Electronic Supplementary Information

Bicyclo[2.2.2]octane-1,4-dicarboxylic acid: Towards Transparent Metal-Organic Frameworks.

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S1. General Conditions

Starting materials, if commercially available, were purchased and used as such. *N*,*N*-dimethylformamide (DMF), *N*,*N*-diethylformamide (DEF) and *N*,*N*-dibuthylformamide (DBF) were distilled before using. All reagent solutions were filtered through a 0.45 μ m PTFE 25mm Syringe Filter. IR spectra were recorded using FT-IR ATR. Microscopic images were taken using Stereoscopic Microscope LEICA M165 FC and Fluorescence Optical Microscope LEICA DM IRBE. DRX powder spectra were performed on a BRUKER AXS D5005 powder diffractometer (Cu radiation, 40 kV, 30 mA, 0.05 steps, 6 s). Single-crystal X-ray diffraction (SXRD) data were collected on a Xcalibur diffractometer (Agilent Technologies, Sapphire 3 CCD detector) using a single wavelength X-ray source with MoK α radiation, $\lambda = 0.71073$ Å and also in a Bruker-Nonius Kappa CCD using a single wavelength X-ray source with MoK α radiation, $\lambda = 0.71073$ Å, and the data reduction was performed with Denzo software.¹ Diffuse Reflectance spectra were performed using an Agilent Technologies CARI60 UV-VIS Spectrometer and a Harrick Video-Barrelino Diffuse Reflection Probe. Elemental analyses were performed in a CE Instruments EA 1110 CHNS. Fluorescence lifetimes were recording with a HAMAMATSU Quantaurus-Tou compact fluorescence lifetime spectrometer C11367

S2. Detailed Synthesis Conditions

Different conditions were applied in order to see differences in the final TMOF structure.

TMOF was obtained using DMF as solvent, at 80°C or 95°C and also using DEF at 80°C. Using DEF at higher temperatures, DBF or DMF at 116°C gave mixtures of amorphous **TMOF2** and **TMOF3**.

Obtained MO	Temperature	Time	Solvent	[Zn(NO ₃) ₂ ·6H ₂ O]	[2]
тмог	80 ºC	72h	DMF	100 mM	40 mM
TIMOF	95 ºC	72h	DMF	100 mM	40 mM
TMOF3	116 ºC	72h	DMF	100 mM	40 mM
TMOF	80 ºC	72h	DEF	100 mM	40 mM
TMOF2	95 ºC	72h	DEF	100 mM	40 mM
TMOF2	116 ºC	72h	DEF	100 mM	40 mM
TIMOF3	80 ºC	72h	DBF	100 mM	40 mM
]	95 ºC	72h	DBF	100 mM	40 mM

The overall yield was around 55±10%.

S3. Single Crystal X-ray Diffraction Analyses

Single-crystal X-ray diffraction (SXRD) data for **TMOF, TMOF2** and **TMOF3** were collected on a Xcalibur diffractometer (Agilent Technologies, Sapphire 3 CCD detector) using a single wavelength X-ray source with MoK α radiation, $\lambda = 0.71073$ Å. **Pyrene@TMOF** crystals data was collected in a Bruker-Nonius Kappa CCD using a single wavelength X-ray source with MoK α radiation, $\lambda = 0.71073$ Å, and the data reduction was performed with Denzo software.

The selected single crystals were mounted using Paratone-N hydrocarbon oil² on the top of a loop fixed on a goniometer head and immediately transferred to the diffractometer. Pre-experiment, data collection, analytical

absorption correction, and data reduction were performed with the Oxford program suite CrysAlisPro.³ Empirical absorption correction was applied using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. The data collection was performed at 120(1) K in all cases.

The crystal structures were solved with $SHELXT^4$, using direct methods and were refined by full-matrix least-squares methods on F^2 with SHELXL2014. All programs used during the crystal structure determination process are included in the OLEX2 software.⁵

The program PLATON⁶ was used to check the results of the X-ray analyses. The electron densities corresponding to the disordered guest molecules of **TMOF2 and Pyrene@TMOF** were flattened using 'SQUEEZE'⁷ option of PLATON. The crystallographic details of both the MOFs are summarized in Table S2. CCDC 1532005-1532008 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

	TMOF	TMOF2	TMOF3	Pyrene@TMOF
Empirical	$C_{46}H_{62}N_2$	$C_{45}H_{69}$	$C_{10}H_{13.50}$	$C_{46}H_{62}N_2$
formula	O ₁₈ Zn ₄	$N_3O_{16}Zn_4$	O _{4.75} Zn	O ₁₈ Zn ₄
Formula weight	1192.45	1169.51	275.08	1192.45
Temperature/K	120.0(1)	120.0(1)	120.0(1)	120.0(1)
Crystal system	monoclinic	trigonal	monoclinic	monoclinic
Space group	P2/n	P3 ₁ 21	I2/a	C2/c
a/Å	6.1341(4)	12.7557(5)	6.1355(4)	6.1210(2)
b/Å	19.5931(11)	12.7557(5)	13.0213(7)	19.5910(9)
c/Å	19.6981(13)	30.6370(8)	14.8255(7)	19.6970(7)
α/°	90	90	90	90
β/°	90.564(6)	90	91.798(5)	90.675(2)
γ/°	90	120	90	90
Volume/Å ³	2367.3(3)	4317.1(3)	1183.86(12)	2361.83(16)
Z	2	3	4	2
$\rho_{calc}g/cm^3$	1.673	1.35	1.535	1.677
µ/mm⁻¹	2.081	1.708	2.074	2.086
F(000)	1232	1824.0	560.0	1232
20 range	6.23 to 50	6.38 to 50	7.34 to 52	4.14 to 50
Radiation		0.71073		
Refl. collected	8680	12519	2838	3902
Independent refl.	4127	5078	1166	2078
R _{int}	0.0698	0.0387	0.0391	0.0266
restraints/param	313/416	323/385	6/110	177/200
GOF	1.069	1.064	1.069	1.076
$\mathbf{P} = \mathbf{W} \mathbf{P} \left[\mathbf{I} \mathbf{y} = 2 \sigma \left(\mathbf{I} \right) \right]$	0.0753,	0.0636,	0.0385,	0.0576,
n ₁ , wn ₂ [ιν-20 (ι)]	0.1989	0.1646	0.0925	0.1671
R. wR.[all data]	0.0945,	0.0758,	0.0432,	0.0638,
\mathbf{n}_1 , $\mathbf{w}\mathbf{n}_2$ [all Gata]	0.2227	0.1745	0.0975	0.1747

Table S2. Crystal data and structure refinement for TMOF, TMOF2, TMOF3 and Pyrene@TMOF.

TMOF

A colourless, block crystal (0.38 x 0.14 x 0.14 mm) of $[Zn(C_{10}H_{12}O_4)]_4$ ·2DMF, was measured at 120(1) K using MoK α radiation, $\lambda = 0.71073$ Å.

The structure was solved by direct methods with SHELXT and was refined with SHELXL in the monoclinic space group P2/n with Z = 2.

The crystal structure exhibits a three-dimensional framework with wide open channels of approximately 4.4×4.1 Å running along the crystallographic *a* axis. Most of the structure is disordered over two sets of positions since it lies about several symmetry elements, inversion centres, two-fold axes and mirror planes.

Some SHELXL restraints (SADI, RIGU) had to be used to correct the geometry of the disordered parts and the thermal parameters of the corresponding atoms. Hydrogen positions were calculated after each cycle of refinement using a riding model, with C-H = 0.97 Å and Uiso(H) = 1.2Ueq(C). The presence of solvent molecules could easily be seen by the residual peaks located in the open channels. There are two different DMF molecules with an occupancy of 0.5 each one.

One of the 1,4-bicyclo[2.2.2]octane-1,4-dicarboxylic acid units is disordered with two different positions for the carbon atoms of the cycle due to a rotation around its central axis and has been modelled with an occupancy of 0.5 for each carbon atom.

The final refinement was conducted with the reflection data within a 0.80 Å resolution limit, a total of 8680 reflections of which 4127 were independent and 3006 were greater than $2\sigma(I)$. Final full matrix least-squares refinement on *F*2 converged to *R*1 = 0.0753 and *wR*2 = 0.2227 (*I*> $2\sigma(I)$) with GOF = 1.069. Crystallographic data and additional details of data collection and refinement are summarized in Table S2. Drawings with atomic labels are represented in Figure S1.



Figure S1. The asymmetric unit present in crystalline **TMOF** with all non–hydrogen atoms represented by thermal ellipsoids drawn at the 50% probability level. All hydrogen atoms were omitted for clarity.

TMOF2

A colourless, hexagonal crystal (0.7 x 0.4 x 0.4 mm) of $[Zn_4O(C_{10}H_{12}O_4)_3(DEF)_2]$ ·3DEF was measured at 120(1) K using MoK α radiation, $\lambda = 0.71073$ Å.

The structure was solved by direct methods with SHELXT and was refined with the SHELXL software package (S3), crystallized in the trigonal P3121 space group with Z = 3.

The crystal structure exhibits a three-dimensional framework with wide open channels of approximately $13.2 \times 6.1 \text{ Å}^8$ running along the crystallographic *a* and *b* axis, and also along the bisection of both axis. Most of the structure is disordered over two sets of positions since it lies about several symmetry elements.

One of the 1,4-bicyclo[2.2.2]octane-1,4-dicarboxylic acid units is disordered with two different positions. These units also have to different positions for the carbon atoms of the cycles due to a rotation around its central axis. They have been modelled with occupancy of 0.5 for each carbon atom. The oxygen atoms (O3 and O4) of the carboxylate group have occupancy of 0.5.

One of the Zinc atoms (Zn2) is coordinated with two different disordered DEF molecules with occupancy of 0.5. The Zn2 is penta-coordinated by three oxygen atoms of three different carboxylate groups, the oxygen of the Zn cluster and the fifth position corresponds to an oxygen atom of a DEF molecule. This DEF has two different positions with an occupancy of 0.5.

Some soft *SHELXL* restraints (*ISOR*, *SADI*, *RIGU*) had to be used to correct the geometry of the disordered parts and the thermal parameters of the corresponding atoms. Hydrogen positions were calculated after each cycle of refinement using a riding model, with C-H = 0.93 Å and Uiso(H) = 1.2Ueq(C) for aromatic H atoms, and with C-H = 0.97 Å and Uiso(H) = 1.2Ueq(C) for methyl H atoms.

The presence of solvent molecules in the channels could easily be seen by the residual peaks located in the open channels. Unfortunately, it could not be modelled even with restraints (without solvent molecules: R1 = 0.0736 for 2492 reflections of $I > 2\sigma(I)$ and wR2 = 0.2073 for all data). Consequently, SQUEEZE (from PLATON) was used to calculate the void space, the electron count and to get a new *HKL* file (With SQUEEZE: R1 = 0.0651 for 2492 reflections of $I > 2\sigma(I)$ and wR2 = 0.2 for all data). According to the SQUEEZE results and the different experimental evidences (see manuscript), a total number of 1 *N*,*N*-diethylformamide (DEF) solvent molecules (electronic density per unit cell = 137 electrons) could be placed in each of the three calculated voids (310 Å³, 311 Å³, 312 Å³) per unit cell.

Crystallographic data and additional details of data collection and refinement are summarized in Table S2. Drawings with atomic labels are represented in Figure S2.



Figure S2. The building block including the asymmetric unit present in crystalline TMOF2 with all non-hydrogen atoms represented by thermal ellipsoids drawn at the 50% probability level. All hydrogen atoms were omitted for clarity.

TMOF3

A colourless, laminar crystal (0.29 × 0.13 × 0.09mm) of $[Zn(C_{10}H_{12}O_4)]$ ·0.75H₂O, was measured at 120(1) K using MoK α radiation, $\lambda = 0.71073$ Å.

The structure was solved by direct methods with SHELXT and was refined with the SHELXL software package (S3), in the monoclinic space group I2/a with Z = 4.

The crystal structure exhibits a three-dimensional framework with wide open channels of approximately 3.7×3.7 Å running along the crystallographic *a* axis.

All hydrogen positions were calculated after each cycle of refinement using a riding model, with C-H = 0.97 Å and Uiso(H) = 1.2Ueq(C). The presence of solvent molecules could easily be seen by the residual peaks located in the open channels. There are two water molecules placed in the middle of the channels with occupancy of 0.125 and 0.25. The hydrogen atoms of the water molecules have not been located.

The 1,4-bicyclo[2.2.2]octane-1,4-dicarboxylic acid is disordered with two different positions for the carbon atoms of the cycle due to a rotation around its central axis. They have been modelled with occupancy of 0.5 for each carbon atom.

The final refinement was conducted with the reflection data within a $\theta_{max} = 26.0^{\circ}$ resolution limit, a total of 2838 reflections of which 1166 were independent and 1055 were greater than $2\sigma(I)$. Final full matrix least-squares refinement on F^2 converged to R1 = 0.0385 and wR2 = 0.0975 with GOF = 1.069. Crystallographic data and additional details of data collection and refinement are summarized in Table S2. Drawings with atomic labels are represented in Figure S3.



Figure S3. The building block including the asymmetric unit present in crystalline **TMOF3** with all non–hydrogen atoms represented by thermal ellipsoids drawn at the 50% probability level. All hydrogen atoms were omitted for clarity.

Pyrene@TMOF

A colorless, block crystal (0.4 × 0.2 × 0.2mm) of $[Zn(C_{10}H_{12}O_4)]_4$ ·2DMF, was measured at 120(1) K using MoK α radiation, $\lambda = 0.71073$ Å.

The structure was solved by direct methods with SHELXT and was refined with the SHELXL software package (S3), in the monoclinic space group C2/c with Z = 2.

The crystal structure exhibits a three-dimensional framework with wide open channels of approximately 4.6×4.1 Å running along the crystallographic *a* axis. Most of the structure is disordered over two sets of positions since it lies about several symmetry elements, inversion centers, two-fold axes and mirror planes.

Some soft SHELXL restraints (RIGU) had to be used to correct the geometry of the disordered parts and the thermal parameters of the corresponding atoms. All hydrogen positions were calculated after each cycle of refinement using a riding model, with C-H = 0.97 Å and Uiso(H) = 1.2Ueq(C). The presence of host molecules in the open channels could not be due to the great disorder of the electronic density points. This could indicate the presence of disordered DMF molecules and pyrene molecules (without solvent molecules: R1 = 0.0958 for 1837 reflections of $l > 2\sigma(l)$ and wR2 = 0.3070 for all data). Consequently, SQUEEZE (from PLATON) was used to calculate the void space, the electron count and to get a new *HKL* file. According to the SQUEEZE the total volume of the voids per unit cell is 436 Å³ (18%) and the total number of electrons placed in the voids is 354 electrons. The number of electrons is almost double that the number of electron calculated in the channels of TMOF (191 electrons, from PLATON). This could indicate the presence of other solvent molecules or the presence of some pyrene molecules inside the channels which can increase the electron density. For the calculation of the molecular formula we have supposed the presence of four DMF in the channels of the unit cell in the same way that in TMOF, even though it does not explain all the electron density present. This feature cannot be considered as a direct proof itself for the presence of pyrene inside TMOF, it is clear that something is generating this effect. Further studies are ongoing in order to understand this phenomenon.

The two different 1,4-bicyclo[2.2.2]octane-1,4-dicarboxylic acid units are disordered with two different positions for the carbon atoms of the bicycles due to a rotation around its central axis in one of them or because the bicyclic atoms had two different possible positions. They have been modelled with an occupancy of 0.5 for each carbon atom.

The final refinement was conducted with the reflection data within a $\theta_{max} = 25^{\circ}$ resolution limit, a total of 3902 reflections of which 2076 were independent and 1837 were greater than $2\sigma(I)$. Final full matrix least-squares refinement on F^2 converged to R1 = 0.0576 and wR2 = 0.1747 with GOF = 1.076. Crystallographic data and additional details of data collection and refinement are summarized in Table S2. Drawings with atomic labels are represented in Figure S5.



Figure S5. The building block including the asymmetric unit present in crystalline **Pyrene@TMOF** with all non–hydrogen atoms represented by thermal ellipsoids drawn at the 50% probability level. All hydrogen atoms were omitted for clarity.

S4. Infrared Spectra



Infrared spectra of byciclo[2.2.2]octane-1,4-dicarboxylic acid (2), TMOF, pyrene and Pyrene@TMOF are shown.







Figure S6. Infrared spectrum of byciclo[2.2.2]octane-1,4-dicarboxylic acid (2), TMOF, pyrene and Pyrene@TMOF.

S5. Microscope Images

Microscopic images (Fig S7 a-d) and Fluorescence Microscopic images (Fig S7 e-h) of **TMOF** and **Pyrene@TMOF** are shown. Presence of pyrene inside the structure of **TMOF** was confirmed by comparison of fluorescence emission of **TMOF** (e-f) and fluorescence emission of **Pyrene@TMOF** (g-h), showing an increase of this emission.



Figure S7. Microscopic images of activated (a-b) and non-activated (c-d) needles of TMOF taken by Stereoscopic Microscope. Microscopic images of TMOF (e-f) and Pyrene@TMOF (g-h) taken with Fluorescence Optical Microscope with and without wavelength filter.

S6. Elemental Analysis

In order to figure out if pyrene molecules were introduced into the cavities of TMOF, elemental analysis of both **TMOF** and **Pyrene@TMOF** were carried out. This experiment did not report any conclusion because concentration of pyrene into TMOF resulted about 10⁻³ m, being difficult to observe changes in elemental analysis.

Table	S3	Elemental	anal	vsis

Sample	Sample Nitrogen		Hydrogen	
Durana@TMOE	0.16%	40.13%	4.67%	
Pyrene@TwiOF	0.21%	40.26%	4.13%	
TMOF	0.14%	40.32%	5.00%	
	0.15%	40.38%	4.85%	

S7. Fluorescence Lifetimes.



	chi	τ ₁ (ns)	τ ₁ (%)	τ2	τ₂(%)
Pyrene (crystals)	1,34	24,65	100,0		
<u>Pyrene@TMOF (480 nm)</u>	1,16	1,71	80,9	22,06	19,1

S8. Pyrene determination by UV/vis

Calibration curve of pyrene absorption was carried out by measuring the UV-Vis profile of pyrene at different concentrations in ethanol (1M in KOH). Starting by a 30.5 μ M solution of pyrene, several dilutions were carried out. As it can be seen in Fig. S8 the absorbance decreased linearly with the dilutions.



Figure S8. Calibration of pyrene.

Calibration curve was performed by plotting the absorbance at 335 nm versus the concentration of pyrene.

Entry	[pyrene] (µM)	Absorbance at 335 nm
1	30,5	1,16
2	22,8	0,85
3	17,4	0,65
4	12,8	0,48
5	9,6	0,35
6	7,2	0,26
7	5,4	0,20
8	4,0	0,17
9	3,0	0,14
10	2,3	0,13
11	1,7	0,11
12	0	0



In order to calculate the amount of pyrene into TMOF, 16 mg of **Pyrene@TMOF** crystals were digested and dissolved with sonication in 3 mL of ethanol (1M in KOH). The solution was filtered through a 0.45 μ M PTFE 25 mm Syringe Filter and its UV-Vis spectrum was recorded. According to the calibration curve, the concentration of pyrene in that solution was 6.5 μ M (3.9 μ g). This amount corresponds to 245 ppm. Taking into account that **TMOF** has been found to act as solid solvent, molality (mol solute/kg solvent) could be calculated, obtaining a value of 1.2×10^{-3} m. Although this value may seem small, it is indeed a high value in UV-Vis or fluorescence techniques (normal values for fluorescence are 10^{-4} - 10^{-5} M).

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