODIPY dyes

Sample	Fluorescence lifetimes, ns		Tavg [*] ,IIS	χ²	Estimated $\Phi_{\rm f}$
	τ1, ns	T2, NS			$\Phi_{\mathrm{f}} = \tau_{\mathrm{avg}} / \tau_{\mathrm{rad}}$
PM605 in acetonitrile	6.76	n/a	6.76	1.136	67.0%
PM6050.05@ZIF-8ILAG	8.20 (87 %)	1.06 (13 %)	7.45	1.160	74.5%
PM6050.5@ZIF-8ILAG	7.22 (84 %)	2.72 (16 %)	6.52	1.087	65.2%
PM6051.5@ZIF-8ILAG	5.18 (79 %)	1.71 (21 %)	4.46	1.234	44.6%
PM6055.0@ZIF-8ILAG	2.26 (43 %)	0.98 (57 %)	1.51	1.047	15.1%

*Amplitude-weighted



Figure S1. Appearance and emission of PM605 when in solution (acetonitrile) as well as in the solid state when visualized under visible (a) as well as UV (b) light.



Figure S2. PXRD patterns of (a) PM605@ZIF-8_{ILAG} and (b) PM605@ZIF-8_{AA} samples containing different wt% of PM605 compared to simulated PXRD pattern of ZIF-8 (CSD code VELVOY).



Figure S3. Fluorescence properties of PM605 in ACN compared to PM605_{0.05}@ZIF-8_{ILAG}: (a) Fluorescence lifetimes of PM605 in ACN (exciting at 467 nm, monitoring at 560 nm) and PM605_{0.05}@ZIF-8_{ILAG} (exciting at 467 nm, monitoring at 590 nm); (b) fluorescence spectra of PM605_{0.05}@ZIF-8_{ILAG} dispersed in ACN (red) and equivalent amount PM605 in ACN in the presence of the same amount of preformed ZIF-8 powder (black).



Figure S4. Normalized emission spectra of (a) PM605@ZIF-8ILAG and (b) PM605@ZIF-8AA where a red-shift in emission maximum is observed upon increasing loading (wt%) of PM605.



Figure S5. (a) Emission spectra of PM605@ZIF-8_{AA} containing different wt% of PM605; (b) Emission spectra of PM605@ZIF-8_{AA} samples compared to PM605@ZIF-8_{ILAG} samples. For PM605 loadings of 0.05-1.5 wt% the AA samples in all cases were less emissive compared to their ILAG counterparts suggesting a better dispersion of PM605 via ILAG method.



Figure S6. Excitation spectra of (a) PM605@ZIF-8_{ILAG} and (b) PM605@ZIF-8_{AA} containing different wt% of PM605. Spectra were recorded from 300 to 580 nm monitoring the fluorescence emission at 600 nm in a well-plate reader.



Figure S7. UV-Vis diffuse reflectance spectra of (a) PM605@ZIF-8_{ILAG} containing different wt% of PM605; (b) PM605@ZIF-8_{AA} samples containing different wt% of PM605.



Figure S8. Fluorescence lifetimes of PM605@ZIF-8_{AA} samples containing different wt% of PM605. In contrast to PM605@ZIF-8_{ILAG} samples, the fluorescence lifetimes of PM605 are less sensitive to increasing loading of PM605 in ZIF-8 framework suggesting that fluorescence quenching in PM605@ZIF-8_{AA} at higher PM605 loadings could be static (formation of "trap sites") rather than dynamic (energy transfer).



Figure S9. PM6050.05@ZIF-8ILAG, PM6050.05@ZIF-8AA and free PM605+ZIF-8 samples and their corresponding dark controls in acetonitrile after the 100 min of irradiation. PM605@ZIF-samples (1 and 2) displayed similar amount of PM605 remained compared to their dark controls (4 and 5), while sample containing free PM605 in solution (3) was visibly photobleached compared to its dark control (6).



Figure S10. Integrated fluorescence intensity of PM605_{0.05}@ZIF-8_{ILAG} and PM605_{0.05}@ZIF-8_{AA} samples and free PM605 in acetonitrile monitored after different irradiation times (solid lines). The extent of PM605 degradation due to photobleaching can be estimated by comparing the fluorescence intensity obtained to that of dark control samples (dashed lines).



Figure S11. TGA thermogram of as-synthesized PM6050.05@ZIF-8ILAG, conducted in dynamic atmosphere of air.



Figure S12. TGA thermogram of as-synthesized PM605_{0.05}@ZIF-8_{AA}, conducted in dynamic atmosphere of air.



Figure S13. TGA thermogram of an unmodified sample of ZIF-8, conducted in dynamic atmosphere of air.



Figure S14. (a) N₂ sorption isotherm of as-synthesized PM6050.05@ZIF-8_{ILAG} (BET surface area 688 m²/g). (b) N₂ sorption isotherm of as-synthesized PM6050.05@ZIF-8_{AA} (BET surface area 791 m²/g).



Figure S15. N₂ sorption isotherm of ZIF-8 $_{ILAG}$ without PM605 (BET surface area 1738 m²/g).

3. References:

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