

Supplementary information for

Crystalline organic monoliths with bicontinuous porosity

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1 Materials

All reagents were used as received unless otherwise noted. *P*-Terphenyl (TP) was purchased from FUJIFILM Wako Pure Chemical and purified by zone melting. Tetramethoxysilane, urea, acetic acid, tris(2-phenylpyridinato)iridium(III) (Ir(ppy)₃), purified by sublimation, hexadecyltrimethylammonium bromide (CTAB), were purchased from TCI. Polyethylene glycol (average Mn 8,500-11,500, flakes; PEG 10,000) was purchased from Sigma Aldrich. Sodium hydroxide was purchased from KISHIDA.

2 General characterization

UV-vis absorption spectra were recorded with a JASCO V-780 spectrophotometer. Photoluminescence spectra were measured with a JASCO FP-8300 spectrofluorometer. The absolute photoluminescence quantum yield was measured in an integrating sphere using a HAMAMATSU multichannel analyzer C10027-01. Time-resolved photoluminescence lifetime measurements were performed using a time-correlated single-photon counting lifetime spectroscopy system, HAMAMATSU Quantaaurus-Tau C11367-21, C11567-02, and M12977-01. Powder X-ray diffraction (PXRD) patterns were measured on a Bruker D2 Phaser (Cu-K α , 30kV, 10 mA). Dynamic light scattering (DLS) and zeta potential measurements were performed using a Malvern Nano-ZS ZEN3600. Scanning electron microscope (SEM) images were obtained using a JEOL JSM-IT700HR InTouchScope™ scanning electron microscope. Mean values and errors of wall width and pore size were estimated using ImageJ software from at least 50 randomly selected points from multiple SEM images. Thermogravimetric analysis (TGA) curves were recorded on Rigaku Thermo Plus EVO2 under N₂. N₂ adsorption isotherm measurements were performed on a Bel BELSORP-max. Samples were activated at room temperature (30°C) under a vacuum overnight prior to measurements. All samples for optical measurements were prepared in an Ar-filled glove box ([O₂] < 0.1 ppm) unless otherwise noted. When an aqueous system was used for optical measurements, 4 freeze-pump-thaw cycles were performed on the sample.

3 Sample preparation

3.1 Synthesis of silica monoliths

Silica monoliths were synthesized following the previous report.¹ 450 mg of urea and 575 mg of polyethylene glycol (MW: 10,000, PEG10,000) were added to 5 mL of aqueous acetic acid solution (10 mM). After complete dissolution, 2.5 mL of tetramethoxysilane (TMOS) was added to the solution in an ice bath and stirred until a transparent solution was obtained. After stirring for 90 minutes, the mixture was placed in a 30°C water bath for overnight gelation. The resulting gel was heated to 100°C for 4 hours. After cooling to room temperature, the resulting gels were washed five times with water and then three times with water/ethanol=2/1. After natural drying by evaporation, the gels were calcined at 600°C for 5 hours to obtain white monolithic gels. The macropore structure was controlled by varying the amount of PEG10,000 at 500, 550, and 575 mg.

3.2 Synthesis of TP-based crystalline organic monoliths (TP-COMs)

10 mg of silica monoliths and 100 mg of *p*-terphenyl (TP) were placed in a glass tube. The glass tube was flame-sealed under reduced pressure. The resulting sample was heated to 230°C, which is above the melting point of TP, to introduce the TP melt into the pore of the silica monoliths for 1 hour. After natural cooling to room temperature, the excess TP was removed using a cutter knife. Most of the excess TP was not attached to the silica monoliths and peeled off on its own, while some TP was attached to the monoliths. TP-loaded monoliths were very hard and could not be cut at all with a cutter knife, while the excess TP could be easily removed with a cutter knife. SEM images of TP-loaded silica monoliths showed both nano-sized interconnected silica particles and micro-sized angular TP crystals (Fig. S2). The resulting composite was immersed in 1 M of aqueous NaOH solution for 1 week to dissolve the silica. After washing with water 3 times, the resulting monoliths were dried under reduced pressure to obtain the TP-COMs.

3.3 Preparation of Ir(ppy)₃ modified TP-COMs

3.64 mg of CTAB (0.01 mmol) was dissolved in 1 mL of water to give a 10 mM aqueous CTAB solution. Next, 25 µL of 2 mM Ir(ppy)₃ in THF solution was added to the aqueous CTAB solution. The mixture was stirred overnight in the dark to remove volatile THF. The resulting mixture was filtered through 0.45 µm PTFE filters to obtain a transparent solution. A piece of TP-COMs (~3 mg) was soaked in Ir(ppy)₃ micellar solution (~300 µL). After 2 hours, the supernatant was removed and washed 3 times with ~300 µL of water, followed by vacuum drying to obtain the Ir(ppy)₃ modified TP-COMs.

4 Supporting figure and table

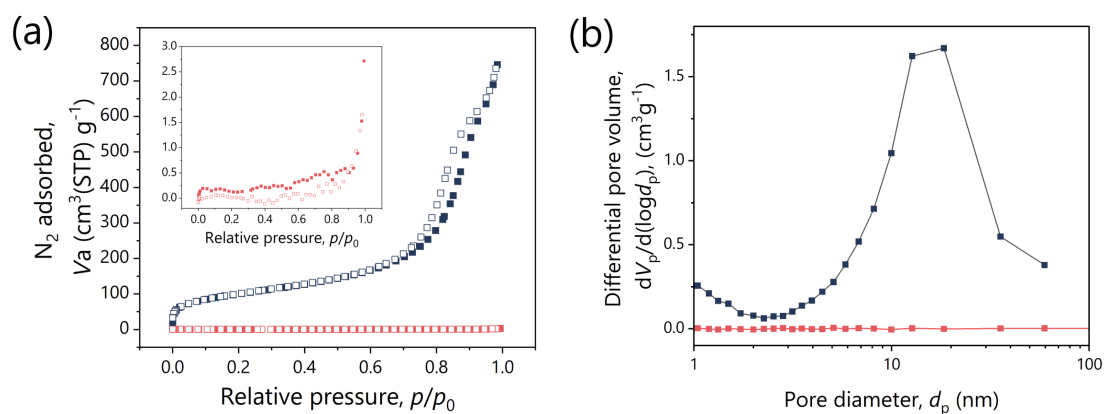


Fig. S1. (a) N₂ adsorption isotherms of silica monoliths (black) and TP-COMs (red). (b) Pore size distributions of silica monoliths (black) and TP-COMs (red) estimated by the BJH method.

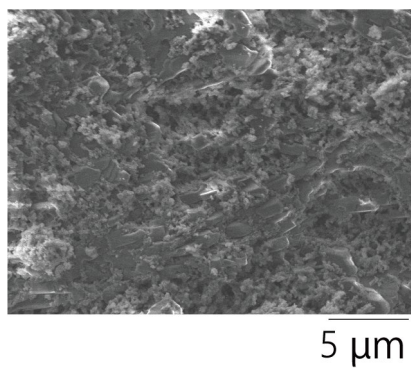


Fig. S2. SEM image of TP-loaded silica monoliths.

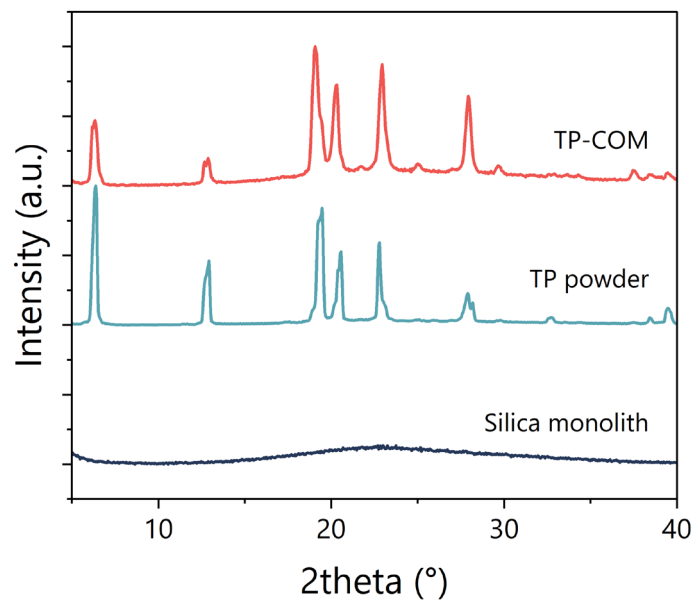


Fig. S3. PXR D patterns of silica monolith (black), TP powder (blue), and TP-COMs (red). TP powder crystallized very slowly by zone melting, whereas TP-COMs crystallized more rapidly because it was prepared by natural cooling from the melt. This difference in crystallization process may have changed the domain size and crystallinity of the crystals.

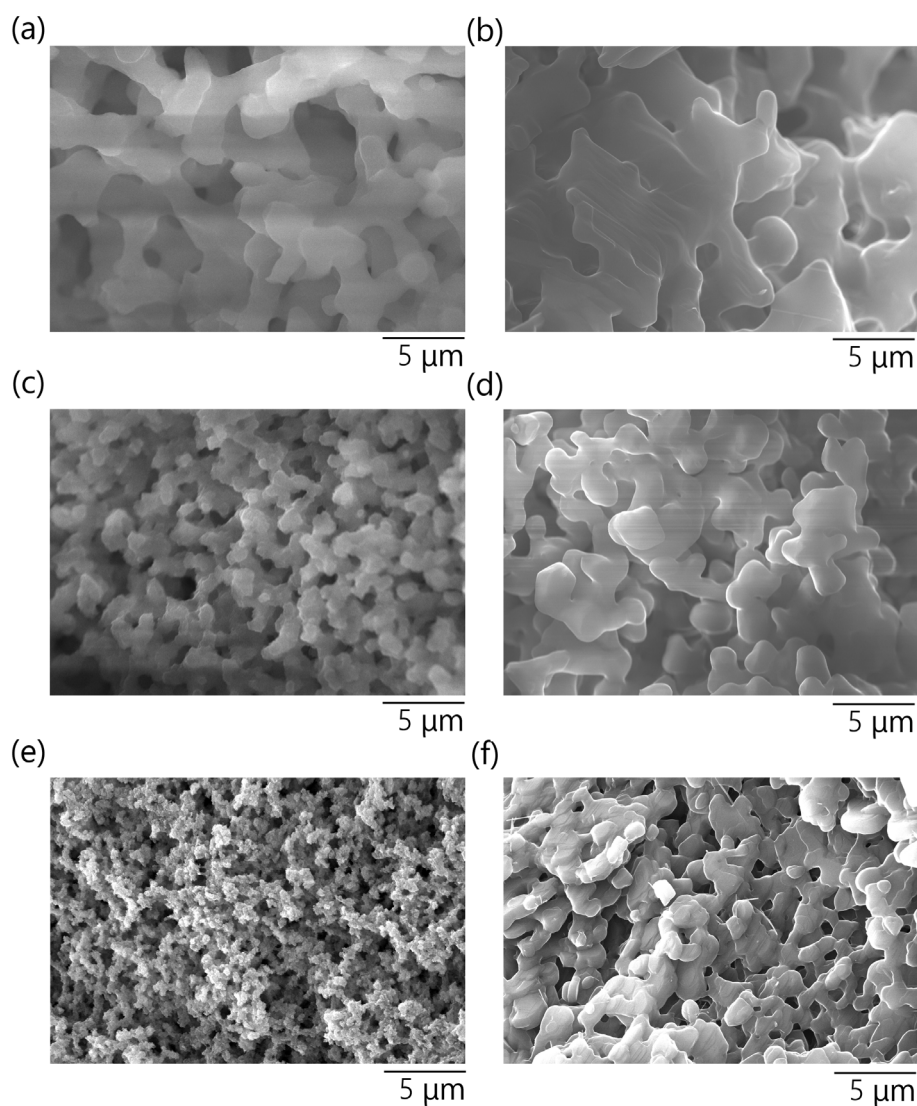


Fig. S4. SEM images of silica monoliths and TP-COMs. (a) Silica monoliths with 500 mg of PEG 10,000, (b) TP-COMs with silica monoliths the 500 mg of PEG10,000, (c) silica monoliths with 550 mg of PEG10,000, (d) TP-COMs used silica monoliths with 550 mg of PEG10,000, (e) silica monoliths with 575 mg of PEG10,000, (b) TP-COMs used silica monoliths with 575 mg of PEG 10,000.

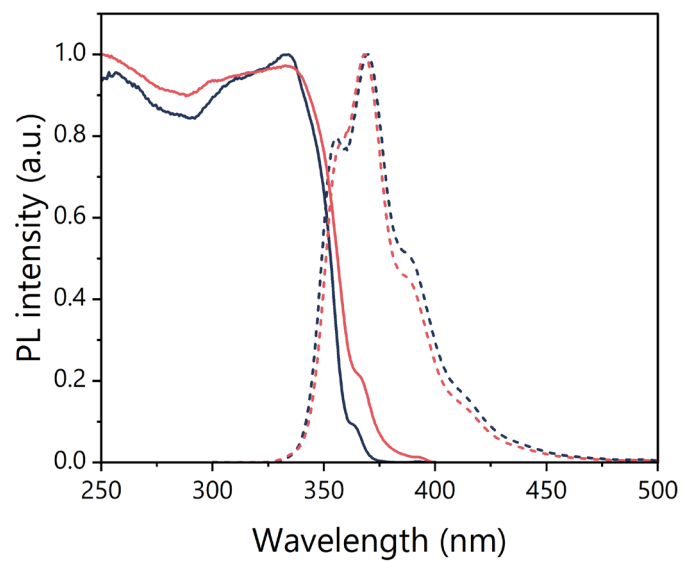


Fig. S5. Excitation (solid line) and fluorescence spectra (dotted line) of TP powder (black) and COMs (red). The emission wavelength was 420 nm, and the excitation wavelength was 280 nm.

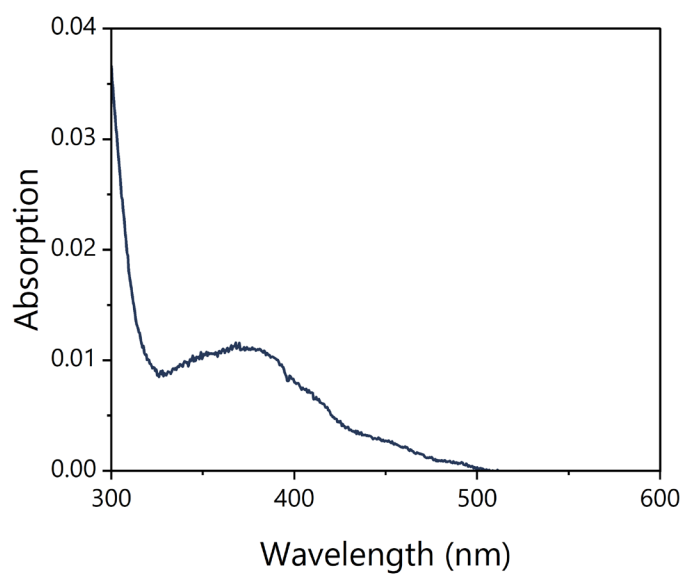


Fig. S6. UV-vis absorption spectrum of Ir(ppy)₃ micelles.

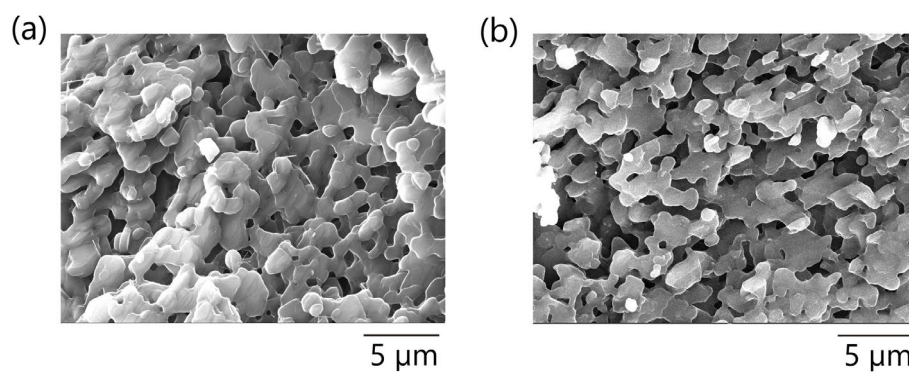


Fig. S7. SEM images of TP-COMs (a) before and (b) after immersion in Ir(ppy)₃ micelles.

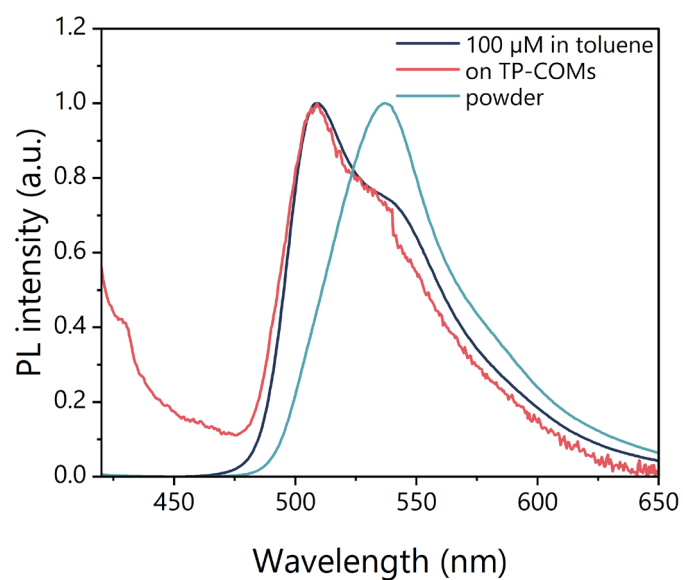


Fig. S8. Photoluminescence spectra of Ir(ppy)₃ 100 μM in toluene (black), on the surface of TP-COMs (red) and powder (blue).

Table S1. Photoluminescence lifetime and triplet energy transfer efficiency of Ir(ppy)₃ on the surface of TP-COMs using toluene solution as a reference. The photoluminescence lifetime was fitted by the following equations.

$$A(t) = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right) + C$$

where A is the excited state concentration, t is the time, and τ is the decay time constant. The triplet energy transfer efficiency was calculated using the following equations.

$$\Phi_{ET} = 1 - \frac{\tau}{\tau_0}$$

where Φ_{ET} is the triplet energy transfer efficiency, τ is the photoluminescence lifetime of Ir(ppy)₃ on the surface of the TP-COMs, and τ_0 is the lifetime of Ir(ppy)₃ in toluene.

	A_1	τ_1	A_2	τ_2	τ (τ_0)	Φ_{ET}
On TP-COMs	4,680	0.376	18.0	2.01	0.38	-
In toluene	3,540	1.30	-	-	1.30	70.6%

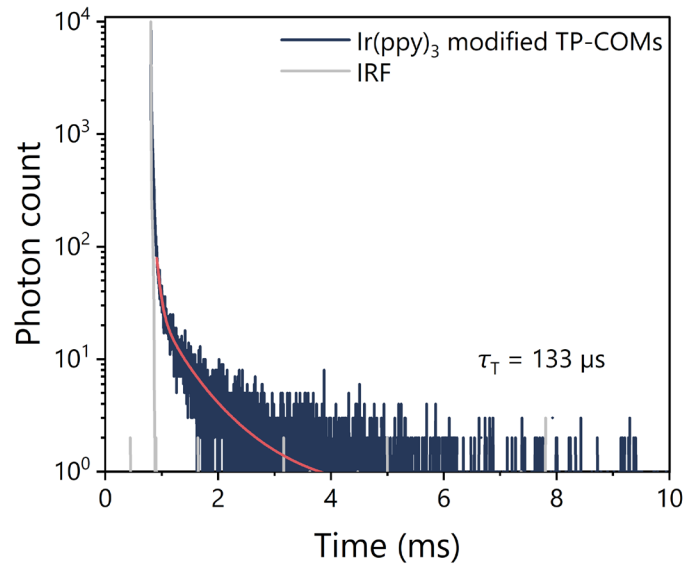


Fig. S9. UCPL decay of Ir(ppy)₃ modified TP-COMs (black) and fitted line (red). The instrument response function (IRF) is shown in gray. Fitting was performed using the following equations.²

$$A(t) = \left(A_1 \frac{1 - \beta_1}{\exp(t/\tau_1) - \beta_1}\right)^2 + \left(A_2 \frac{1 - \beta_2}{\exp(t/\tau_2) - \beta_2}\right)^2 + C$$

where A is the triplet concentration, t is the time, and β is the dimensionless parameter indicating the TTA efficiency ($0 < \beta < 1$). τ_T was estimated by averaging these two components from the resulting parameters $A_1 = 51,400$, $\beta_1 = 0.670$, $\tau_1 = 0.117$, $A_2 = 391$, $\beta_2 = 0.993$, and $\tau_2 = 2.26$, respectively.

References

1. K. Nakanishi, H. Shikata, N. Ishizuka, N. Koheiya and N. Soga, *J. High Resolut. Chromatogr.*, 2000, **23**, 106-110.
2. A. Olesund, V. Gray, J. Mårtensson and B. Albinsson, *J. Am. Chem. Soc.*, 2021, **143**, 5745-5754.