Supporting Information

Electroluminescence response promoted by dispersion and interaction of perylene-3,4,9,10-tetracarboxylic dianhydride inside MOF5

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1. **General conditions:**

All reactants were purchased from Sigma Aldrich and used without extra purification. Raman spectra were recorded at room temperature with a 514 nm laser excitation at 2 W power on a *Renishaw In Via* Raman spectrometer equipped with a CCD detector. X-ray powder diffraction data was measured on a PANalytical Empyrean diffractometer (CuKα radiation) in transmission mode. SEM images were recorded with a JEOL JSM6300. Laser flash photolysis (LFP) experiments were performed using a Q-switched Nd:YAG laser (Quantel Brilliant, 355 nm, 20 mJ per pulse, 5 ns fwhm) coupled to a mLFP-111 Luzchem miniaturized equipment. This transient absorption spectrometer includes a ceramic xenon light source, 125 mm monochromator, Tektronix 9-bit digitizer TDS-3000 series with 300 MHz bandwidth, compact photomultiplier and power supply, cell holder and fiber optic connectors, fiber optic sensor for laser-sensing pretrigger signal, computer interfaces, and a software package developed in the LabVIEW environment from National Instruments. The LFP equipment supplies 5 V trigger pulses with programmable frequency and delay. The rise time of the detector/digitizer is ∼3 ns up to 300 MHz (2.5 GHz sampling). The monitoring beam is provided by a ceramic xenon lamp and delivered through fiber optic cables. The laser pulse is probed by a fiber that synchronizes the LFP system with the digitizer operating in the pretrigger mode. All transient spectra were recorded using 10 mm × 10 mm quartz cells with a capacity of 4 mL and were bubbled for 30 min with Ar before signal acquisition. The absorbance of the samples was 0.2 at the laser excitation wavelength (307 nm). Fluorescence data were measured using 10 mm × 10 mm quartz cells of 4 mL total volume using a Jacso FP-8500 spectrofluorometer. UV/vis data were measured using 10 mm × 10 mm quartz cells of 4 mL total volume using a Jacso FP-650 spectrofluorometer. The absorbance of the sample was set at an optical density of 0.3. Optical picture were obtained with a Leica microscope, under different excitation/filter wavelengths (Figure S1). Fluorescence lifetime were measured with Easylife microbeam spectrosfluorimeter.

![Figure S1: Different excitation/filter wavelengths used.](image-url)
2. Preparation of materials

Preparation of Microcrystalline MOF5

Terephthalic acid (0.8 mg, 5 mmol), Zn(NO$_3$)$_2$·6H$_2$O (4.5 g, 15 mmol) and DMF (300 mL) were mixed and sonicated in a 500 mL glass flask under argon atmosphere. After complete dissolution of the reagents, the reaction was heated at 140 ºC for 12 h. After this time, formation of crystals was observed. The mother liquid was removed by filtration over a Nylon membrane (0.2 μm pore) and the crystals were washed/exchanged 3 times with DMF (10 h) and 3 times with chloroform. Samples were activated heating at 120 ºC under vacuum for 48 h. The samples were stored with Argon to prevent degradation.

**Figure S2:** Powder X-ray diffractogram of MOF5.

**Figure S3:** SEM images and optical microscope (down right) of MOF5.
200 μm MOF5 and NH₂-MOF5

Terephthalic acid (83 mg, 0.5 mmol), Zn(NO₃)₂·6H₂O (450 mg, 1.52 mmol) and DMF (98 mL) were mixed and sonicated for 10 minutes prior to introduction in 4 mL flask (2 mL each, 25) sealed and heated to 110 °C for 7 h. After this time, formation of crystals was observed. The mother liquid was removed and the crystals were washed/exchanged 3 times with DMF (10 h) and 3 times with chloroform. Samples were activated heating at 120 °C under vacuum for 48 h. The samples were stored under Argon to prevent degradation.

Figure S4: Optical microscope pictures (polarized light) of MOF5 and NH₂-MOF5.
PDA@MOF5 preparation

Three strategies were employed for the preparation of PDA@MOF5, however just one of them afforded homogeneous distribution of PDA inside the pores. Activation of MOF5 prior to PDA diffusion revealed essential, because without activation PDA appeared on the surface of the crystals and no fluorescence was observed.

Inside the same flask employed for the synthesis of MOF, PDA in DMF solution (0.5 mg/10 mL) was introduced in the flasks. After 3 days at 60ºC the solution was carefully removed and the corresponding coloured crystals were washed 3 times with DMF and then 3 with methylene chloride. The PDA@MOF5 material was dried under vacuum at 100 ºC for 12 h.

Figure S5: Different strategies for the incorporation of PDA inside MOF5.

Figure S6: Optical microscope images for the materials obtained after de different strategies: left - MOF5 without activation; centre - with activation of MOF5; and right - introduction of PDA in the MOF5 synthesis.
Figure S7: Optical microscope pictures normal (up) and under 470 nm wavelength excitation (down) for the materials obtained after different strategies: left - MOF5 without activation; centre - with activation of MOF5; and right - introduction of PDA in the MOF5 synthesis.
Figure S8: Optical microscope images under transmission mode (left) and under 350 nm (centre) and 470 nm (right) excitation for NH$_2$-MOF5 (top), and the attempt of obtaining PDA@NH$_2$-MOF5 (bottom). The arrows indicate the location of PDA aggregates on the external surface of the MOF.

After activation of microcrystalline MOF5, MOF5 (250 mg) was immersed and stirred at 25 ºC with a PDA solution in DMF (0.5 or 1 mg/1mL). After 3 days at 60ºC the solution was carefully removed and the corresponding coloured crystals were washed 3 times with DMF and 3 times with methylene chloride. Then material was dried under vacuum at 100 ºC for 12 h.
Figure S9: Optical microscope images under transmission mode (left) and under 470 nm excitation (right) for microcrystalline MOF5 and PDA@MOF5.
### 3. Diffusion experiments

**Table S1**: Emission intensities for the corresponding diffusion experiments.

<table>
<thead>
<tr>
<th>MOF-5 (530nm)</th>
<th>(I_{\text{fluor}})</th>
<th>((I-I_0)/I_0)</th>
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<tr>
<td>t (h)</td>
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<tr>
<td>24</td>
<td>0.11143</td>
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</table>
4. Quantification methodology

Scheme S1: PDA and PDA@MOF5 reaction under basic medium.

Figure S10: UV/vis calibration of PDA under basic medium.
5. Fluorescence Characterization

**Figure S11.** Normalized emission spectra of PDA@MOF5 in different solvents (1 mg / 3 mg, $\lambda_{exc} = 475$ nm). A red shift is observed for apolar solvents, due to a higher stabilization of the excited state when compared with polar solvents.
6 Electroluminescence device preparation

All samples were prepared on ITO-coated glass substrates purchased from Psiotec Ltd. with an approximate area of 1×1 cm², which were first cleaned by ultrasonication in acetone and isopropanol. The cleaned ITO glass was then coated first with a TiOx layer (20 nm) by depositing 40 µL of a TiOx solution (titanium(IV) isopropoxide, 2-methoxyethanol and ethanolamine, for more details concerning the preparation of this solution see reference 1) and spin coating at 2000 rpm for 50 s. Then the glass was sintered at 450 °C for 30 min. To prepare the second layer, corresponding to the active material, a suspension of PDA@MOF5 (5 mg) or MOF5 (5 mg) or PDA (the corresponding amount present in 5 mg of 0.9% w/w PDA@MOF5) in 50 µL DMF is sonicated (80 W) until a slurry is obtained (~30 min), then 25 µL of PEDOT:PSS (1.3 wt% in H₂O, Aldrich) are diluted in 25 µL of DMF and the resulting suspension is added dropwise to the MOF slurry in DMF. The resulting suspension is homogenized by magnetic stirring (10 min) and drop-casted from a pipette of this suspension (25-30 µL) was casted at the center of the ITO substrate containing the TiOx layer and spread with a plastic tip obtaining a uniform wet layer and allowed to evaporate overnight in a well-ventilated fume hood. The resulting films are then heated to 105 °C under inert atmosphere for 1.5 h. MoOx layer (20 nm) was deposited by thermal evaporation using MoO₂ powder as precursor. Finally, a gold layer (100 nm) was deposited by thermal evaporation using a shadow mask obtaining an active area pixel of 0.048 cm². The thickness of the films was measured by a MicroXAM-100 3D surface profilometer. Figure S11 shows the cross section of the active materials (PDA, ~570 nm and PDA@MOF5, ~1200 nm).

a) 

b)
Figure S12. Optical profilometry section for the devices containing PDA (a) or PDA@MOF5 (b) as active material.

Figure S13. Electroluminescence spectra of PDA@MOF5 (20 V and 100 mA, black line), PDA (30 V and 100 mA, green line) and MOF5 (30 V and 100 mA, blue line).

Figure S14. Schematic energy-level diagram for the electroluminescence devices (ITO/TiO$_2$/PDA/MoO$_x$/Au)
7 Measurements of Electroluminescence

Immediately after preparation of the electrochemical cells were characterised by connecting the device electrodes to a Keithley 2601 source-meter and several values of constant voltage between 0 and 40 V were applied for the time required to record the electrochemical spectra (scan rate of 1 nm/sec). The emission of the electroluminescent material was monitored in the range from 400 to 750 nm by placing the cell inside the sample chamber of a modified (PTI) LPS-220B spectrofluorimeter that has been previously calibrated with a luminance meter Mavo-Monitor USB MM-5032 (GOSSEN).
8 Electrical Stress Measurements

In order to study the stability of the PDA@MOF5, 20 mg was placed in a sample holder with an area of 0.5 cm$^2$ and pressed at 10 Ton/cm$^2$. Then, the sample was submitted to more than ten cycles of voltage ranging from 0 to 40 V (simulating experimental conditions of the electroluminescent devices) and using an AMEL potentiostat (model 7050) connected with a PC to control the scan. A full description of the equipment used can be found in the literature. The sample was characterized by PXRD before and after the electrical stress.

Figure S15. Current – voltage (J-V) and luminance curves for the EL devices containing PDA@MOF5 (a) or PDA (b) submitted to more than ten cycles of voltage ranging from 0 to 40 V only in the case of J – V curves.
Figure S16. EL - Current – Time curves for the EL devices containing PDA@MOF5 at 40 Volt, and measured during 40 min.

Figure S17. UV- vis in situ spectroelectrochemical experiment of PDA thin film prepared on ITO coated glass substrate and submitted at 40 Volt. Curves measured every 2.5 min during 40 min.
References
