Supporting Information

Turn-on fluorescence triggered by selective internal dye replacement in MOFs

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Materials

$Cr(NO_3)\cdot 9H_2O$ (99%, Aldrich), terephthalic acid (99%, *Aldrich*), 40 % aq. Hydrofluoric acid (Fluka, Buchs Switzerland), millipore water ($\rho > 18$ MΩcm), Ethanol (99,5%, Aldrich), chloroform (99%, Aldrich), pyridine (99.0%, Aldrich), benzene (99.0%, Aldrich), aceton (99.0%, Aldrich) 4-aminopyridine (99%, Acros), formanilide (99%, Acros) 9-(1-hexylheptyl)-2-benzopyrano[6',5',4':10,5,6]anthra[2,1,9-*def*]isoquinoline-1,3,8,10-tetraone was prepared according to the literature [1].

Characterization

XRD patterns were recorded with a D8 Discover Bruker diffractometer.

Thermal analysis experiments were performed on a STA 449C Netzsch instrument. The measurements were performed in air atmosphere from 25 °C to 900 °C with a heating rate of 10 K min^{-1}. The C, H, N contents were determined using an Elementar micro cube instrument. FT-IR spectra of KBr pellets (256 scans with a resolution of 4 cm^{-1}) were recorded on a Bruker Equinox 55 spectrometer. 200 mg dry KBr and 2 mg sample were mixed in an agate mortar and subsequently pressed at 2000 kN for 5 min. IR spectra for the analysis of the organic compounds were acquired with a Perkin Elmer BX II FT-IR System with an ATR unit. The band intensity is reported as follows: very strong (*vs*), strong (*s*), medium (*m*) and weak (*w*).

Surface properties of the samples were determined using N_2 sorption at 77 K with a NOVA 4000e Quantachrome instrument. Samples were degassed under vacuum at 150 °C. The surface area was calculated according to the BET method.

Scanning electron microscopy was performed on a JEOL JSM-6500F electron microscope at 5 kV acceleration voltage and and an Oxford analysis system.

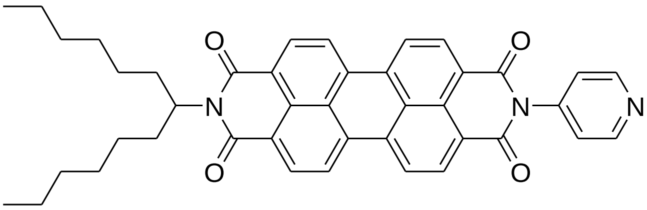
NMR spectra were recorded with a Bruker AMX 600 with TMS as internal standard. Multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet or combinations of the above.

UV-VIS spectra were performed on a Varian Cary 5000, fluorescence spectra on a Varian Cary Eclipse.

The mass spectra were acquired by use of positive-ion fast atom bombardment FAB-(+) with 3-nitrobenzylalcohol as matrix. The mass of the detected ions is given as *m*/*z*.

Experimental section

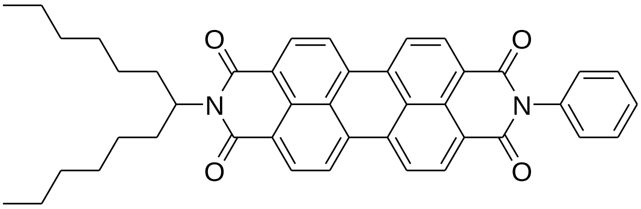
1.1 2-(1-Hexylheptyl)-9-pyridin-4-ylanthra[2,1,9-*def*;6,5,10-*d'e'f'*]diisoquinoline-1,3,8,10-tetraone (1)



9-(1-Hexylheptyl)-2-benzopyrano[6',5',4':10,5,6]anthra[2,1,9-*def*]isoquinoline-1,3,8,10-tetraone (0.30 g, 0.52 mmol), 4-aminopyridine (98 mg, 1.0 mmol) and imidazole (10 g) were heated at 150 °C for 3 h and then allowed to cool. While still warm, the solution was treated with aqueous HCl (2 M, 75 mL). The precipitate was collected by vacuum filtration, dried at 110 °C, purified by column separation (silica gel, chloroform/ethanol 50:1) and finally precipitated with methanol from chloroform and dried at 110 °C.

Yield: 0.22 g (65%) red solid, m.p. > 250 °C. R_f value (silica gel, chloroform/ethanol 50:1) = 0.35. IR (ATR): ν = 2922.9 (m), 2852.9 (w), 1695.4 (s), 1652.6 (s), 1589.7 (s), 1576.0 (m), 1505.6 (w), 1456.0 (w), 1431.1 (w), 1402.8 (m), 1339.1 (s), 1250.0 (m), 1173.8 (m), 1149.8 (w), 1124.0 (w), 1064.9 (w), 964.1 (w), 964.1 (w), 843.9 (w), 825.5 (w), 809.2 (s), 787.0 (m), 742.9 (s), 702.1 (w), 697.9 (w), 667.8 cm^{-1} (w). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C, Figure S1): δ = 0.82 (t, ^{3}J(H,H) = 7.0 Hz, 6 H, 2 × CH_3), 1.17-1.36 (m, 16 H, 8 × CH_2), 1.83-1.90 (m, 2 H, β-CH_2), 2.19-2.27 (m, 2 H, β-CH_2), 5.14-5.20 (m, 1 H, N-CH), 7.36 (dd, ^{3}J(H,H) = 4.5 Hz, ^{4}J(H,H) = 1.7 Hz, 2 H, 2 × CH_pyridine), 8.58-8.71 (m, 8 H, 8 × CH_perylene), 8.85 ppm (dd, ^{3}J(H,H) = 4.5 Hz, ^{4}J(H,H) = 1.7 Hz, 2 H, 2 × CH_pyridine). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C, Figure S2): δ = 14.0, 22.6, 26.9, 31.7, 32.3, 54.9, 122.7, 123.0, 123.5, 124.0, 126.3, 126.7, 129.5, 129.8, 131.8, 132.0, 134.0, 135.5, 143.0, 151.2, 162.8 ppm. UV/Vis ($CHCl_3$): λ_max (ε) = 460.0 (19300), 491.0 (52500), 527.6 nm (85300). Fluorescence ($CHCl_3$): λ_max (I_rel) = 536.1 (1.00), 580.3 (0.51) nm 626.2 (0.12). Fluorescence quantum yield ($CHCl_3$, λ_exc = 491 nm, $E_{491\,\mathrm{nm}/1\,\mathrm{cm}}$ = 0.0130, reference 2,9-bis-(1-hexylheptyl)anthra[2,1,9-*def*;6,5,10-*d'e'f'*]diisoquinoline-1,3,8,10(2*H*,9*H*)-tetraone RN110590-84-6 with Φ = 1.00): 1.00. MS (FAB^{+}): m/z (%): 650.8 (100) [M^{+}+H], 649.8 (13) [M^{+}], 468.5 (39), 373.3 (32). HRMS ($C_{42}H_{39}N_3O_4$): Calcd. 649.2941; found 649.2933, Δ = - 0.0008. $C_{42}H_{39}N_3O_4$ (649.3): Calcd. C 77.63, H 6.05, N 6.47; found C 77.30, H 6.11, N 6.28

1.2 (1-Hexylheptyl)-9-phenylanthra[2,1,9-*def*;6,5,10-*d'e'f'*]diisoquinoline-1,3,8,10-tetraone (2)



9-(1-Hexylheptyl)-2-benzopyrano[6’,5’,4’:10,5,6]anthra[2,1,9-*def*]isochinoline-1,3,8,10-tetraone (0.15 g, 0.26 mmol), formanilide (63 mg, 0.52 mmol) and imidazole (5.0 g) were heated at 150 °C for 3 h and then allowed to cool. While still warm, the solution was treated with aqueous HCl (2 M, 50 mL). The precipitate was collected by vacuum filtration, dried at 110 °C, purified by column separation (silica gel, chloroform) and finally precipitated with methanol from chloroform and dried at 110 °C. Yield: 0.13 g (77%) red solid, m.p. > 250 °C. R_f value (silica gel, chloroform) = 0.25. IR (ATR): ν = 2921.0 (w), 1695.9 (m), 1652.9 (s), 1592.0 (m), 1575.9 (m), 1505.3 (w), 1433.2 (w), 1403.4 (m), 1341.8 (s), 1252.9 (m), 1177.2 (m), 1027.9 (w), 966.0 (w), 860.0 (w), 847.1 (w), 837.6 (w), 809.1 (s), 744.1 (s), 698.9 (m), 688.1 (w), 668.0 cm^{-1} (w). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C, Figure S3): δ = 0.82 (t, ^3J(H,H) = 6.9 Hz, 6 H, 2 × CH_3), 1.17-1.37 (m, 16 H, 8 × CH_2), 1.82-1.90 (m, 2 H, β-CH_2), 2.19-2.29 (m, 2 H, β-CH_2), 5.15-5.21 (m, 1 H, N-CH), 7.33-7.36 (m, 2 H, 2 × $CH_{arom.}$), 7.49-7.52 (m, 1 H, $CH_{arom.}$), 7.56.7.59 (m, 2 H, 2 × $CH_{arom.}$), 8.62-8.75 ppm (m, 8 H, 8 × $CH_{perylene}$). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C, Figure S4): δ = 14.0, 22.6, 26.9, 29.2, 29.7, 31.7, 32.4, 54.8, 123.1, 123.3, 126.4, 126.7, 128.6, 128.9, 129.5, 129.8, 129.8, 131.1, 131.8, 134.3, 135.1, 163.6 ppm. UV/Vis ($CHCl_3$): λ_{max} (ε) = 459.2 (20400), 490.4 (54700), 527.0 nm (90500). Fluorescence ($CHCl_3$): λ_{max} (I_{rel}) = 496.4 (1.00), 538.7 (0.48), 588.4 nm (0.11). Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 490 nm, $E_{490\ nm/1\ cm}$ = 0.0127, reference 2,9-bis-(1-hexylheptyl)anthra[2,1,9-*def*;6,5,10-*d'e'f'*]diisoquinoline-1,3,8,10(2*H*,9*H*)-tetraone RN110590-84-6 with Φ = 1.00): 1.00. MS (DEP/EI): *m*/*z* (%): 648.3 (17) [M^+], 443.2 (32), 181.6 (34). HRMS ($C_{43}H_{40}N_2O_4$): Calcd. 648.2988; found 648.2980, Δ = - 0.0008. $C_{42}H_{40}N_3O_4$ (648.3): Calcd. C 79.60, H 6.21, N 4.32; found C 79.43, H 6.24, N 4.27.

2.1 Synthesis of MIL-101(Cr)

MIL-101(Cr) was synthesized as reported elsewhere: G. Ferey, C.M.-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surble, I. Margiolaki, *Science* **2005**, *309*, 2040-2042.

A solution of $Cr(NO_3)\cdot 9H_2O$ (4.20 g, 10.5 mmol, 1.00 eq.), terephtalic acid (1.74 g, 10.5 mmol, 1.00 eq.) and 40 % aq. HF (315 µL, 7.12 mmol, 0.68 eq.) in H_2O (50 mL, 265 eq.) was introduced into an autoclave and placed in a preheated oven at 220 °C for 18 h. After cooling to room temperature the solvent was removed by filtration and the green reaction mixture was purified in several steps. Between each step the solvent was exchanged. First the crude MIL-101(Cr) was stirred for 12 h in H_2O at room temperature. Then the same mixture was refluxed for 8 h, followed by another stirring for 12 h at room temperature, and again refluxed for 6 h. Subsequently the solvent was removed by filtration, and EtOH were added to the solid product. The mixture was stirred for 12 h at room temperature, followed by refluxing for 6 h, stirring for another 12 h at room temperature and again refluxing for 8 h, followed by cooling to room temperature and filtration. Yield after purification: 3.58 g of the green, crystalline product.

2.2 Synthesis of MOF-dye 1 adduct

2-(1-Hexylheptyl)-9-pyridin-4-ylanthra[2,1,9-*def*;6,5,10-*d'e'f'*]diisoquinoline-1,3,8,10-tetraone (**1**) (0.13 g, 0.20 mmol) and MIL-101(Cr) (0.50 g) were suspended in toluene (20 mL) and refluxed for 8 h. The cooled suspension was filtered, washed with plenty of chloroform (about 50 mL) and the solid was dried at 110 °C. Yield: 0.61 g red solid.

2.3 Synthesis of MOF-reference dye 2 adduct

The second dye (1-hexylheptyl)-9-phenylanthra[2,1,9-*def*;6,5,10-*d'e'f'*]diisoquinoline-1,3,8,10-tetraone (**2**) (10 mg, 15 µmol) and MIL-101(Cr) (40 mg) were suspended in toluene (5 mL) and refluxed for 8 h. The cooled suspension was filtered, washed with plenty of chloroform (about 50 mL) and the solid was dried at 110 °C. Yield: 38 mg green solid.

2.4 Solvent stability experiment of MOF-dye 1 adduct

MOF-dye **1** (37.5 mg) adduct was suspended in 10 mL of one of the following solvents each (chloroform, pyridine, water, benzene or acetone) in snap-cap vials and agitated with an orbital shaker (100 cycle rotations per minute) for 7 d at room temperature. Subsequently, the suspensions were filtered yielding red solid products. XRD, IR, TGA, elemental analysis and sorption measurements were performed to study the structure, composition, thermal behavior and the surface properties of these materials.

2.5 Soxhlet extraction of MOF-dye 1 adduct with pyridine

A Soxhlet extraction of the MOF-dye **1** adduct was carried out with pyridine for 1 d. Soxhlet extraction with pyridine gave rise to a green powder. XRD, IR, TG, elemental analysis and sorption measurements of the powders were performed.

2.6 Release of dye 1 from MOF-dye 1 adduct upon treatment with ammonia

MOF-dye **1** adduct (50 µg) was treated with ammonia (0.5 M in THF, 2 mL) in a quartz cuvette. The sample was put into a fluorimeter and the measurements were started (3 min interval, 8 repetitions). For comparison the MOF-dye **1** adduct (50 µg) was treated with pure THF (2 mL) or pure $CHCl_3$.

Figures

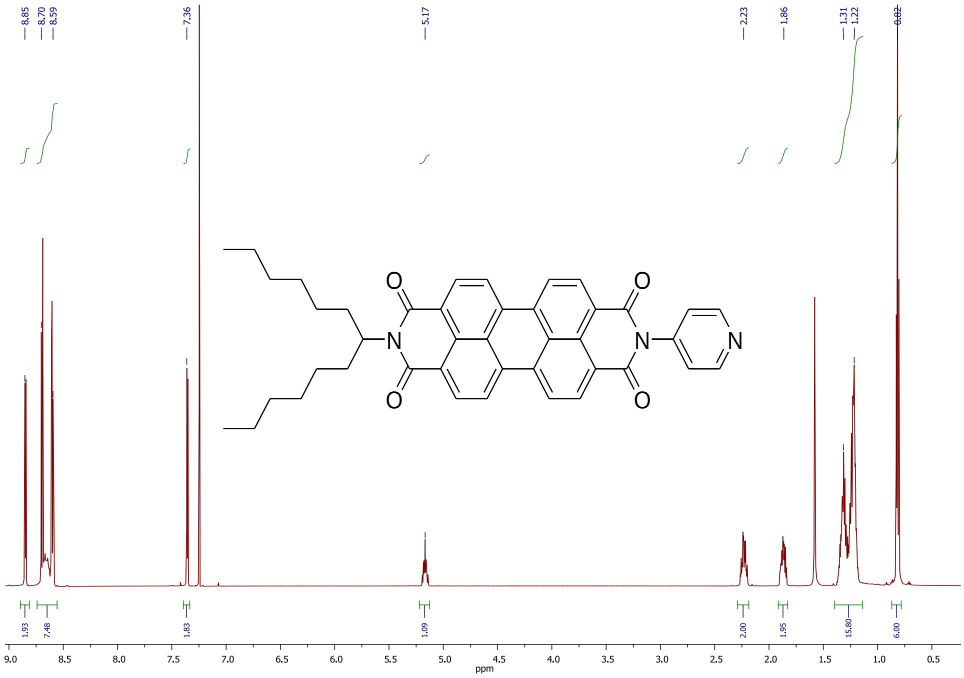


Figure S1. ^{1}H NMR Spectrum of 2-(1-Hexylheptyl)-9-pyridin-4-ylanthra[2,1,9-*def*;6,5,10-*d'e'f'*]diisoquinoline-1,3,8,10-tetraone (**1**)

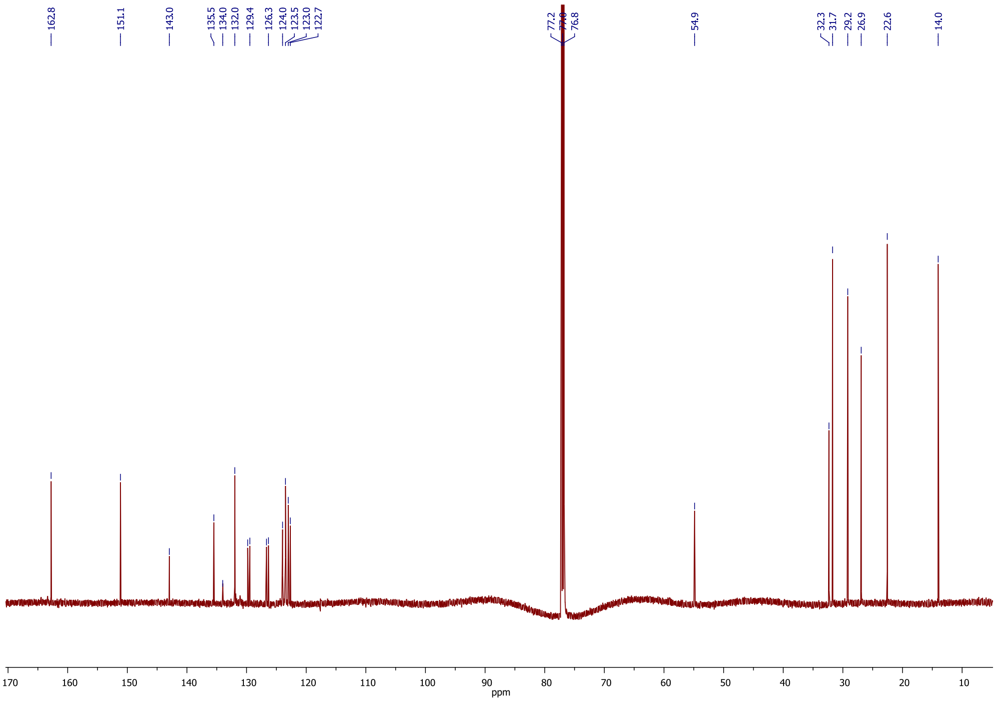


Figure S2. ^{13}C NMR Spectrum of 2-(1-Hexylheptyl)-9-pyridin-4-ylanthra[2,1,9-*def*;6,5,10-*d'e'f'*]diisoquinoline-1,3,8,10-tetraone (**1**)

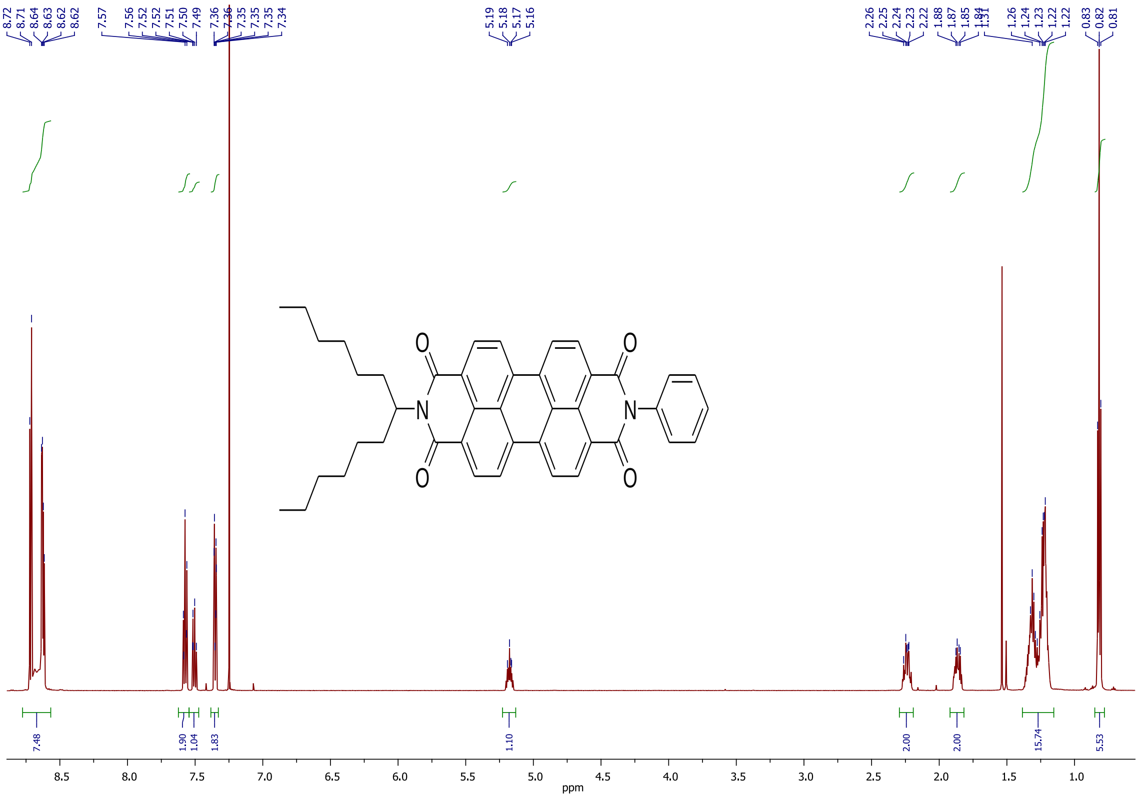


Figure S3. ^{1}H NMR Spectrum of 2-(1-Hexylheptyl)-9-phenylanthra[2,1,9-*def*;6,5,10-*d'e'f'*]diisoquinoline-1,3,8,10-tetraone (**2**)

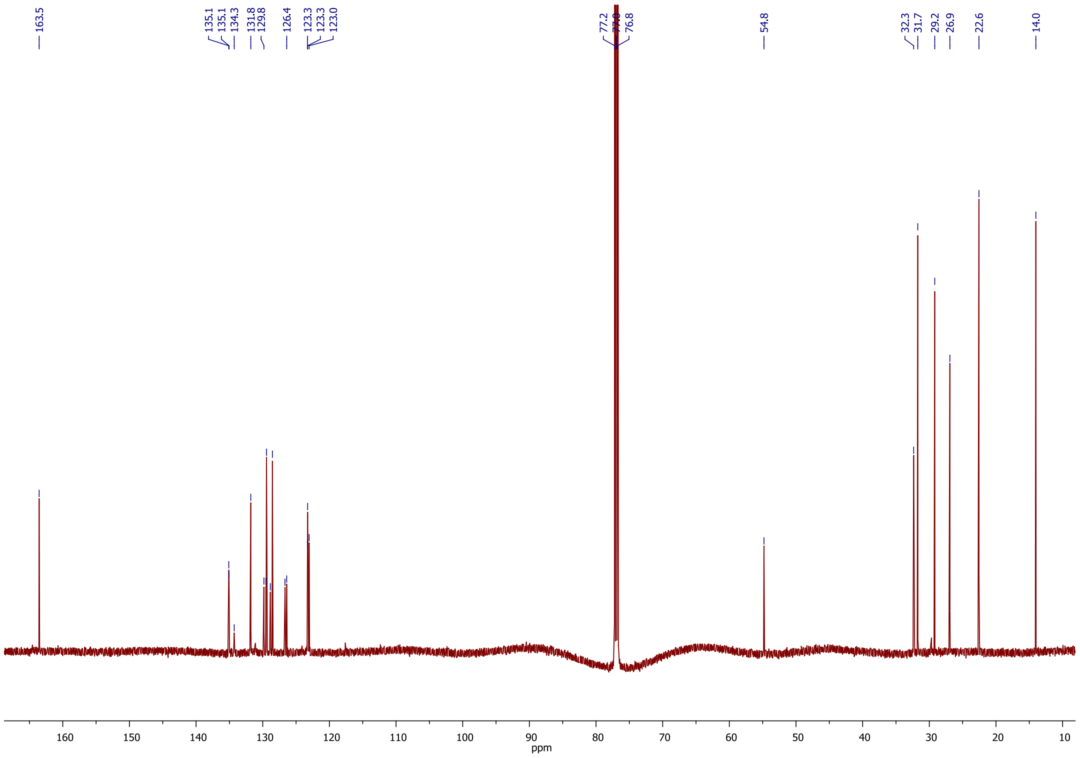


Figure S4. ^{13}C NMR Spectrum of 2-(1-Hexylheptyl)-9-phenylanthra[2,1,9-*def*;6,5,10-*d'e'f'*]diisoquinoline-1,3,8,10-tetraone (**2**)

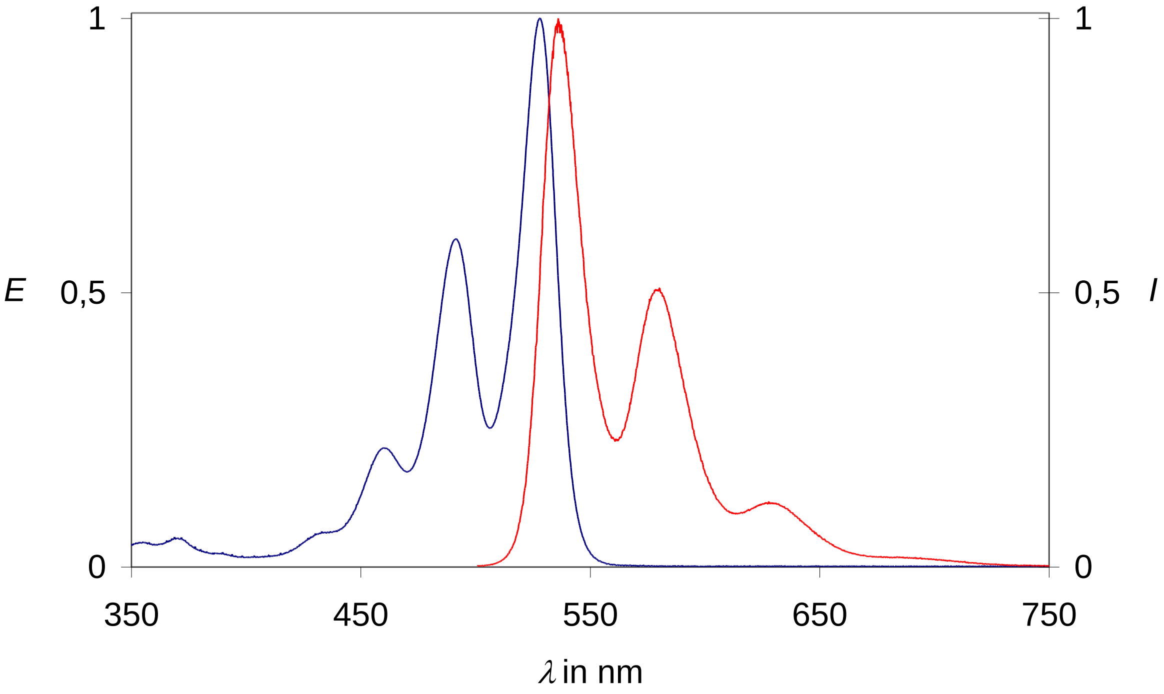


Figure S5. UV/Vis and fluorescence (excitation λ_{exc} = 491 nm) spectra of 2-(1-Hexylheptyl)-9-pyridin-4-ylanthra[2,1,9-*def*;6,5,10-*d'e'f'*]diisoquinoline-1,3,8,10-tetraone (**1**)

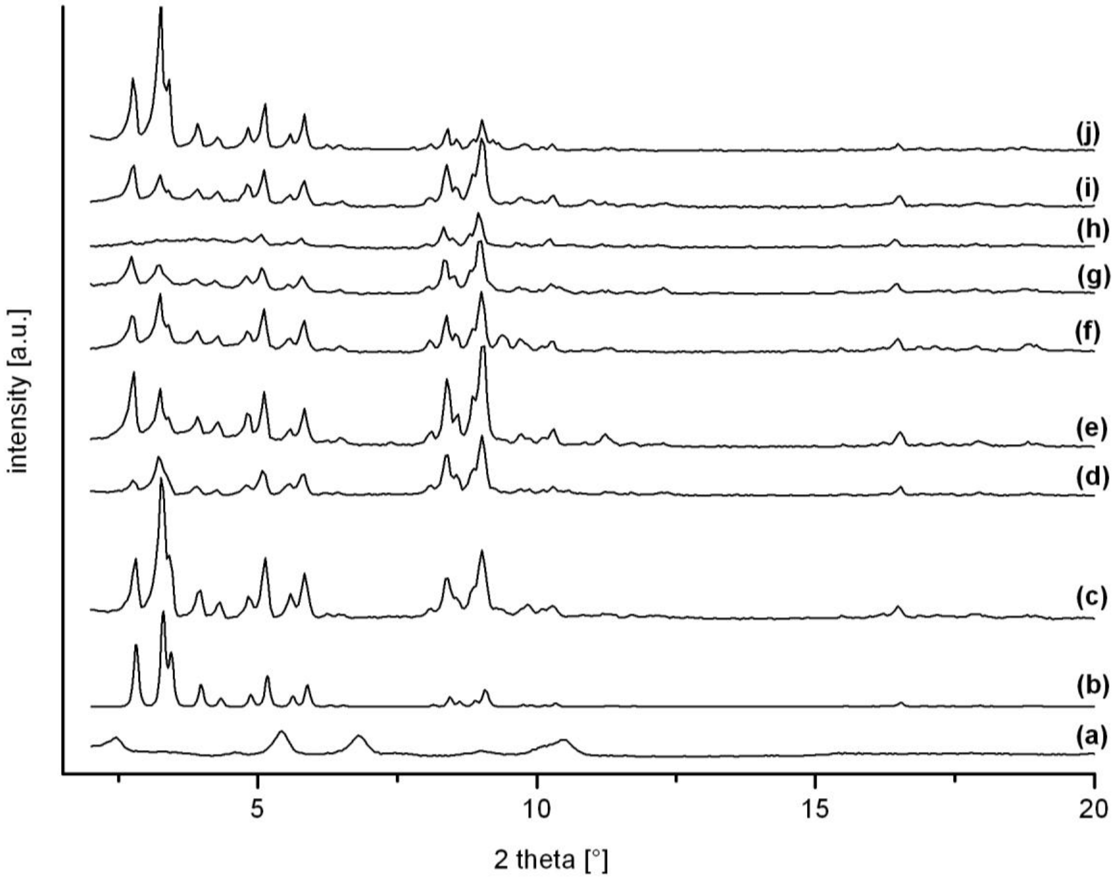


Figure S6. X-ray powder diffraction patterns of dye **1** (**a**), simulated XRD pattern of MIL-101(Cr) (**b**),[2] MIL-101(Cr) (**c**), MOF-reference dye **2** adduct after washing with chloroform (**d**), MOF-dye **1** adduct after 7 d treatment with water (**e**), MOF-dye **1** adduct after 7 d treatment with pyridine (**f**), MOF-dye **1** adduct after 7 d treatment with chloroform (**g**), MOF-dye **1** adduct after 7 d treatment with benzene (**h**), MOF-dye **1** adduct after 7 d treatment with acetone (**i**) and MOF-dye **1** adduct after Soxhlet extraction with pyridine (**j**).

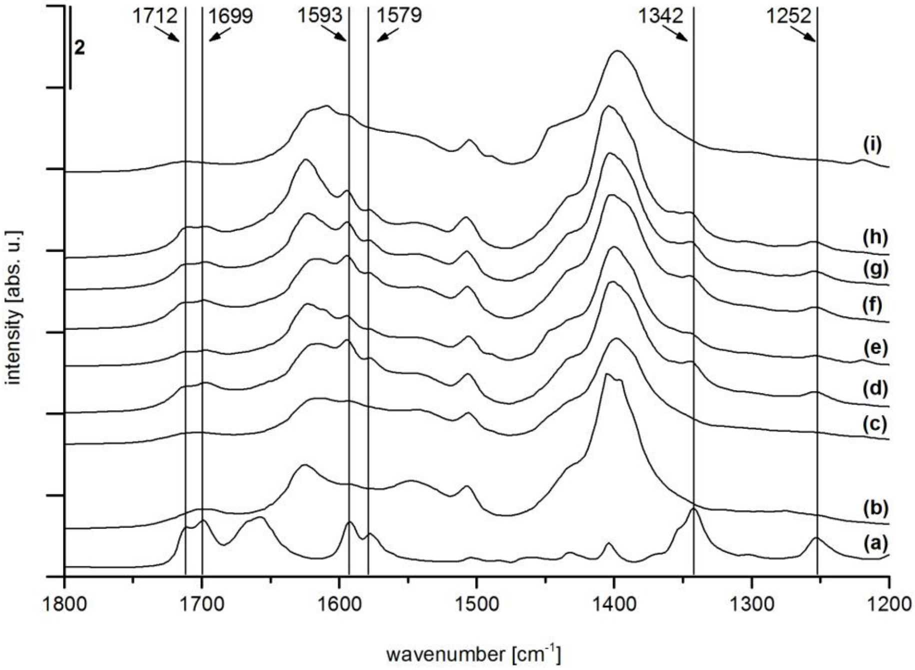


Figure S7. IR-spectra of dye **1** (**a**), MIL-101(Cr) (**b**), MOF-reference dye **2** adduct after washing with chloroform (**c**), MOF-dye **1** adduct after 7 d treatment with water (**d**), MOF-dye **1** adduct after 7 d treatment with pyridine (**e**), MOF-dye **1** adduct after 7 d treatment with chloroform (**f**), MOF-dye **1** adduct after 7 d treatment with benzene (**g**), MOF-dye **1** adduct after 7 d treatment with acetone (**h**) and MOF-dye **1** adduct after Soxhlet extraction with pyridine (**i**).

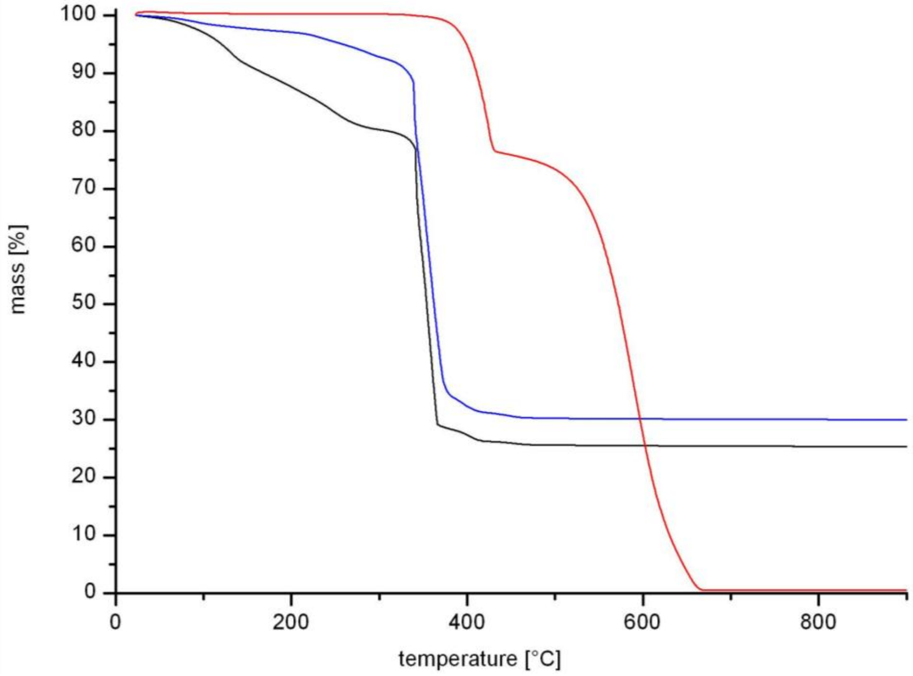


Figure S8. Thermogravimetric analysis of MIL-101(Cr) (**black**), MOF-reference dye **2** adduct after washing with chloroform (**blue**) and dye **1** (**red**) (in air, heating rate 10 K/min).

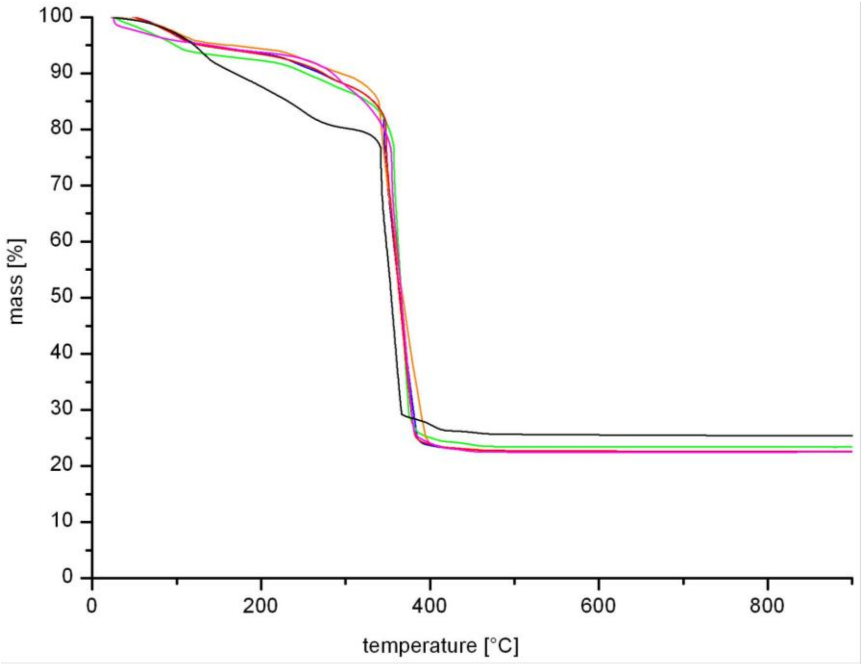


Figure S9. Thermogravimetric analysis of MIL-101(Cr) (**black**), MOF-dye **1** adduct after 7 d treatment with water (**orange**), MOF-dye **1** adduct after 7 d treatment with chloroform (**green**), MOF-dye **1** adduct after 7 d treatment with benzene (**blue**), MOF-dye **1** adduct after 7 d treatment with acetone (**red**) and MOF-dye **1** adduct after 7 d treatment with pyridine (**magenta**) (in air, heating rate 10 K/min).

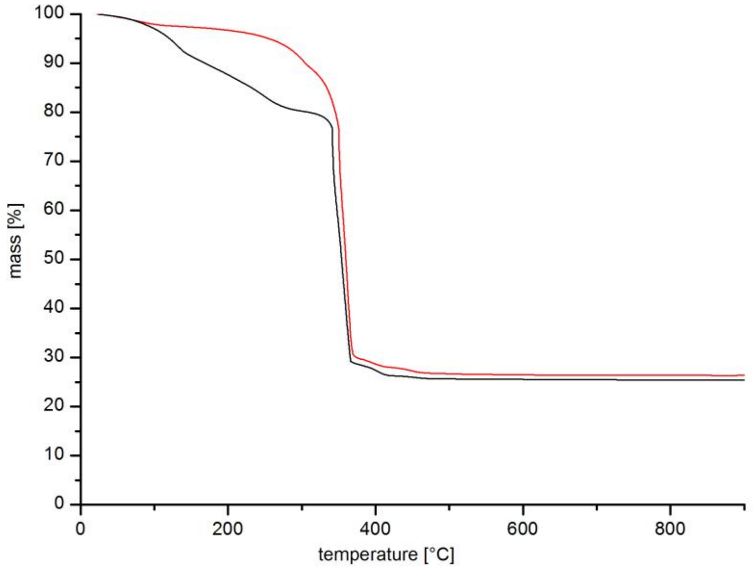


Figure S10. Thermogravimetric analysis of MIL-101(Cr) (**black**) and MOF-dye **1** adduct after Soxhlet extraction with pyridine (**red**) (in air, heating rate 10 K/min).

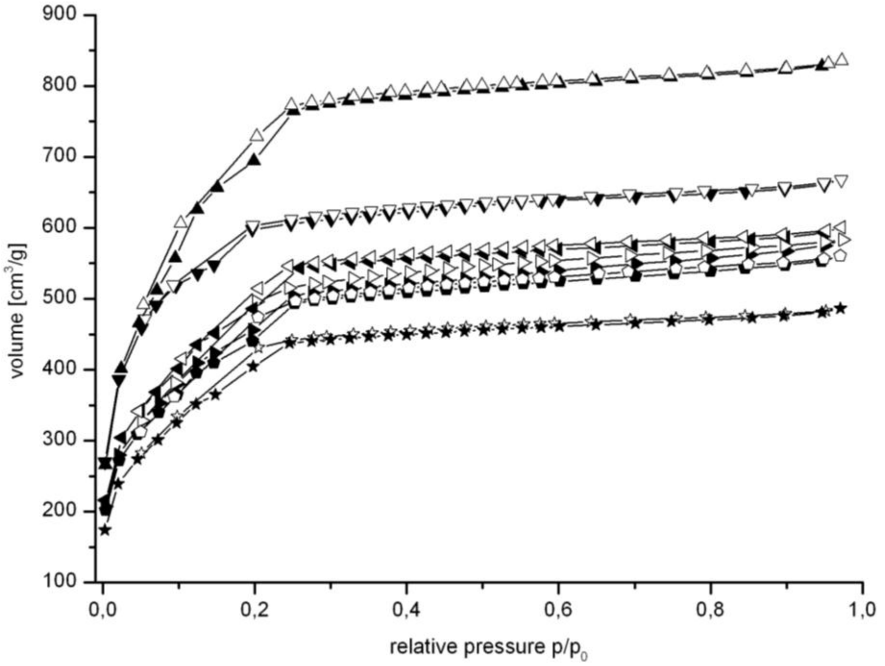


Figure S11. Nitrogen sorption isotherms of MOF-dye **1** adduct after 7 d treatment with water (☆,★), MOF-dye **1** adduct after 7 d treatment with benzene (⬠,⬟), MOF-dye **1** adduct after 7 d treatment with acetone (▷,▶), MOF-dye **1** adduct after 7 d treatment with chloroform (◁,◀), MOF-dye **1** adduct after 7 d treatment with pyridine (▽,▼) and MIL-101(Cr) (△,▲). Filled symbols represent adsorption isotherms, empty symbols represent desorption isotherms.

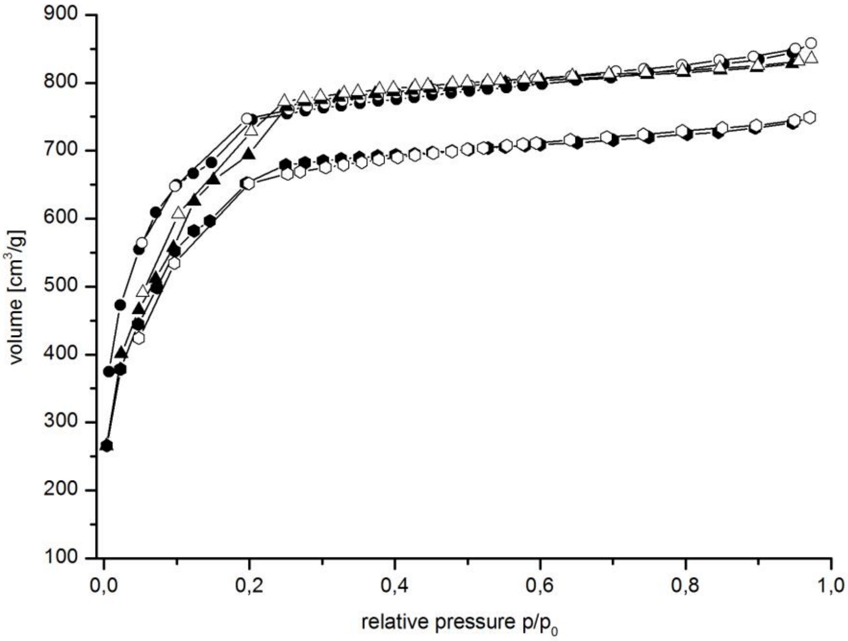


Figure S12. Nitrogen sorption isotherms of MIL-101(Cr) (△,▲), MOF-reference dye **2** adduct after washing with chloroform (⬡,⬢**)** and MOF-dye **1** adduct after Soxhlet extraction with pyridine (○,●). Filled symbols represent adsorption isotherms, empty symbols represent desorption isotherms.

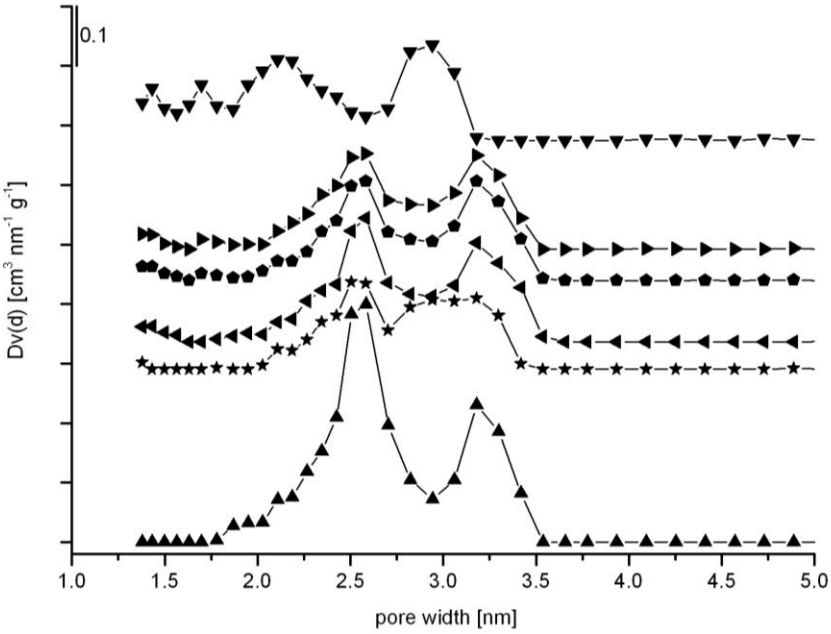


Figure S13. NLDFT pore size distribution of MIL-101(Cr) (▲), MOF-dye **1** adduct after 7 d treatment with water (★), MOF-dye **1** adduct after 7 d treatment with chloroform (◀), MOF-dye **1** adduct after 7 d treatment with benzene (⬟), MOF-dye **1** adduct after 7 d treatment with acetone (▶) and MOF-dye **1** adduct after 7 d treatment with pyridine (▼).

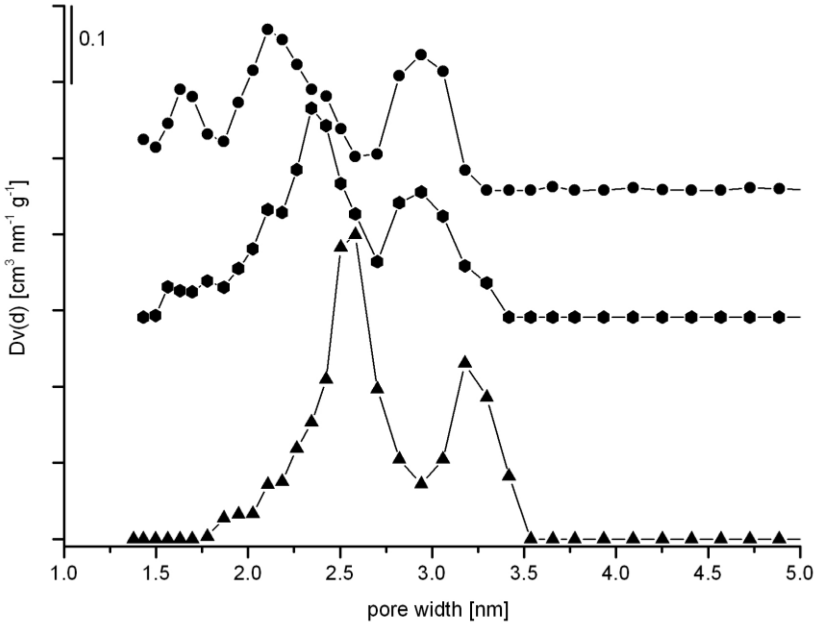


Figure S14. NLDFT pore size distribution of MIL-101(Cr) (▲), MOF-reference dye **2** adduct after washing with chloroform (⬢) and MOF-dye **1** adduct after Soxhlet extraction with pyridine (●).

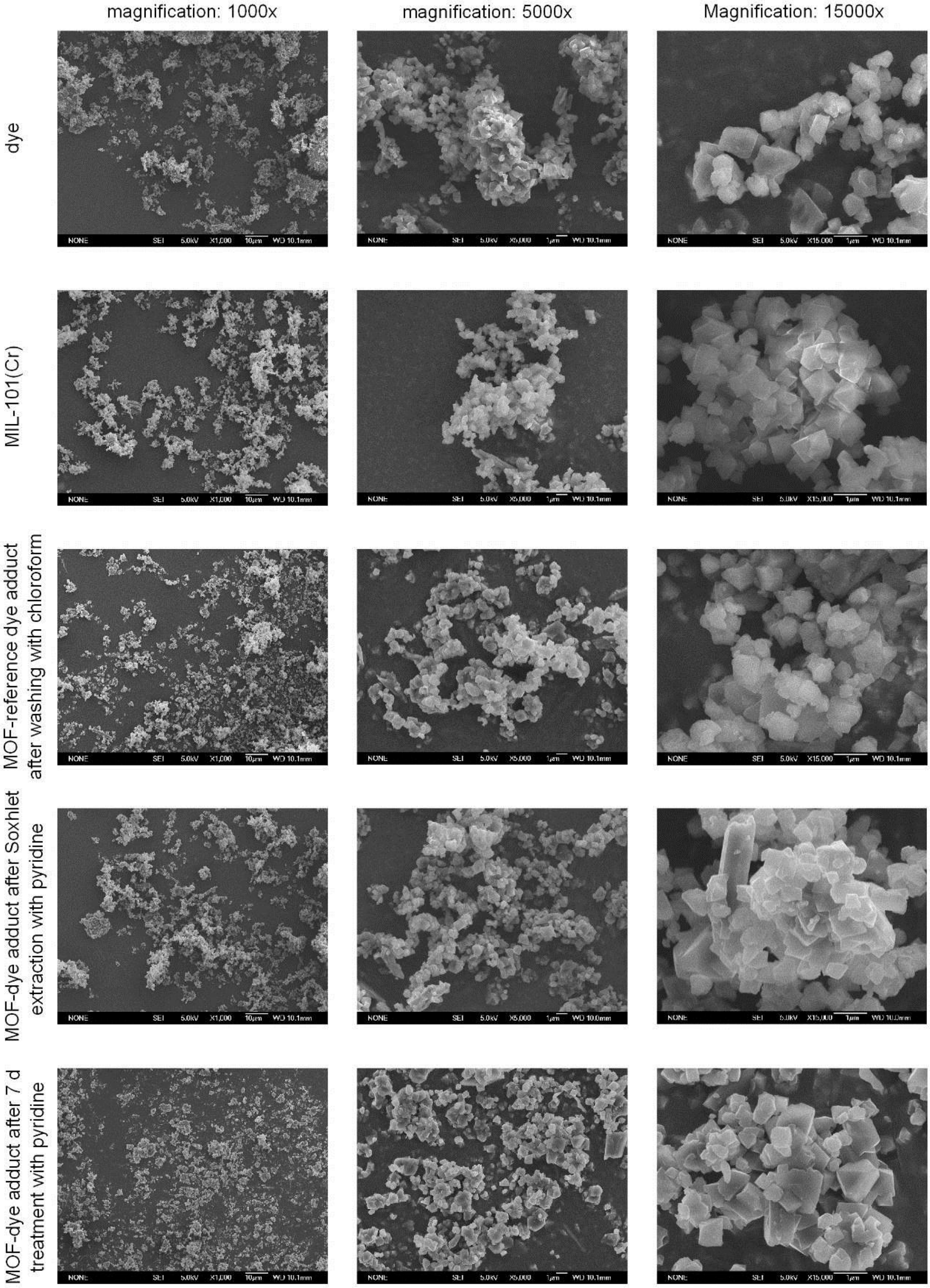


Figure S15. SEM images of dye **1**, MIL-101 (Cr), MOF-reference dye **2** adduct after washing with chloroform, MOF-dye **1** adduct after Soxhlet extraction with pyridine and MOF-dye **1** adduct after 7 d treatment with pyridine.

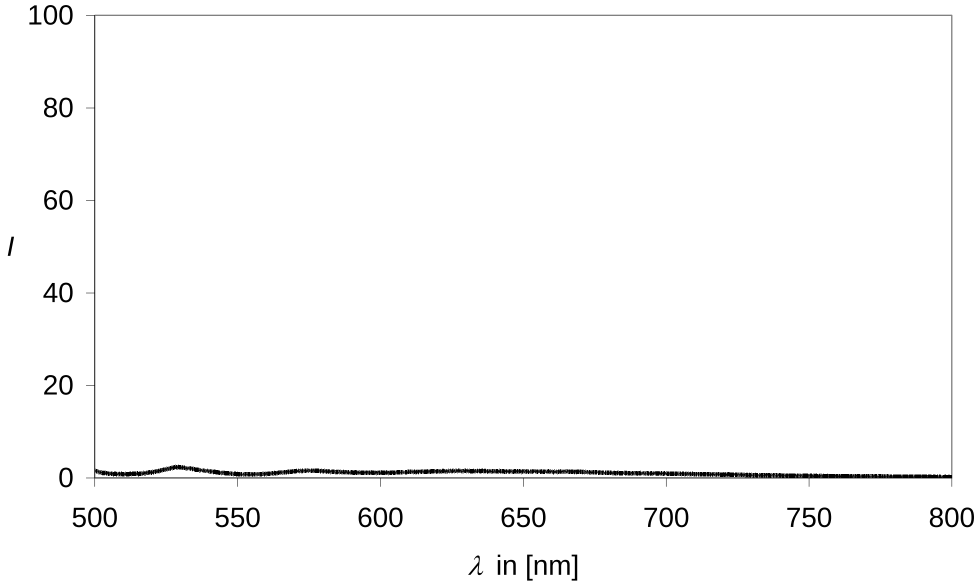


Figure S16. Solid-state fluorescence spectra of MOF-dye **1** adduct.

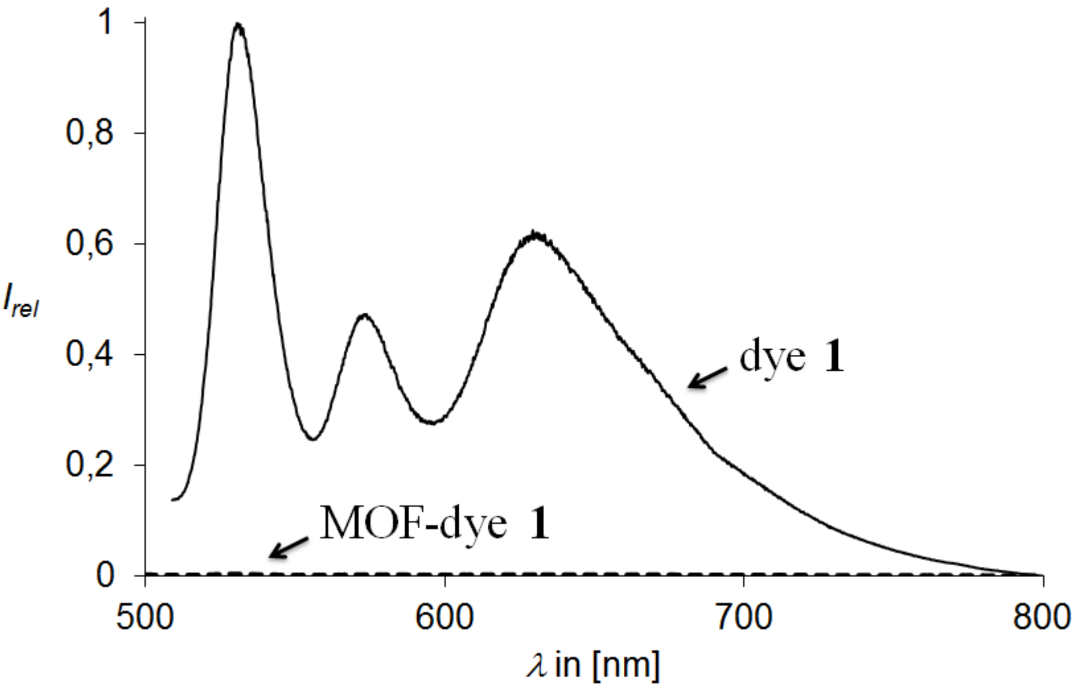


Figure S17. Solid-state fluorescence spectra of MOF-dye **1** adduct and dye **1**.

Tables

Table 1. CHN Analysis

MIL-101(Cr) : C 39.90, H 6.04, N 0.75

Dye 1 : C 77.30, H 6.11, N 6.28

MIL-101(Cr)-dye 1 adduct : C 45.45, H 4.00, N 2.12.

Solvent	**Solvent composition after 7 days extraction**
Benzene	C 45.19 H 3.67 N 2.22
Pyridine	C 46.74 H 3.20 N 4.05
Acetone	C 44.73 H 3.61 N 2.21
Chloroform	C 44.30 H 3.61 N 2.17
Water	C 45.68 H 3.71 N 2.19

Table 2. BET surface areas and total pore volumes of the MOF-dye adducts as a result of stability experiments.

Sample	BET surface area [m^2/g]	Total pore volume [cm^3/g]	p/p_0 for calculation of total pore volume
MOF-dye **1** adduct after 7 d treatment with:			
acetone	1692	0.78	0.25
benzene	1632	0.76	0.25
chloroform	1806	0.84	0.26
pyridine	2134	0.92	0.20
water	1504	0.68	0.25
MIL-101(Cr)	2639	1.18	0.25
MOF-reference dye **2** adduct after washing with chloroform	2431	1.05	0.25
MOF-dye **1** adduct after Soxhlet extraction with pyridine	2650	1.17	0.25

References

[1] H. Kaiser, J. Lindner, H. Langhals, *Chem. Ber.* **1991**, *124*, 529-535.

[2] G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surblé, I. Margiolaki, *Science* **2005**, *309*, 2040-2042.