Supporting Information for:

Near-infrared Emitting Ytterbium Metal-organic Frameworks with Tunable Excitation Properties

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1. Reagents, General Procedures, and Spectroscopy.

Starting materials and reagents were obtained from commercial sources or synthesized by procedures noted below. ¹H NMR (300 MHz) and ¹³C NMR (75 MHz) were recorded on a Bruker Avance 300. Fourier transform infrared (FT-IR) spectra were measured on a Nicolet Avatar 360 FT-IR spectrometer using KBr pellet samples. Absorptions are described as very strong (vs), strong (s), medium (m), weak (w), shoulder (sh), and broad (br) and stretches (st) are labeled symmetric (sym) or asymmetric (as). Data was analyzed using the Omnic Software Package. Mass spectra were obtained with a VG AutoSpec Q.

X-ray powder diffraction patterns were taken using a Bruker AXS D₈ Discover powder diffractometer at 40 kV, 40 mA for Cu K α , ($\lambda = 1.5406$ Å) with a scan speed of 0.20 sec/step and a step size of .02018°. The data were analyzed for d-spacing measurements using the EVA program from the Bruker Powder Analysis Software package. The simulated powder patterns were calculated using PowderCell 2.4. The purity and homogeneity of the bulk products were determined by comparison of the simulated and experimental X-ray powder diffraction patterns. Solvent exchange of the DMF and H₂O guest molecules in **Yb-PVDC-1** and **Yb-PVDC-2** was performed using anhydrous solvents as follows: 30 min soak in exchange solvent (ES) followed by solvent removal (3X); overnight soak in ES and then solvent removal; 24 h soak in ES and solvent removal; addition of fresh solvent. The elemental microanalysis was performed by the University of Illinois, Department of Chemistry, Microanalytical Laboratory using an Exeter Analytical CE440.

Single X-ray Diffraction Studies

Single crystal XRD data was collected on a Bruker SMART APEX II CCD-based X-ray diffractometer equipped with a normal focus Mo-target X-ray tube ($\lambda = 0.71073$ Å) operated at 2000 W power (45 kV and 35 mA). The detector was placed at a distance of 6.002 cm from the crystal. 1800 frames were collected with a scan width of 0.3° in omega and phi with an exposure time of 10 s/frame. Crystals were mounted in glass capillaries, and the X-ray intensities were measured at 253K and 298K for **Yb-PVDC-1** and **Yb-PVDC-2**, respectively. Crystal data and details of data collection are given in **Tables S2-3**.

Spectroscopic Methods

Absorption spectra were recorded on a Perkin-Elmer Lambda 9 Spectrometer coupled with a personal computer using software supplied by Perkin-Elmer.

Emission and excitation spectra in the visible range were measured using a Varian Cary Eclipse Fluorescence Spectrophotometer coupled to a personal computer with software provided by Varian. Spectra in the near infrared range were measured using a Jobin Yvon–Horiba Fluorolog-322 spectrofluorimeter equipped with an Electro-Optical Systems, Inc. DSS-IGA020L detector for the NIR domain. Emission and excitation spectra of the **Yb-PVDC-1 and Yb-PVDC-2** were collected as solid samples under chloroform (Figure S1a,b) on the JY Horiba Fluorolog-322 Spectrofluorimeter fitted with an integrating sphere developed by Prof. Frédéric Gumy and Prof. Jean-Claude G. Bünzli (Laboratory of Lanthanide Supramolecular Chemistry, École Polytechnique Féderale de Lausanne (EPFL), BCH 1402, CH-1015 Lausanne, Switzerland) as an accessory to the Fluorolog FL3-22 spectrometer (Patent pending) using quartz tube sample holders.

S3

a)





Figure S1. Pictures of Yb-PVDC-1 and Yb-PVDC-2 samples under chloroform for excitation and emission measurements.

Relative quantum yield measurements were obtained with the integration sphere on the Jobin Yvon-Horiba Fluorolog-322 using ytterbium tropolate, $[Yb(trop)_4]^-$ in DMSO ($\Phi_{Yb} = 1.9\%$).^[1]

Measurements of the near infrared luminescence lifetimes were performed using a Nd:YAG Continuum Powerlite 8010 laser (354nm, third harmonic) as the excitation source. Emission was collected at a right angle to the excitation beam, and wavelengths were selected by a Spectral Products CM 110 1/8 meter monochromator. The signal was monitored by a Hamamatsu R316-02 photomultiplier tube coupled to a 500 MHz band pass digital oscilloscope (Tektronix TDS 754D). Signals from >1000 flashes were collected and averaged. The results have been obtained from data resulting from at last three independent experiments. Luminescence decay curves were treated with Origin 7.0 software using exponential fitting models. The oscilloscope afforded the ability to collect luminescence decay profiles with 50,000

point resolution (average of at least 1000 individual acquisitions), which allows enhanced statistical fitting capabilities. The experimental luminescent decay profiles were fit using OriginPro 7.0 nonlinear fitting modules, using the following equation:

$$y = A_1 e^{(-x/t_1)} + A_2 e^{(-x/t_2)} + \dots + A_N e^{(-x/t_N)} + y_0$$

where N = number of components in fitting and t1 through tN are the luminescent lifetimes. The decay curves were fit with increasing numbers of lifetime components, and the reduced chisquared and R² values were monitored to determine the quality of the fit. The number of components was increased until the changes in chi-squared and R² values became insignificant. An example of these values produced for a series of fittings for a decay profile collected on YbPVDC1 are shown in Table S1. A four component exponential decay was chosen as the best fit of the data based on these criteria. The experimental decay profile and graphical representation of the calculated fit are shown in **Figure S2**.

Table S1. The chi-squared and R ²	values for a series of exponential decay fittings of an Yb-
PVDC-1 ytterbium centered decay	profile.

Fitting Components	Chi-squared test	R ² value
1	$6.62 \ge 10^{-10}$	0.97091
2	2.78×10^{-11}	0.99878
3	$1.10 \ge 10^{-11}$	0.99952
4	8.99 x 10 ⁻¹²	0.99961
5	8.86 x 10 ⁻¹²	0.99961



Figure S2. Experimental luminescence decay profile (black) of ytterbium centered luminescence for YbPVDC1 and the graphical representation of the calculated fit (red).

Photophysical analysis of H₂-PVDC

For analysis of the photophysical properties of H₂-PVDC, a solution of 5.0×10^{-4} M was prepared by dissolving 1.50 mg of the ligand in 6.97 mL of dimethylsulfoxide (DMSO). This stock solution was diluted for UV-visible absorbance measurements and fluorescence analysis, spectra shown in **Figure S3**.



Figure S3. Photophysical analysis of H_2 -PVDC in DMSO: absorbance spectrum (blue), emission spectrum (wine), and excitation spectrum (red) of emission at 485 nm.

The absorbance spectrum of H_2 -PVDC displays two bands, with apparent maxima centered at 340 and 415 nm. Excitation at both these band maxima produced a single fluorescence band centered at 485 nm. The excitation spectrum of the fluorescence at 485 nm correlated well with the absorbance spectrum, also with two bands at 340 and 415 nm.

Photophysical analysis and characterization of the Yb-PVDC complex

In order to investigate the ability of H₂-PVDC to bind to and sensitize Yb³⁺ cations, solutions were prepared in the following manner: 0.60 mL of 5×10^{-4} M H₂-PVDC was deprotonated with 1 equivalent of tetraethylamine hydroxide (0.1 M solution in DMSO). 1 equivalent of ytterbium cation (from chloride salt in DMSO solution) was added to this solution to yield a final stoichiometric ratio of 1:1, metal to ligand. The solution was then diluted with DMSO to bring the total volume to 3.0 mL and the final concentration to 1.0×10^{-4} M for each reagent. The solution was allowed to stand overnight to allow complete complexation prior to analysis. This complex was analyzed by mass spectrometry, which revealed that the ytterbium cation binds to PVDC in a stoichiometric ratio of 1:1 metal to ligand. HRMS (EI+) Calcd for C₂₆H₂₁O₆Yb [M]⁺ 599.0686, found 599.0677. The Yb-PVDC solution was analyzed in 1.0 mm path length quartz cuvettes (purchased from NSG Precision Cells, Inc).

Upon monitoring the Yb³⁺ emission at 980nm for the Yb-PVDC complex in DMSO, an excitation spectrum was obtained (**Figure S4**). The excitation spectrum displayed two bands with maxima at 340 and 415 nm, which correlate with the absorbance spectrum of H₂-PVDC indicating sensitization of Yb³⁺ by PVDC via the "antenna effect." Exciting through either of these two bands produced characteristic Yb³⁺ emission in the NIR range, centered at 980nm, shown in **Figure S4**.



Figure S4. Photophysical analysis of Yb-PVDC complex in DMSO solution; the Yb³⁺ emission spectrum (orange), Yb³⁺ excitation spectrum (red) on emission at 980 nm, and the absorbance spectrum of H₂-PVDC (blue).

2. Synthesis of H₂-PVDC

1,4-Bis(bromomethyl)-2,5-dimethoxybenzene (1):



(1)

This intermediate was prepared following an established procedure,^[2] which is detailed below. To a stirred solution of 1,4-dimethoxybenzene (Aldrich, 10.00 g, 72.37 mmol) in glacial acetic acid (Fisher, 50 mL), paraformaldehyde (Aldrich, 4.27 g, 144.75 mmol) and HBr/AcOH (Fluka, 33%, 30 mL) were added slowly. The mixture was stirred at 50 °C for one hour and hydrolyzed in water (200 mL) after cooling to room temperature. The white solid was collected by filtration, suspended in CHCl₃ (50 mL), and refluxed for 10 min. After cooling to room temperature, the white solid was again collected by filtration and washed with water (15.75 g, 67%). ¹H NMR (300 MHz, CDCl₃) δ 6.88 (s, 2H), 4.54 (s, 4H), 3.87 (s, 6H) ppm; ¹³C NMR (75 MHz, CDCl₃) δ 151.9, 128.0, 114.5, 56.9, 29.1 ppm; FTIR (KBr pellet): 2962 (w), 2934 (w), 2834 (w), 1509 (vs), 1461 (s), 1428 (w), 1404 (vs), 1319 (m), 1228 (vs), 1205 (s), 1179 (w), 1103 (w), 890 (w), 874 (w), 718 (w) cm⁻¹. HRMS (EI+) Calcd for C₁₀H₁₂O₂Br₂ [M]⁺ 321.9204, found 321.9209

(2,5-Dimethoxy-1,4-phenylene)bis(methylene)bis(triphenylphosphonium bromide) (2):



A mixture of 1,4-bis(bromomethyl)-2,5-dimethoxybenzene **1** (9.59 g, 29.60 mmol) and triphenylphosphine (Aldrich, 18.63 g, 71.04 mmol) was refluxed in dry toluene (Acros, 99.8%, 80 mL) under Argon for 6 hours. The crude white powder was obtained by filtration and used for subsequent reaction without further purification.

Dimethyl 4,4'-(1*E*,1'*E*)-2,2'-(2,5-dimethoxy-1,4-phenylene)bis(ethane-2,1-diyl)dibenzoate (3):



The following procedure was adapted from a previously reported synthesis.^[3] A mixture of (2,5-Dimethoxy-1,4-phenylene)bis(methylene)bis(triphenylphosphonium bromide) **2** (25.68g, 30.26 mmol) and methyl 4-formylbenzoate (TCI, 12.42 g, 75.66 mmol) were dissolved in dry methanol (Aldrich, 99.8%, 120 mL) under argon. NaOMe (Aldrich, 0.5 M in methanol, 160 mL) was added via cannula. A yellow precipitate formed immediately. The reaction was stirred under argon for 4 h. After addition of water (140 mL), the yellow powder was filtered and washed with aqueous ethanol (60%,3 x 75 mL). Pure trans product was isolated via crystallization from toluene in the presence of few crystals of iodine (11.95 g, 86%) ¹H NMR (300 MHz, CHCl₃) δ 8.02 (d, J=8.7, 4H), 7.59 (m, 6H), 7.16 (m, 4H), 3.95 (s, 6H), 3.93 ppm (s, 6H); ¹³C NMR (75 MHz, CHCl₃) δ 167.5, 152.4, 142.9, 130.6, 129.4, 128.8, 127.2, 127.0, 126.3, 109.9, 56.9, 52.66 ppm; FTIR (KBr pellet): 3007 (w), 2943 (w), 2835 (w), 1714 (vs), 1604 (m), 1493 (w), 1464 (w), 1437 (sh), 1410 (m), 1277 (vs), 1209 (s), 1183 (m), 1111 (s), 1041 (m), 1014 (w), 971 (trans =C-H, w), 875 (sh), 849 (w), 766 (m), 702 cm⁻¹ (w). HRMS (EI+) Calcd for C₂₈H₂₆O₆ [M]⁺ 458.1729, found 458.1727

4,4'-(1E, 1'E)-2,2'-(2,5-dimethoxy-1,4-phenylene)bis(ethene-2,1-diyl)dibenzoic acid (4):



(4)

To dimethyl 4,4'-(1*E*, 1'*E*)-2,2'-(2,5-dimethoxy-1,4-phenylene)bis(ethane-2,1diyl)dibenzoate (5.46 g, 11.9 mmol) was added KOH (Alfa Aesar, 6.2 g, 121 mmol), methanol (60 mL), THF (60 mL), and H₂O (30 mL). The mixture was refluxed overnight, cooled, and H₂O (60 mL) was added, resulting in a clear yellow solution. The solution was acidified with 2N HCl and the resulting yellow solid was collected by filtration and was then recrystallized from DMF to yield a bright yellow powder (4.24 g, 83%). ¹H NMR (300 MHz, DMSO) δ 12.87 (s, 2H), 7.95 (d, J=7.5, 4H), 7.70 (d, J=8.4, 4H), 7.51 (d, J=21.9, 2H), 7.45 (d, J=15.9, 2H), 7.39 (s, 2H), 3.93 ppm (s, 6H); ¹³C NMR (75 MHz, DMSO) δ 168.14, 152.30, 142.64, 130.94, 130.43, 129.33, 127.45, 126.94, 126.01, 110.59, 57.27 ppm; FTIR (KBr pellet): 2938 (b), 2831 (b), 2543 (m), 2361 (w), 1680 (C=O, s), 1600 (s), 1536 (w), 1491 (w), 1462 (m), 1315 (m), 1290 (s), 1209 (m), 1045 (m), 959 (trans =C-H, w), 859 (w), 771 cm⁻¹ (w). HRMS (EI+) Calcd for C₂₆H₂₂O₆ [M]⁺ 430.1416, found 430.1401







Figure S6. (a)¹H NMR of **3** (CDCl₃, 300 MHz); (b)¹³C NMR of **3** (CDCl₃, 75 MHz).

Figure S7. (a)¹H NMR of **4** (DMSO, 300 MHz); **(b)** ¹³C NMR of **4** (DMSO, 75 MHz).



3. Synthesis of Yb-PVDC-1 and Yb-PVDC-2

(a) Synthesis of Yb-PVDC-1: $Yb_2(C_{26}H_{20}O_6)_3(H_2O)_2 \bullet (DMF)_6(H_2O)_{8.5}$

In a glass vial (4 mL), a solution of 4,4'-(1*E*,1'*E*)-2,2'-(2,5-dimethoxy-1,4phenylene)bis(ethene-2,1-diyl)dibenzoic acid (H₂-PVDC) (8.60 mg, 0.020 mmol) in DMF (0.4 mL) was added to a solution of Yb(NO₃)₃ • 5H₂O (6.75 mg, 0.015 mmol) and 1M HNO_{3(aq)} (20.0 μ L) in DMF (0.3 mL) to produce a neon green solution. The vial was capped and placed in an 85 °C isotemp oven for 48 hours to produce yellow crystalline needles of the product. The crystals were collected, washed with DMF (4 x 3 mL), and air dried (8.6 mg, 42.4 %).

EA Calcd. (%) for Yb₂(C₂₆H₂₀O₆)₃(H₂O)₂ • (DMF)₆(H₂O)_{8.5}: C, 51.04; H, 5.49; N, 3.72. Found: C, 50.97; H, 4.57; N, 3.91. EA. Calcd. (%) for the chloroform exchange product, Yb₂(C₂₆H₂₀O₆)₃(H₂O)₂ • (CHCl₃)_{2.75}(DMF)_{0.3}: C, 48.61; H, 3.44; N, 0.21. Found: C, 48.79; H, 3.10; N, 0.21. FT-IR (KBr 4000-700 cm⁻¹): 3432 (br), 2933 (w), 1665 (DMF C=O, m), 1600 (m), 1538 (s), 1414 (COO⁻, vs), 1256 (w), 1209 (s), 1180 (w), 1106 (w), 1042 (s), 962 (m), 861 (w), 780 (trans C=C-H, s), 709 cm⁻¹(w).

Notes on molecular formula determination:

The molecular formulas for the as-synthesized and chloroform-exchanged materials were determined through analysis of the X-ray crystal data and elemental analysis data. While the absolute framework composition is unambiguous, it is more difficult to obtain accurate estimations of the quantity of guest molecules within the pores. This problem is exacerbated by the fact that these materials have very large cavities which easily lose guest molecules upon standing. Therefore, it is difficult to directly compare the number of estimated guest molecules determined from EA and TGA. Our reported formulas are the best possible match to the EA

data. Nevertheless, we include the TGA data for comparison. The TGA for as-synthesized Yb-PVDC-1 (**Figure S8**) reveals a total weight loss of 35 % at 300° C. We estimate from the EA data a weight loss of 27.8 % upon complete removal of coordinated water and uncoordinated guest molecules. The TGA for chloroform-exchanged Yb-PVDC-1 (**Figure S9**) reveals a total weight loss of 25 % at 300° C. We estimate from the EA data a weight loss of 17.4 % upon complete removal of uncoordinated guest molecules. We note that the EA samples could have lost significant amount of solvent prior to analysis, as they were sent to the University of Illinois for analysis. We expected to predict fewer solvent molecules from the EA data compared to the TGA data, given the delay time for analysis; indeed, this was the case. Such discrepancies are not uncommon for materials with such large cavities.







Figure S9. Thermogravimetric analysis of CHCl₃-exchanged Yb-PVDC-1.

(b) Synthesis of Yb-PVDC-2: $Yb_2(C_{26}H_{20}O_6)_3 \bullet (DMF)_{12}(H_2O)_{10}$

In a glass vial (20 mL), a solution of 4,4'-(1*E*, 1'*E*)-2,2'-(2,5-dimethoxy-1,4phenylene)bis(ethene-2,1-diyl)dibenzoic acid (H₂-PVDC) (86.0 mg, 0.20 mmol) in DMF (4 mL) was added to a solution of Yb(NO₃)₃•5H₂O (22.5 mg, 0.05 mmol) and 1M HNO_{3(aq)} (10 μ L) in DMF (1 mL) to yield a neon green solution. The vial was capped and placed in an 105 °C isotemp oven for 36 hours to produce orange block-like crystals of the product. The crystals were collected, washed with DMF (4 x 5 mL) and air dried (48 mg, 51.9 %).

EA Calcd. (%) for Yb₂(C₂₆H₂₀O₆)₃ • (DMF)₁₂(H₂O)₁₀: C, 50.93; H, 6.15; N, 6.25. Found: C, 50.95; H, 5.40; N, 6.47. EA. Calcd. (%) for the chloroform exchange product, Yb₂(C₂₆H₂₀O₆)₃ • (CHCl₃)_{7.5}(H₂O)_{0.5}(DMF)_{0.5}: C, 40.62; H, 2.82; N, 0.27. Found: C, 40.66; H, 2.75; N, 0.23. FT-IR (KBr 4000-700 cm⁻¹): 3433 (br), 2930 (w), 1655 (DMF C=O, m), 1602 (s), 1536 (m), 1418 (COO⁻,vs), 1208 (s), 1180 (w), 1103 (w), 1041 (w), 960 (trans =C-H, w), 862 (w), 780 cm⁻¹ (m).

Notes on molecular formula determination:

The molecular formulas for the as-synthesized and chloroform-exchanged materials were determined through analysis of the X-ray crystal data and elemental analysis data. While the absolute framework composition is unambiguous, it is more difficult to obtain accurate estimations of the quantity of guest molecules within the pores. This problem is exacerbated by the fact that these materials have very large cavities which easily lose guest molecules upon standing. Therefore, it is difficult to directly compare the number of estimated guest molecules determined form EA and TGA. Our reported formulas are the best possible match to the EA data. Nevertheless, we include the TGA data for comparison. The TGA for as-synthesized Yb-

PVDC-2 (Figure S10) reveals a total weight loss of 31 % at 300° C. We estimate from the EA data a weight loss of 39.3 % upon complete removal of coordinated water and uncoordinated guest molecules. The TGA for chloroform Yb-PVDC-2 (Figure S11) reveals a total weight loss of 38.5 % at 300° C. We estimate from the EA data a weight loss of 36.6 % upon complete removal of uncoordinated guest molecules. We note that the EA samples could have lost significant amount of solvent prior to analysis, as they were sent to the University of Illinois for analysis. We expected to predict fewer solvent molecules from the EA data compared to the TGA data, given the delay time for analysis; indeed, this was the case. Such discrepancies are not uncommon for materials with such large cavities









4. Powder X-ray Diffraction Patterns of Yb-PVDC-1 and Yb-PVDC-2

(a) . Figure S12 Powder X-ray Diffraction Pattern of Yb-PVDC-1



5. Crystallographic data and structure refinement for Yb-PVDC-1 and Yb-PVDC-2 a) Single Crystal X-ray Diffraction Study for Yb-PVDC-1

An X-ray crystal structure was determined for $C_{39}H_{30}O_{10}Yb$, **Yb-PVDC-1**, using a single crystal on a Bruker Smart Apex CCD diffractmeter with graphite-monochromated MoK α (λ = 0.71073 Å) radiation. The parameters used during the collection of diffraction data are summarized in Table S1. The crystal was mounted in a glass capillary and placed in a cold N₂ stream (253 K) for data collection.

Unit-cell parameters and systematic absences indicated **Yb-PVDC-1** crystallized in orthorhombic *F* ddd. Unit-cell dimensions were derived from the least-squares fit of the angular settings of 2973 reflections. Data were corrected for absorption using the Bruker program Sadabs. The crystal was weakly diffracting with no observed intensities beyond $2\theta=46^{\circ}$.

The structure was solved via direct methods, which located Yb³⁺ and most of the remaining non-hydrogen atoms. Remaining non-hydrogen atoms were gradually found from several subsequent difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically, although C(10) required an isotropic restraint (SHELXTL ISOR command) to avoid going non-positive definite. Idealized atom positions were calculated for all hydrogen atoms (d-(C_{methyl}-H) = 0.96 Å, d-C_{phenyl}-H)=0.93 Å, U= 1.2 U_{iso} of attached carbon).

Calculations from Platon indicated solvent accessible voids accounting for 64.5% of the unit-cell volume (eight voids measuring 5175 Å³ with 790 electrons each). We were unable to identify or model specific solvent molecules within the voids. The diffuse electron density was treated with the SQUEEZE routine from the PLATON software package.

The large voids in the structure allow for considerable flexing and uncertainty in the positions of the framework atoms and this is evidenced in large atomic displacement parameters for many of the benzene carbons and a large number of atypical bond lengths and angles. It was

necessary to fit the rings to rigid hexagons (dC-C = 1.39 Å) and constrain a number of other bond lengths in the structure in order get a stable refinement. Several 1,3 distances were restrained to provide reasonable geometries. The numerous checkcif alerts are attributable to the uncertainty in the atomic positions and the low percentage of observed diffraction intensities. It was necessary to constrain or restrain a number of bond lengths and angles in the structure in order get a stable refinement and chemically reasonable model. Phenyl rings were fit to rigid hexagons (dC-C = 1.39 Å). For the linker phenyl ring located on the inversion center all 1,1 and 1,2 C-C distances were constrained (1.39 Å for 1,1; 2.408 Å for 1,2 distances); the symmetry operator was used to do this across the inversion center. Cphenyl-O distances were constrained to 1.36 Å and O-C_{methyl} distances at 1.42 Å. Ethylene C=C distances were fixed at 1.31 Å. All carbon and oxygen atoms were restrained to have similar ADP's as their neighbors (SIMU and DELU restraints with a standard deviation of 0.03 each). Chemically equivalent 1,1 and 1,2 C-C distances to the ethylene carbon atoms in all units were restrained to be the same within a standard deviation of 0.02 Å. Numerous checkcif alerts are generated for high R_{int} values, unusual atomic displacement parameters. These are attributable to the uncertainty in the atomic positions and the low percentage of observed diffraction intensities. There is also a checkcif alert regarding the very large voids.

The final Fourier map showed maximum and minimum peaks of 0.52 and -0.37 e⁻Å⁻³, respectively, which were close to Yb(1). All computer programs used in the data collection and refinements are contained in the Bruker program packages SMART (vers. 5.625), SAINT (vers. 6.22), and SHELXTL (vers. 6.14) and Platon.^[4]

Table S2. Crystal data and structure refinement for Yb-PVDC-1

Identification code	Yb-PVDC-1	
Empirical formula	C39 H30 O10 Yb	
Formula weight	831.67	
Temperature	253(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	F d d d	
Unit cell dimensions	a = 16.247(6) Å	α= 90°.
	b = 48.939(19) Å	β= 90°.
	c = 80.84(3) Å	$\gamma = 90^{\circ}$.
Volume	64280(43) Å ³	
Ζ	32	
Density (calculated)	0.688 Mg/m ³	
Absorption coefficient	1.189 mm ⁻¹	
F(000)	13248	
Crystal size	0.32 x 0.23 x 0.21 mm ³	
Theta range for data collection	3.54 to 23.25°.	
Index ranges	-17<=h<=18, -54<=k<=54, -89<=l<=87	
Reflections collected	95070	
Independent reflections	11506 [R(int) = 0.1522]	
Completeness to theta = 23.25°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7883 and 0.7021	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	11506 / 455 / 404	
Goodness-of-fit on F ²	0.884	
Final R indices [I>2sigma(I)]	R1 = 0.0575, $wR2 = 0.1252$	
R indices (all data)	R1 = 0.1599, wR2 = 0.1484	
Largest diff. peak and hole	0.522 and -0.366 e.Å ⁻³	

Figure S14. The asymmetric unit present in crystalline **Yb-PVDC-1** with all atoms represented by thermal ellipsoids drawn at the 30% probability level. All hydrogen atoms were omitted for clarity.







b) Single Crystal X-ray Diffraction Study for Yb-PVDC-2

An amber block-shaped crystal (0.45 x 0.5 x 0.45 mm) of Yb₂(C₂₆H₂₀O₆)₃, **Yb-PVDC-2**, was mounted in a glass capillary on a Bruker SMART APEX II CCD-based X-ray diffractometer equipped with a normal focus Mo-target X-ray tube ($\lambda = 0.71073$ Å) operated at 2000 W power (45 kV and 35 mA). The X-ray intensities were measured at 298 K. The detector was placed at a distance of 6.002 cm from the crystal. 1800 frames were collected with a scan width of 0.3 degrees in omega and phi with an exposure time of 10 s/frame.

An initial unit cell was established using the Apex2 software proved to be ambiguous and thus 708 reflections were read in form several hundred frames and were exported into Cell-Now, resulting in a suggested I centered orthorhombic unit cell with the dimensions a = 16.063, b = 22.697, c = 38.454, $\alpha = 90.07$, $\beta = 90.03$, $\gamma = 89.93$. 5.5% of the reflections were not consistent with an I centered lattice (versus 50% for e.g. a C-centered lattice), and the unit cell was integrated in this setting, a unit cell was assigned in XPREP and attempts were made to solve the structure. These attempts, however, failed, and thus the data were again integrated using a primitive orthorhombic instead of the I centered orthorhombic cell with the same metric parameters as that established by Cell_Now. Inspection in XPREP then also suggested an I-centered orthorhombic cell with I/sigma for reflections obeying I centering being 1.7 versus 5.2 for all reflections, but again the primitive cell was chosen instead. Based on systematic absences the space group Pnna was chosen and the data were cut off at a d-spacing of 0.75.

The structure was then solved with the help of Patterson methods using the program XS, which revealed two ytterbium atoms and some of the metal bound oxygen atoms. Using Fourier transform recycling additional possible oxygen atoms were identified during the next refinement cycles. Tentatively correct oxygen positions were chosen based on the Yb-O distances and angles. Successive improvement of the difference map then allowed for the identification of the aromatic rings bonded to the carboxylate groups, and the model was augmented to include all of the $O_2C-C_6H_4$ groups. At this point it became obvious that the remainder of the linking molecules exhibit large vibrational motion with less than atomic resolution for the 2,5-dimethoxy phenylene units. The overall electron density nevertheless allowed for identification of the units as a whole and disorder for one of the two crystallographically independent linkers became obvious. The - caused by flip disorder of one of the two ethylene units - involves both etheylene units of this linker, the 2,5-dimethoxy phenylene and one of the carboxylate bonded aromatic rings, and the occupancy ratio refined to 0.63(1) to 0.37(1). The other linker - located on a crystallographical inversion center - showed no disorder but only very pronounced thermal motion.

In order to obtain a chemically meaningful model and refinement a range of restraints was introduced at this point. For the benzene ring located on the inversion center all 1,1 and 1,2 C-C distances were restrained to be each the same (the respective symmetry operator was used to do this across the inversion center). All other benzene rings were restrained to resemble ideal hexagons with C-C distances of 1.39 Å. All carbon atoms but the carboxylate ones were restrained to be isotropic within a standard deviation of 0.02 Å², and all carbon and oxygen atoms were restrained to have similar ADPs as their neighbors (SIMU and DELU restraints with a standard deviation of 0.03 each). Chemically equivalent 1,1 and 1,2 C-C distances to the ethylene carbon atoms in all units were restrained to be the same within a standard deviation of 0.02 Å. The methoxy units were restrained to have the same 1,1 and 1,2 distances in all units and to lie within the planes of the phenylene units they are bonded to. The carbon atoms C2a to C7a were set to have the same ADPs as their disordered counterparts C2b to C7b (which they significantly overlap). Application of these restraints did not cause any significant increase in R values or decrease in any other structure quality indicators, and none of the restraints applied had an error significantly larger than 0.1 Å or $Å^2$ for bond distance and ADP restraints, respectively.

The residual electron density in the voids between the inorganic-organic hybrid network did not exhibit any chemically meaningful pattern and was ignored during the refinement process. No correction was applied for the residual electron density. The two largest peaks exhibit electron densities of 2.44 and 1.89 electrons per cubic Ångstrom.

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Identification code	Yb-PVDC-2	
Empirical formula	C ₇₈ H ₆₀ O ₁₈ Yb ₂	
Formula weight	1631.34 g/mol	
Temperature	298(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pnna	
Unit cell dimensions	a = 16.0798(14) Å	$\alpha = 90^{\circ}$
	<i>b</i> = 22.7096(19) Å	β= 90°
	c = 38.484(3) Å	$\gamma = 90^{\circ}$
Volume	14053(2) Å ³	
Ζ	4	
Density (calculated)	0.771 Mg/m ³	
Absorption coefficient	1.358 mm ⁻¹	
F(000)	3248	
Crystal size	0.5 x 0.45 x 0.45 mm ³	
Theta range for data collection	3.44 to 28.29°.	
Index ranges	$-21 \le h \le 21, -30 \le k \le 30,$	
	-51≤ <i>l</i> ≤51	
Reflections collected	123644	
Independent reflections	17435 [R(int) = 0.0580]	
Completeness to theta = 28.29∞	99.8 %	
Absorption correction	Semi-empirical from	
	equivalents	
Max. and min. transmission	0.543 and 0.468	
Refinement method	Full-matrix least-	
	squares on F ²	
Data / restraints / parameters	17435 / 1228 / 529	
Goodness-of-fit on F ²	1.028	
Final R indices [I>2sigma(I)]	R1 = 0.0581, w $R2 =$	
	0.2103	
R indices (all data)	R1 = 0.1046, wR2 =	
	0.2528	
Largest diff. peak and hole	2.921 and -0.541 e.Å $^{-3}$	

Table S3. Crystal data and structure refinement for Yb-PVDC-2.

Figure S16. The building unit and asymmetric unit present in crystalline **Yb-PVDC-2** with all atoms represented by thermal ellipsoids drawn at the 30% probability level. All hydrogen atoms were omitted for clarity.





Figure S17. Unit cell packing for Yb-PVDC-2.

6. References

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