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Supplementary Information

for

Photonic Hybrid Crystals Constructed from In Situ Host-Guest Nanoconfinement of a Light-Emitting Complex in Metal-Organic Framework Pores

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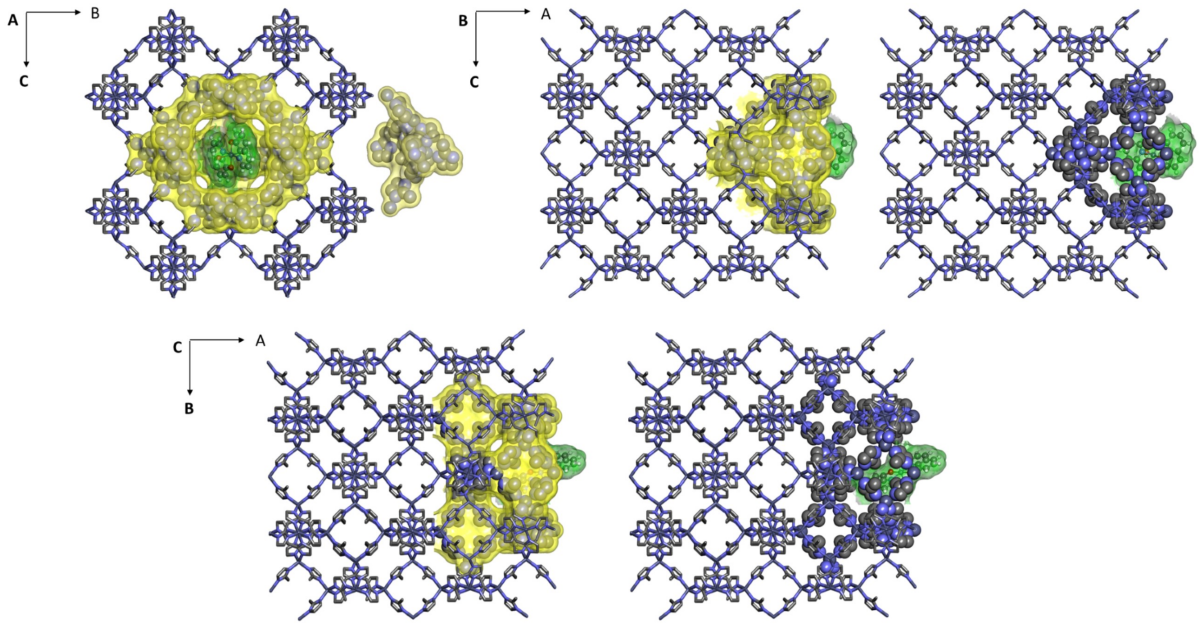

Figure S1. Structural representation of the cross-section of ZIF-8 internal void (yellow: van der Waals surfaces) and the proposed spatial nanoconfinement of a ZnQ guest complex (green: vdW surface of ZnQ), viewed along three crystallographic axes. For clarity, the corresponding figures to the right are depicted with vdW surface of only the ZnQ guest, and not for the host's void.

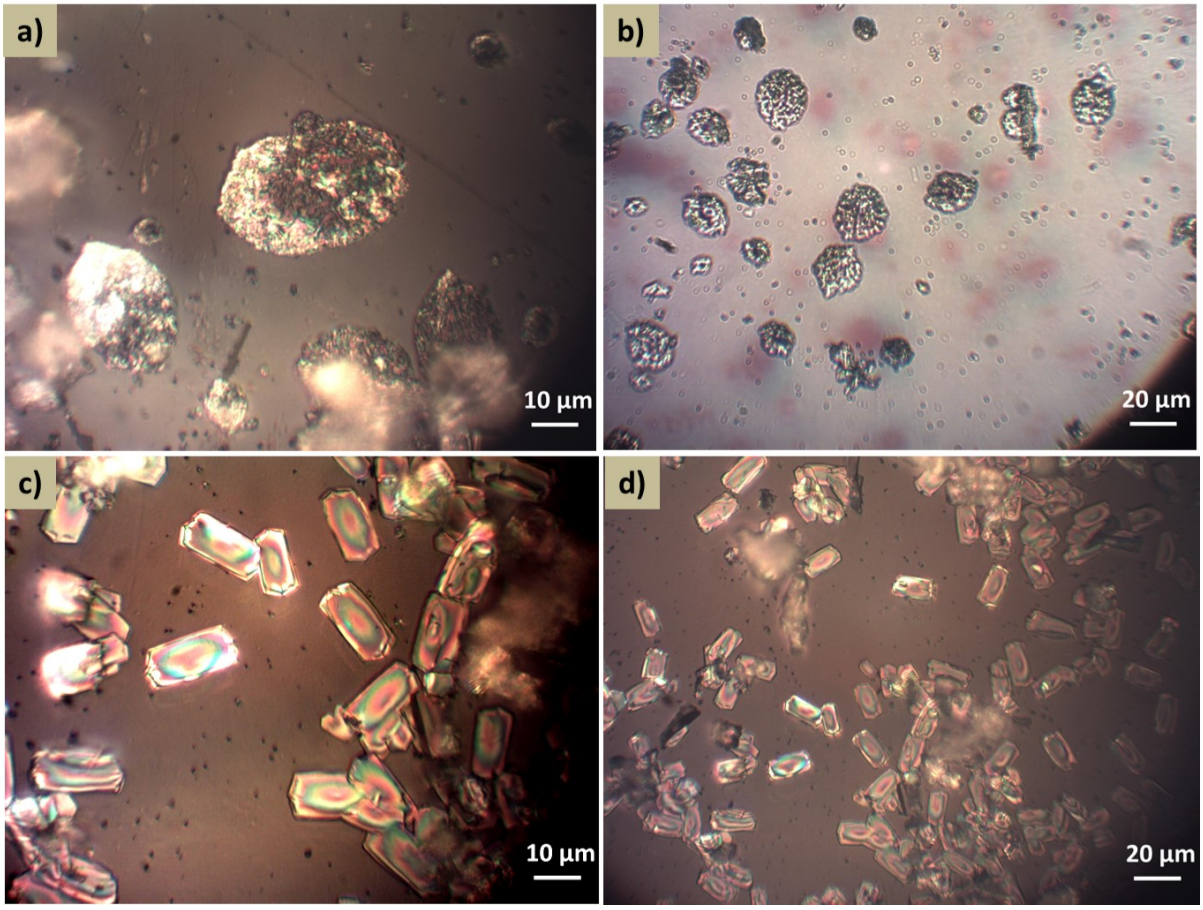

Figure S2. Optical images of a mixture of crystals obtained in the (sub-optimal) reactions **I** and **II** (c.f. Table 1 of main manuscript). (a-b) show partially-formed ZnQ hexagonal crystals whose crystal faces are decorated by small crystallites of other unknown side-products. (c-d) show hexagonal microplates of ZnQ complex obtained in the product mixture, which correspond to the 2-D hexagonal crystal morphology[1] identified in an isolated synthesis to yield phase pure ZnQ.

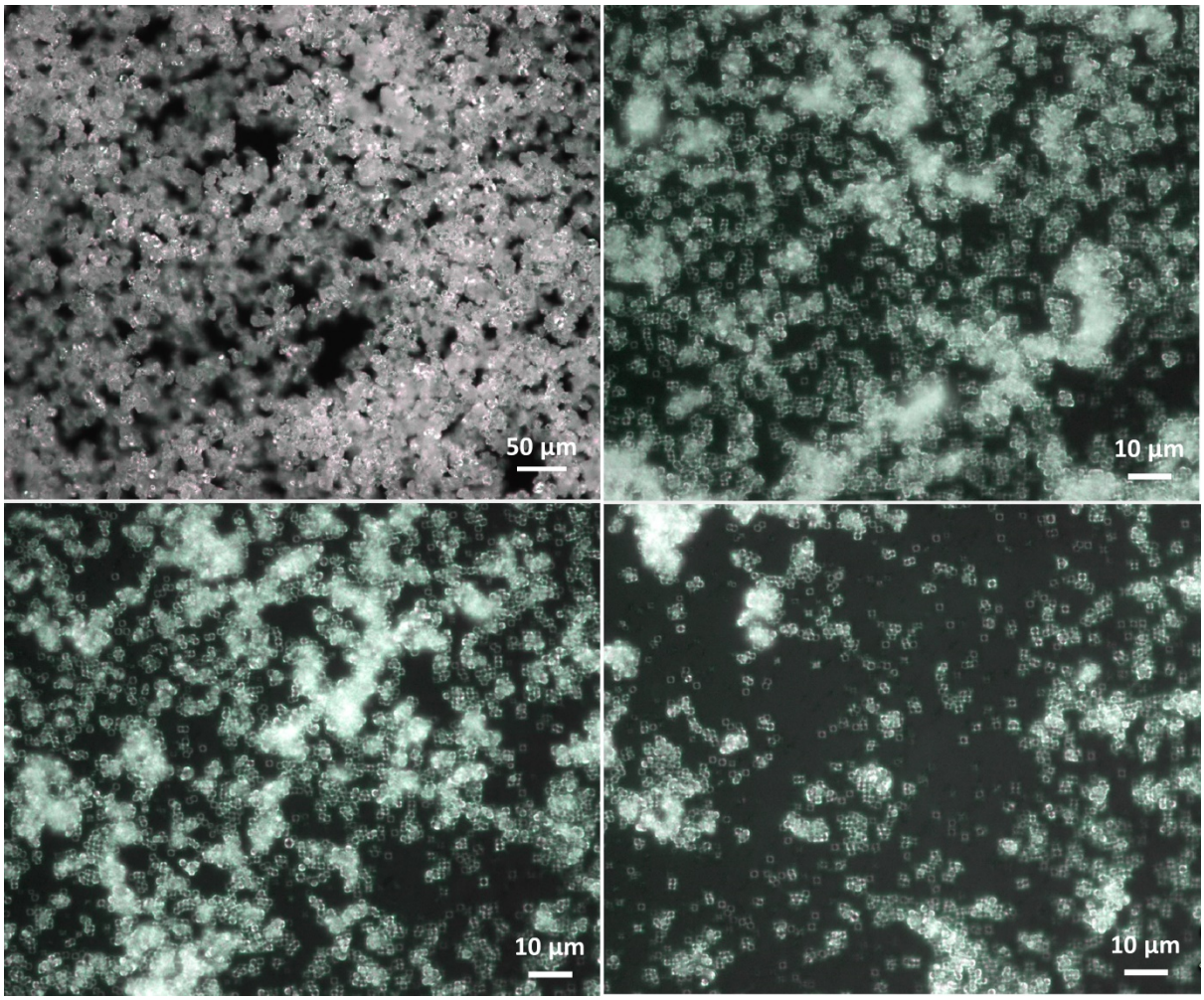

Figure S3. Optical microscopy images for **ZIF-8⊃ZnQ** hybrid host-guest compound obtained from the (optimal) reaction **IV**, yielding a phase pure product exhibiting uniform crystal size.

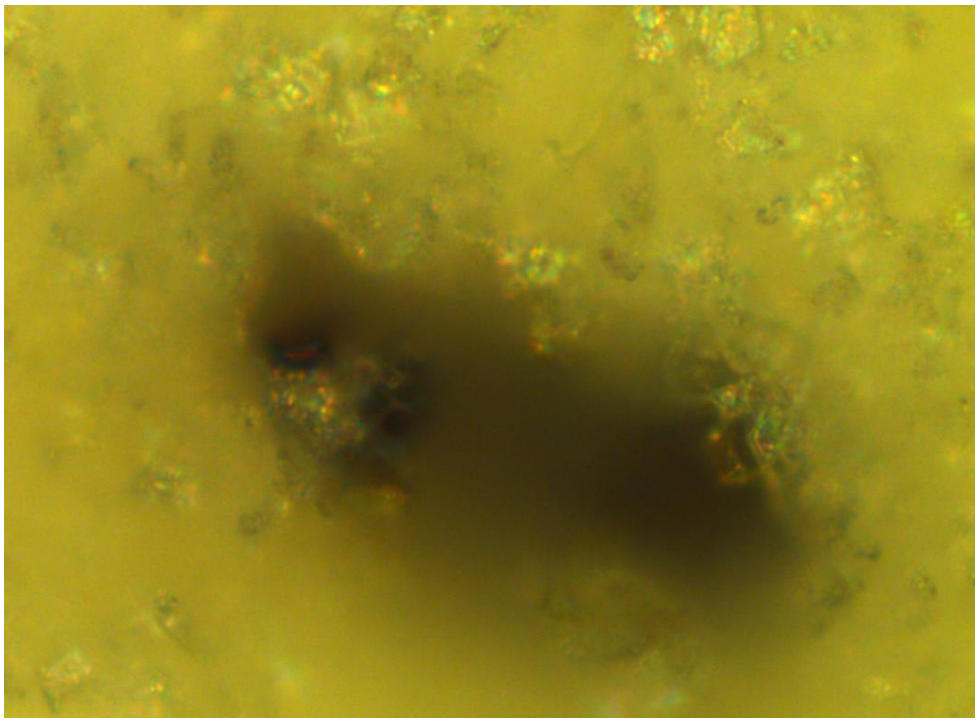

Figure S4. Darken middle region corresponding to the burnt sample of ZnQ (crystalline powder) under irradiation using 50 mW visible light at 532 nm using the Raman spectrometer laser source. The image size is approximately 100 µm across.

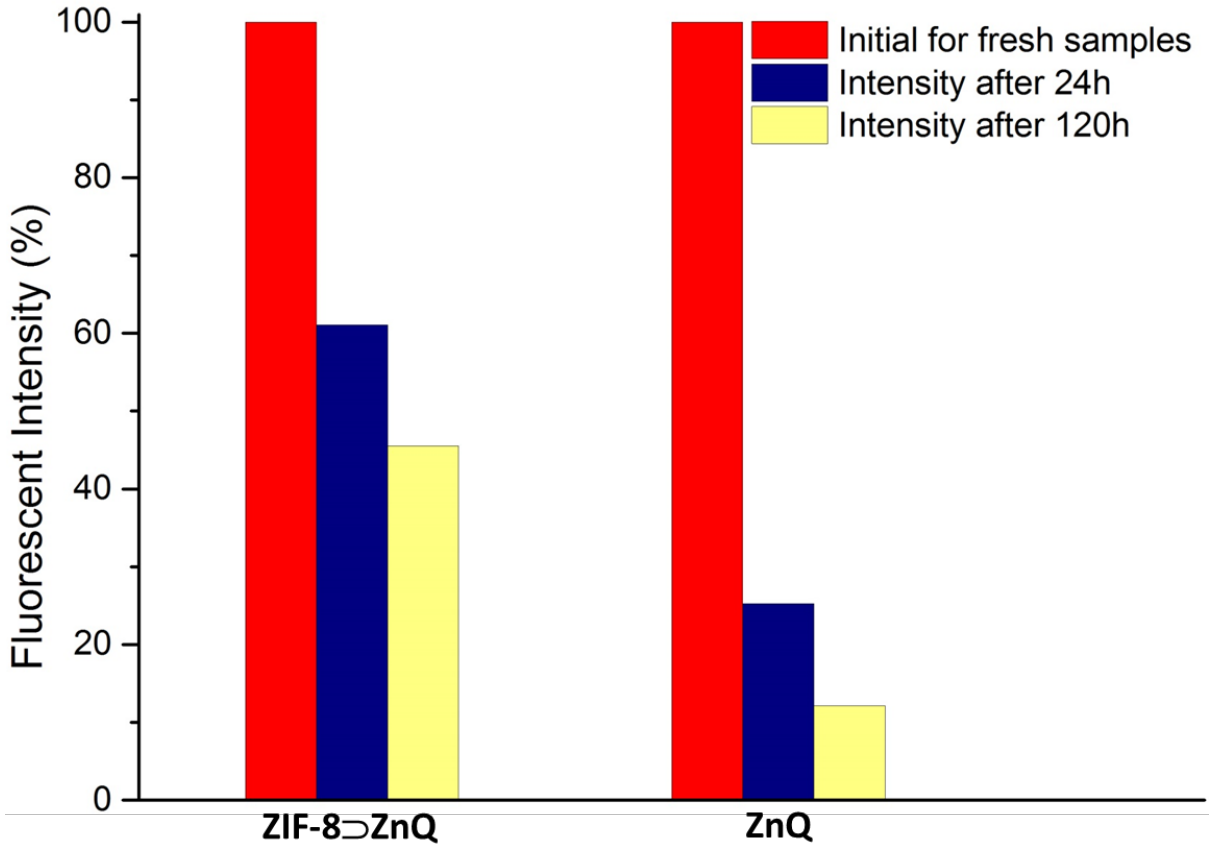

Figure S5. Emission intensity variation for the encapsulated form of ZnQ within ZIF-8 pores (ZIF-8⊃ZnQ host-guest system) compared against the pure ZnQ species after exposure to sunlight irradiation for a period of 5 days. Note that the intensity for each thin film sample was normalized to 100% of its initial emission, and the change in photostability was determined by monitoring the same two thin film samples. It is evident that the photostability of the ZnQ emitter when shielded by the ZIF-8 pores are at least twice more stable than the unprotected ZnQ species.

Molecular Orbital Energy Calculations

Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels for both species (i.e. ZIF-8 and ZnQ) were calculated considering 1x1x1 unit cell and a single molecule respectively, using the DMol3 density functional theory (DFT) code implemented in Accelrys Material Studio. The generalized-gradient approximation (GGA) exchange-correlation functional by Perdew and Wang, PW91, was adopted to determine the HOMO-LUMO band gaps (*cf*. Figure 5(a) of the main manuscript).

The calculation parameters used are listed below.

Task parameters
Scf_density_convergence : 1.000000e-006
Scf_charge_mixing :2.000000e-001
Scf_spin_mixing : 5.000000e-001
Scf_diis : 6 pulay
Scf_iterations : 50

Electronic parameters
Spin_polarization: unrestricted
Charge: 0
Basis: dnp
Pseudopotential: none
Functional: gga(p91)
Aux_density : octupole
Integration_grid : fine
Occupation : fermi
Cutoff_Global : 4.4000 angstrom

Calculated properties
Print_eigval_window : -1.d9
Plot : homo
Plot : lumo
Grid msbox 3 0.2500 0.2500 0.2500 3.0000

Reference:

1. Sun, Y. Q.; Lei, Y. L.; Gao, J.; Sun, X. H.; Lin, S. H.; Bao, Q. L.; Liao, Q.; Lee, S. T.; Liao, L. S., Two-Dimensional Optical Waveguiding and Luminescence Vapochromic Properties of 8-Hydroxyquinoline Zinc (Znq_2) Hexagonal Microsheets. *Chem. Commun.* **2014,** *50*, 10812-4.