ZIF-8 encapsulation improves the antifungal activity of benzaldehyde and methyl anthranilate in biopolymeric films

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Supporting Information

ZIF-8 NPs characterization

Dynamic Light Scattering measurements

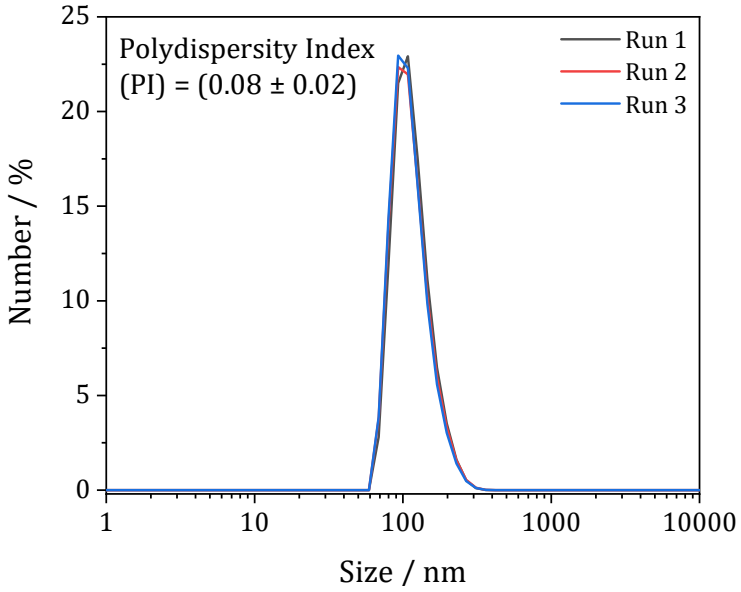

Figure S1: Hydrodynamic size of the pristine ZIF-8 nanoparticles in a methanol suspension.

Preparation of biomolecule@ZIF-8 composites

HPLC Calibration curves

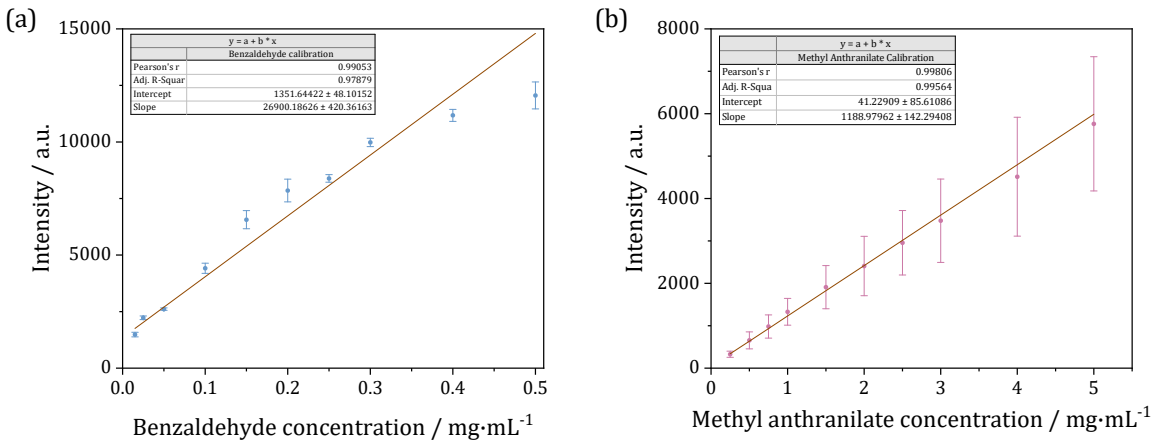

Figure S2. Calibration curves in acetonitrile of benzaldehyde (a) and methyl anthranilate (b). Statistics table is included in each graph.

Encapsulation kinetics

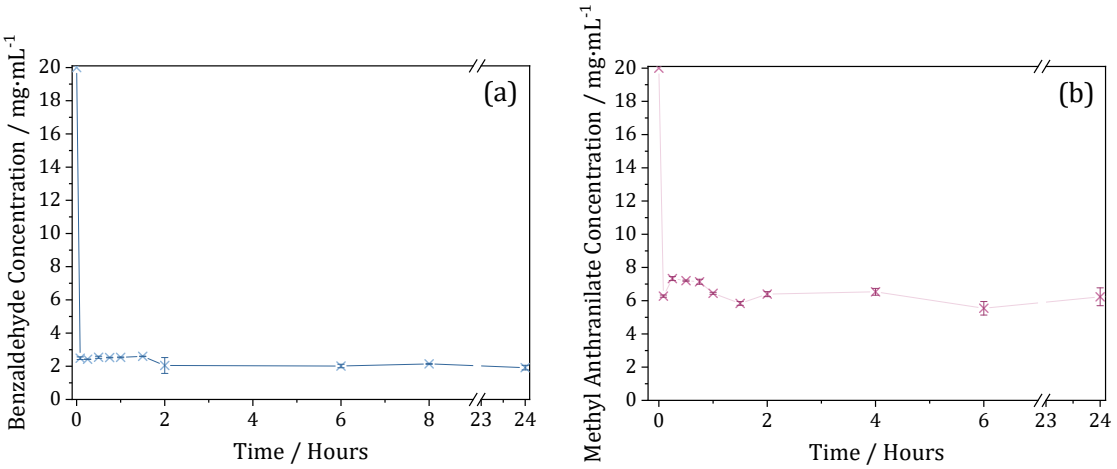

Figure S3. Benzaldehyde (a) and methyl anthranilate (b) concentration remanent in the encapsulation media after different encapsulation times quantified by means of HPLC

Characterization of biomolecule@ZIF-8 composites

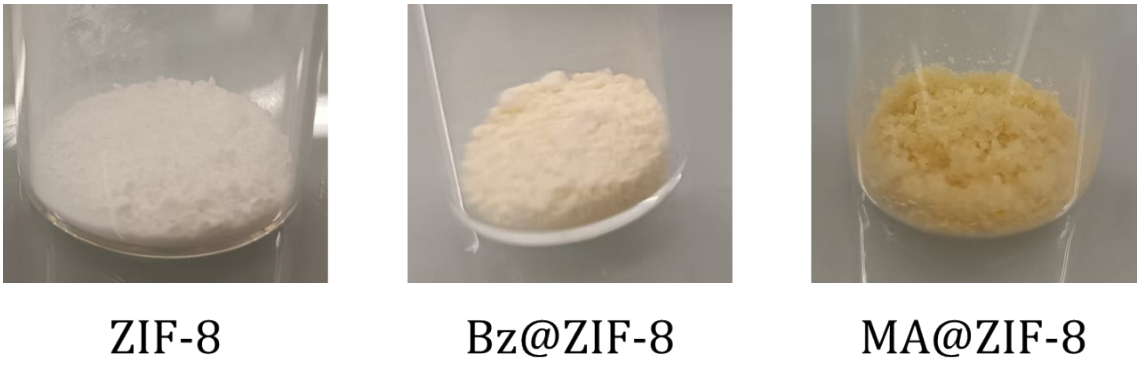

Figure S4. Image of the encapsulated materials, compared with pristine ZIF-8.

Infrared Spectroscopy

Table S1. Position and assignation of the principal bands of pristine ZIF-8 and the two active molecules employed in this study.

Compound	Band position / cm^{-1}	Assignation
ZIF-8	3135 and 2929	aromatic and aliphatic ν_{as}(C-H)
	1583	$\nu_{C=N}$
	1460–1309	skeletal vibration of the imidazolate ring
	1180 and 1146	aromatic ν_{C-N}
	995	δ_{C-N}
	760	δ_{C-H}
	420	ν_{Zn-N}
Benzaldehyde	3064	aromatic ν_{C-H}
	2816 and 2734	aldehyde-related ν_{C-H}
	1696	aldehyde $\nu_{C=O}$
	1595 and 1583	aromatic $\nu_{C=C}$
	1454	aldehyde δ_{C-H}
Methyl anthranilate	3479 and 3370	$\nu(NH_2)$
	2951	ν_{C-H}
	1612, 848 and 798	$\delta(NH_2)$
	1685	$\nu_{C=O}$
	1242	ν_{as}(CO-O)
	1098	ν_{as}(O-C-C)

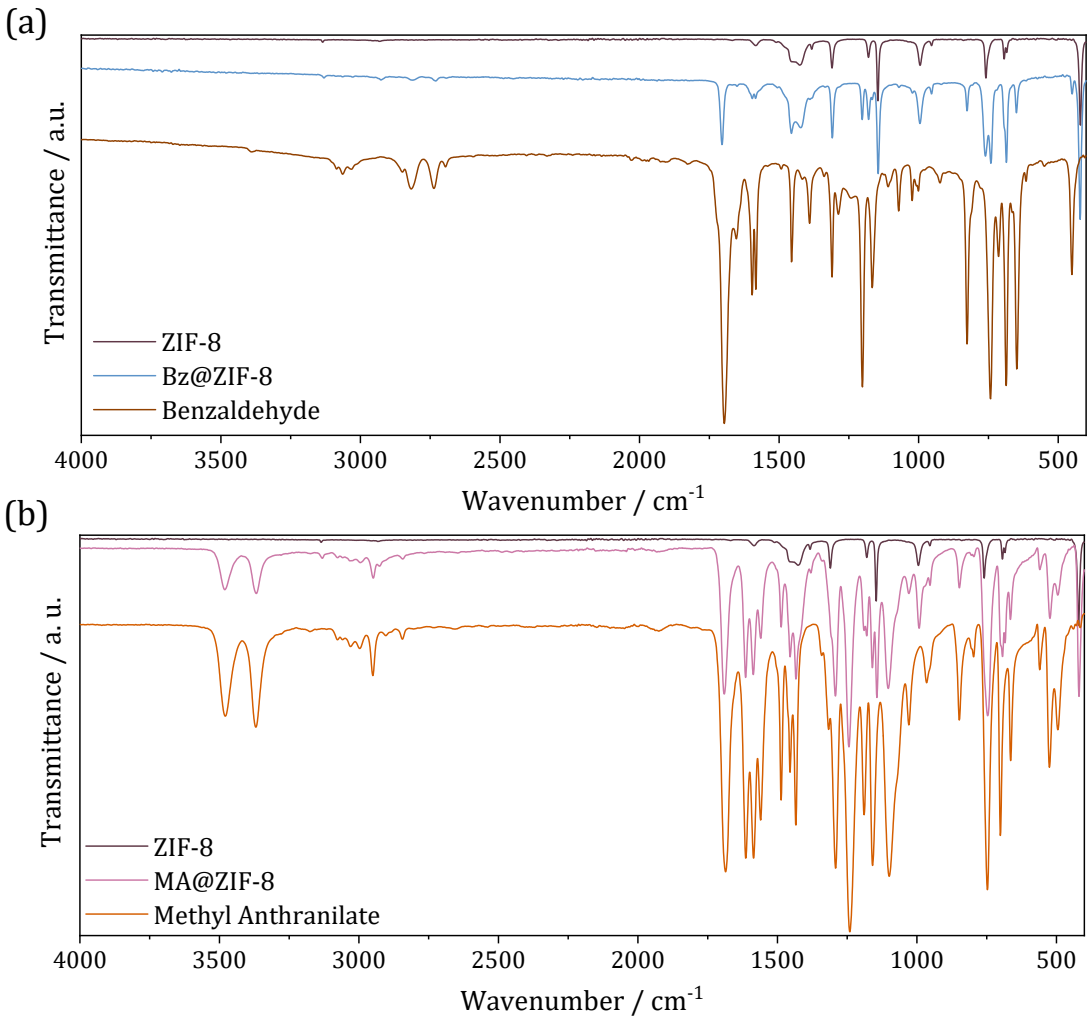

Figure S5. (a) FTIR spectra of Bz@ZIF-8 (blue) compared with ZIF-8 (purple) and benzaldehyde (yellow). (b) FTIR spectra MA@ZIF-8 (pink) compared with ZIF-8 (purple) and methyl anthranilate (orange).

Thermogravimetric analysis

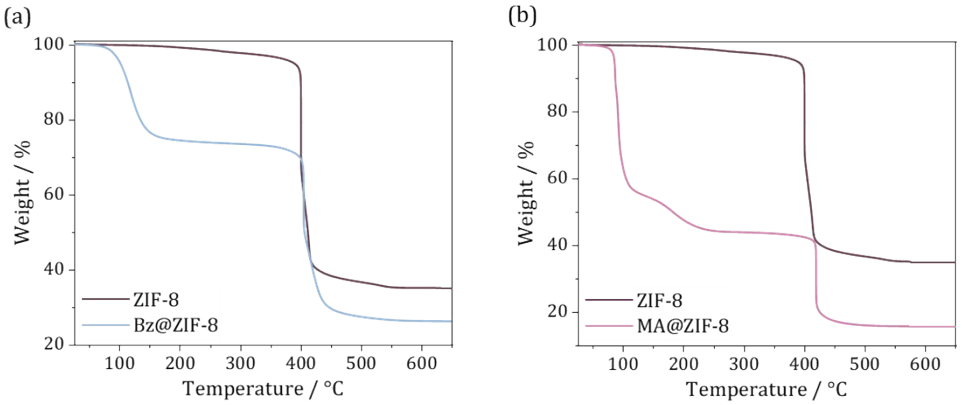

Figure S6. Thermogravimetric analysis of the obtained biomolecule@ZIF-8 composites compared with pristine ZIF-8 nanoparticles. To maximize solvent removal while retaining the active molecules, ZIF-8 NPs and Bz@ZIF-8 composite were pre-treated by heating at 100 °C for 3 hours, with an extended 16 hours for MA@ZIF-8 due to its gel nature.

Table S2. Summary of the ligand decomposition temperature, inorganic residue value and the estimated molecule loading for each material, as compared to the control empty ZIF-8 and related theoretical value (theo).

	Ligand decomp. T / °C	**Inorganic residue (D.B.) / % (w/w)**	**Loading / % (w/w)**
ZIF-8 (theo)	-	36.0	-
ZIF-8	405	36.1	-
Bz@ZIF-8	410	28.4	21.3
MA@ZIF-8	400	23.9	33.8

N_2 sorption isotherms at 77 K

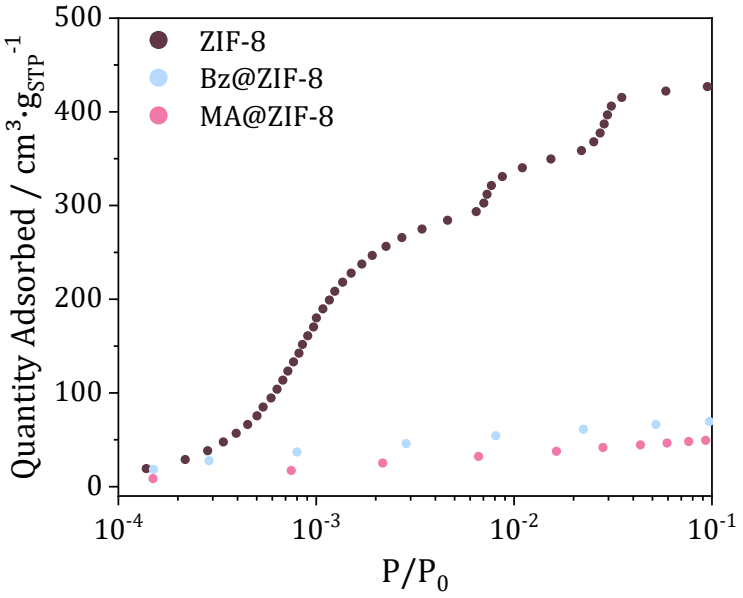

Figure S7. Logarithmic representation of N_2 adsorption isotherms at 77 K of Bz@ZIF-8 and MA@ZIF-8, compared with ZIF-8 in the micropore region.

***In vitro* evaluation of antifungal activity**

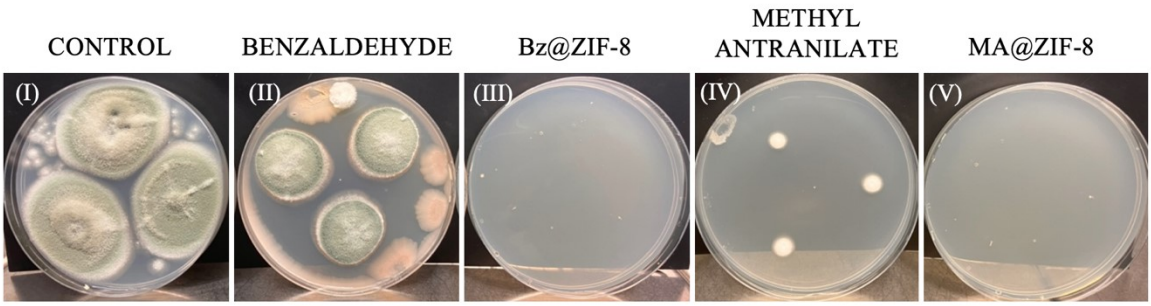

Figure S8. (a) Images of the microatmosphere test carried out to determine the activity of Bz@ZIF-8 and MA@ZIF-8 containing films against Penicilium expansum: images of the Petri dishes showing 3 droplets of the fungal suspension for control (I), free benzaldehyde (II), Bz@ZIF-8 composite (III), free methyl anthranilate (IV) and MA@ZIF-8 composite (V). The images correspond to 9 days of incubation.

Bz release kinetics

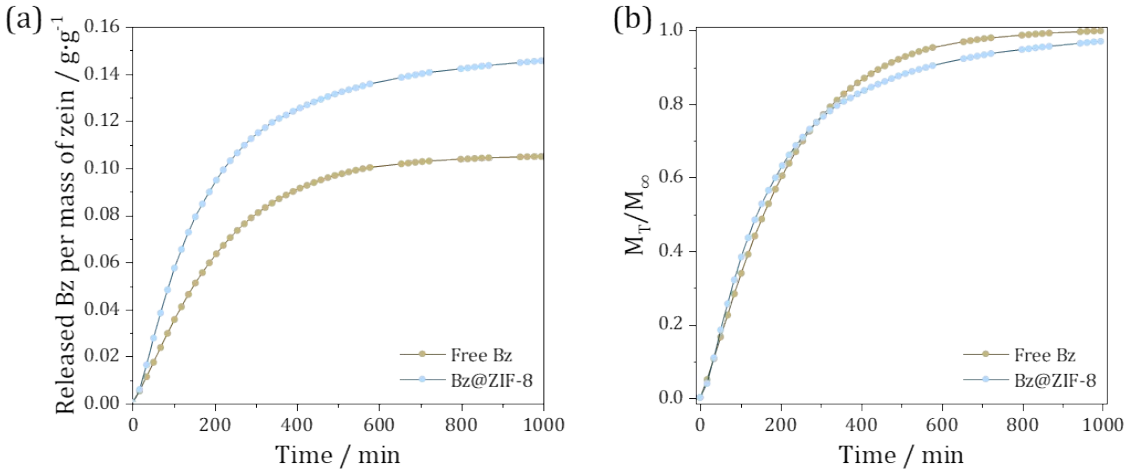

Figure S9. (a) Accumulated mass of Bz released over time for the studied films. (b) Ratio of mass release at time "t" vs the mass at infinite time. Lines and symbols in yellow correspond to film with free Bz, blue lines and symbols correspond to films with Bz@ZIF-8.