

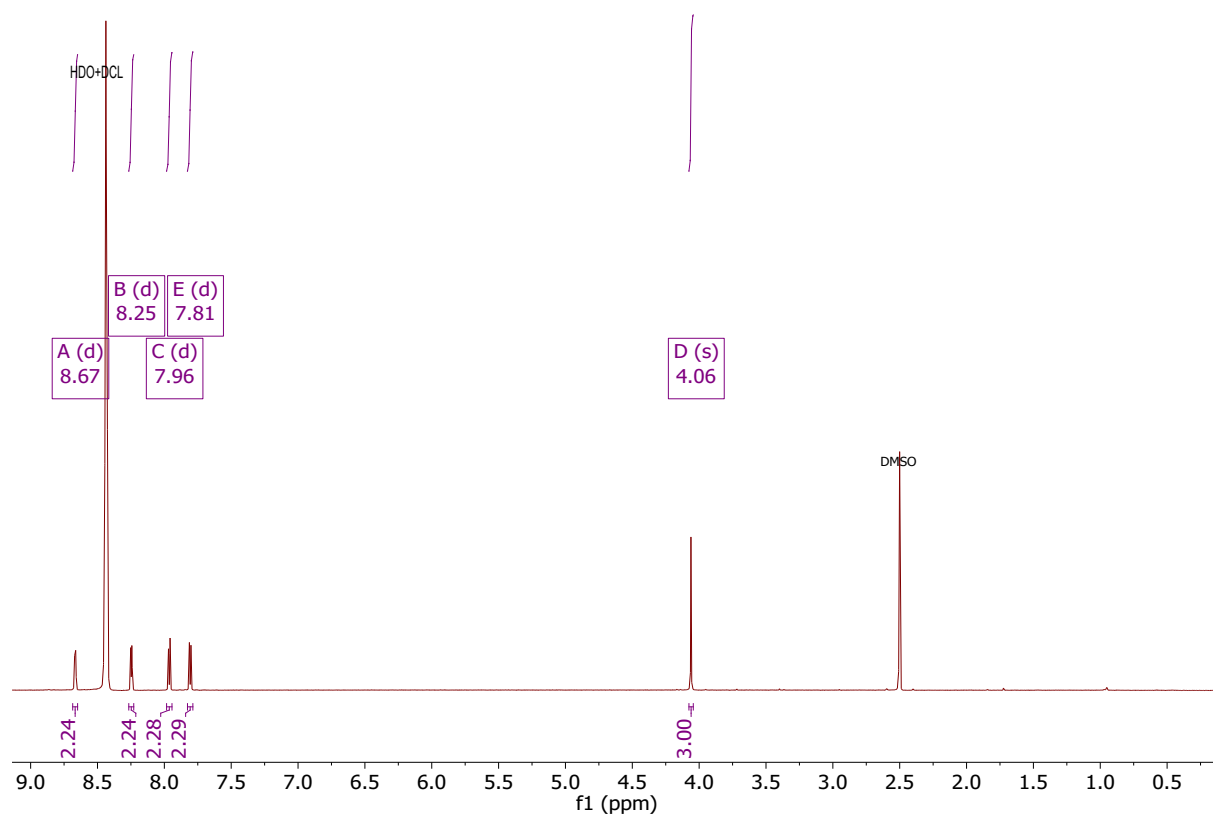
# CHEM**NANO**MAT

## Supporting Information

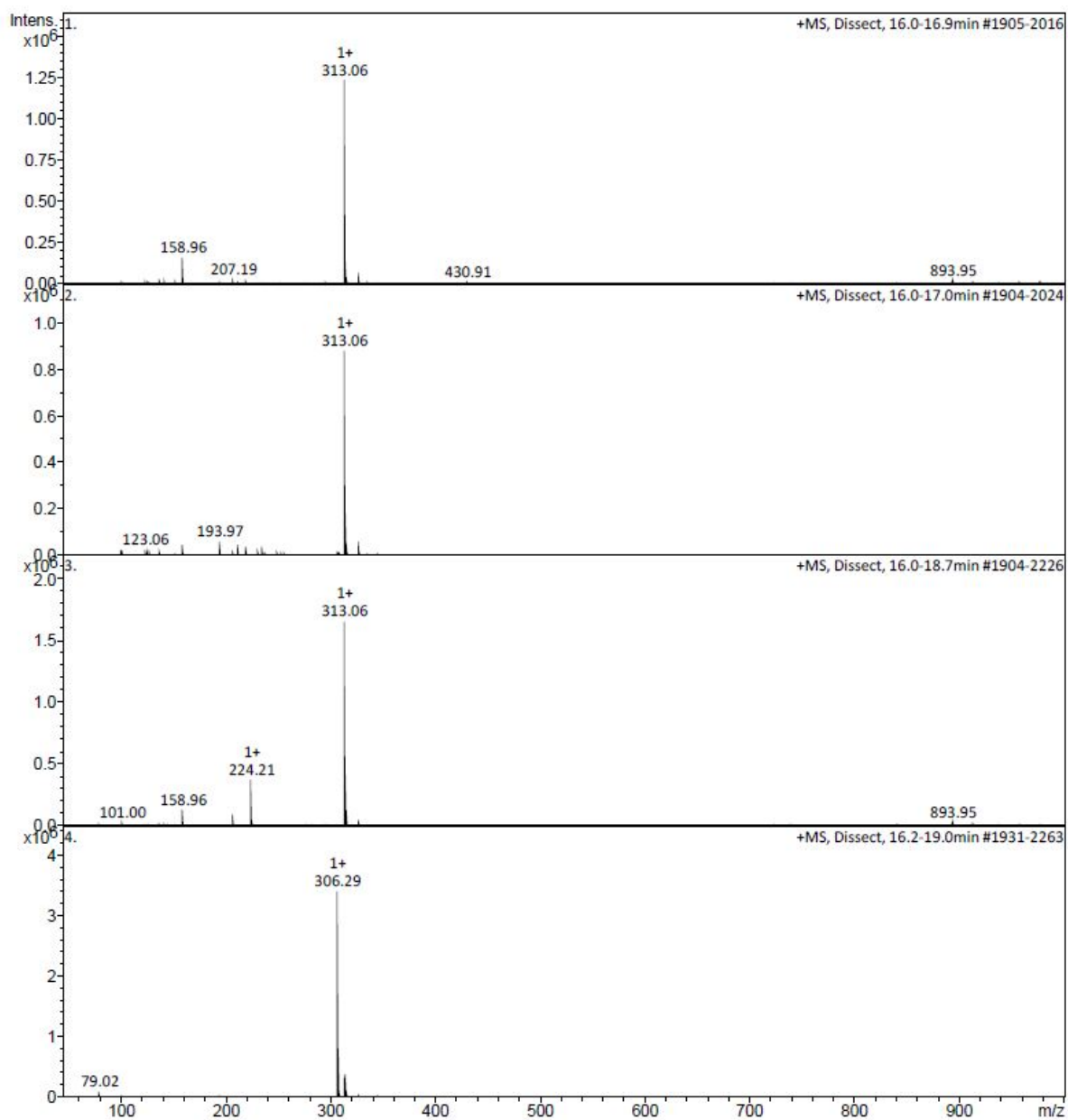
### **The Interplay of Nanoconfinement and pH from the Perspective of a Dye-Reporter Molecule**

Robert Brilmayer<sup>+</sup>, Martin Brodrecht<sup>+</sup>, Christoph Kaiser, Hergen Breitzke, Bharti Kumari, Josef Wachtveitl, Gerd Buntkowsky,\* and Annette Andrieu-Brunsen\*

## Characterization Data for MPT-Ph (Compound 2)

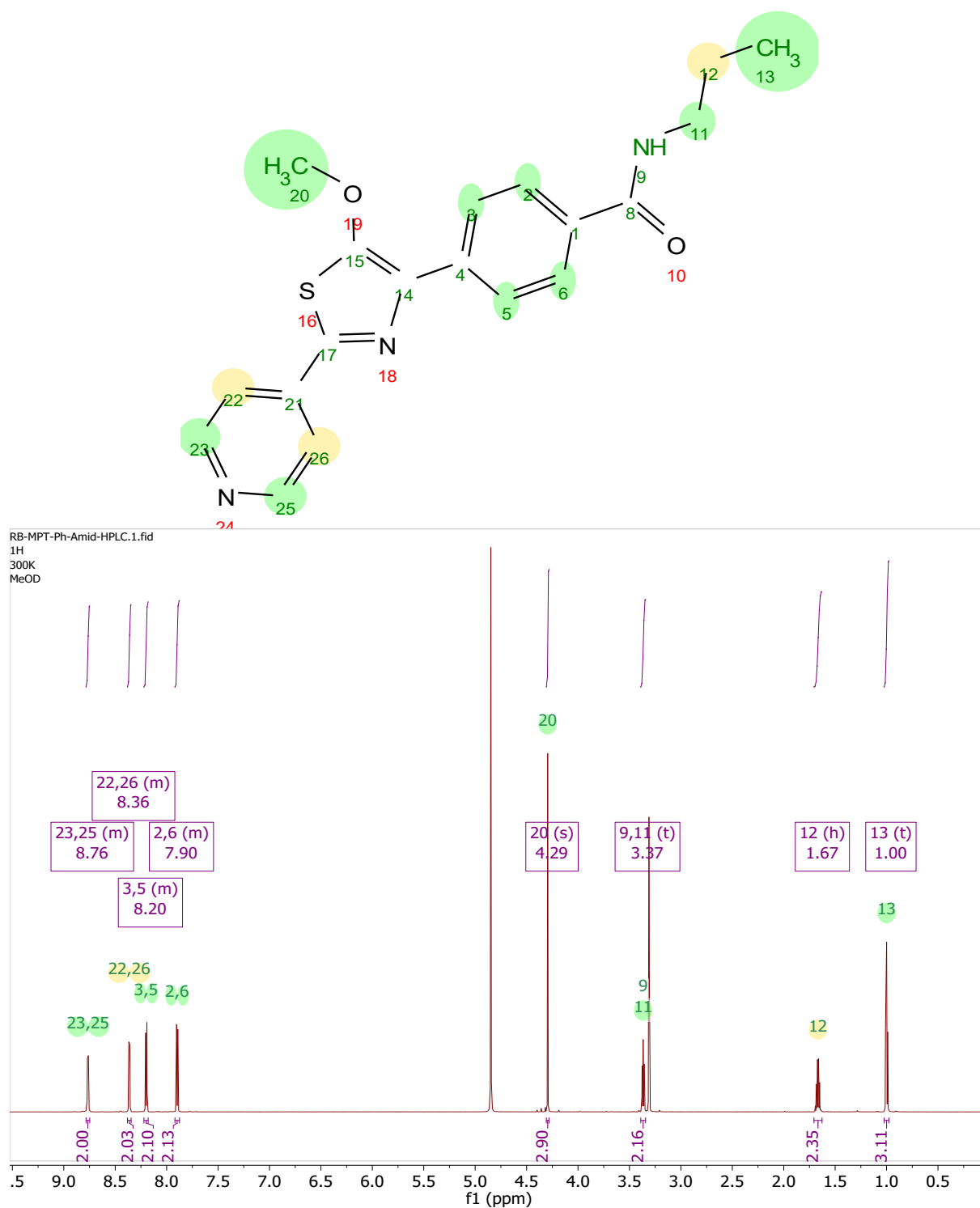


**Figure S1.**  $^1\text{H-NMR}$  of compound 2 MPT-Ph.  $^1\text{H NMR}$  (700 MHz,  $\text{DMSO-d}_6$ )  $\delta$  8.67 (d,  $J = 5.7$  Hz, 2H), 8.25 (d,  $J = 6.0$  Hz, 2H), 7.96 (d,  $J = 8.2$  Hz, 2H), 7.81 (d,  $J = 8.2$  Hz, 2H), 4.06 (s, 3H).

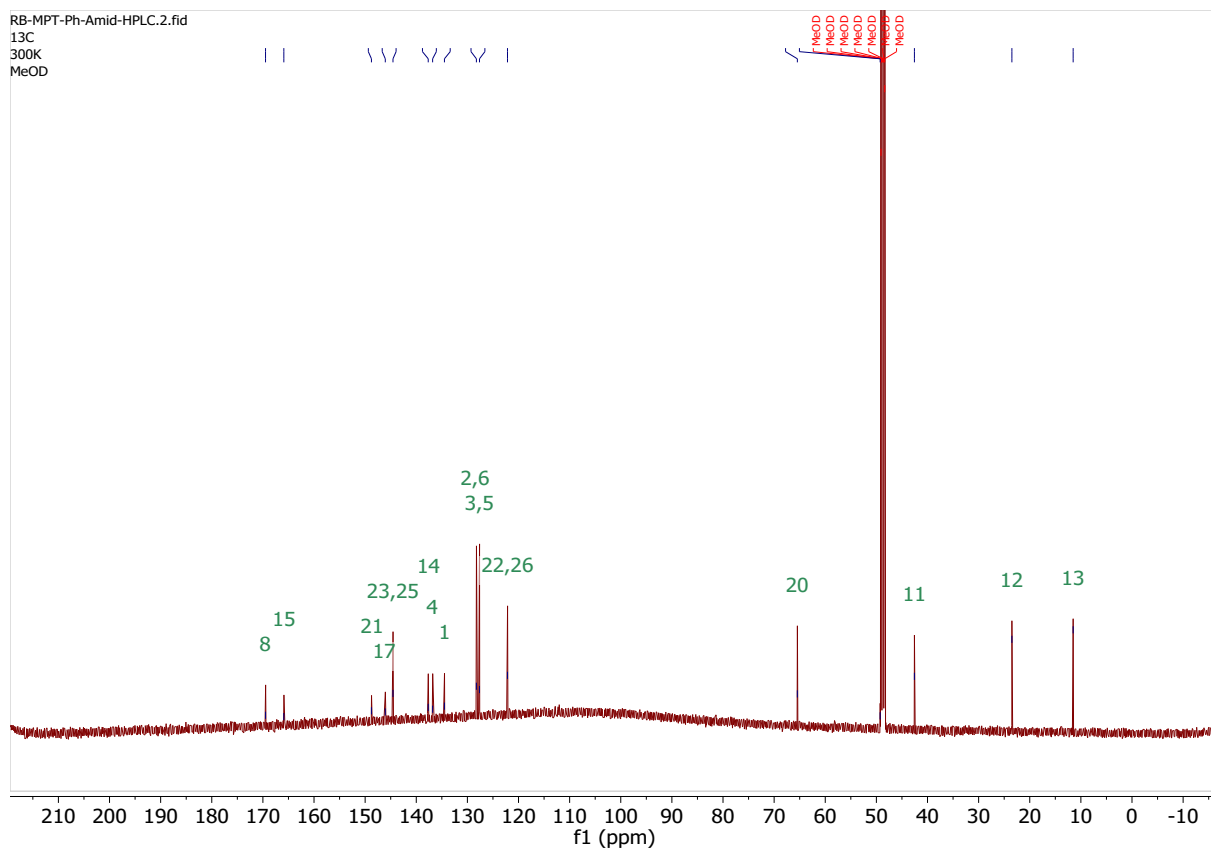


**Figure S2.** ESI-MS spectrum of compound 2 MPT-Ph.

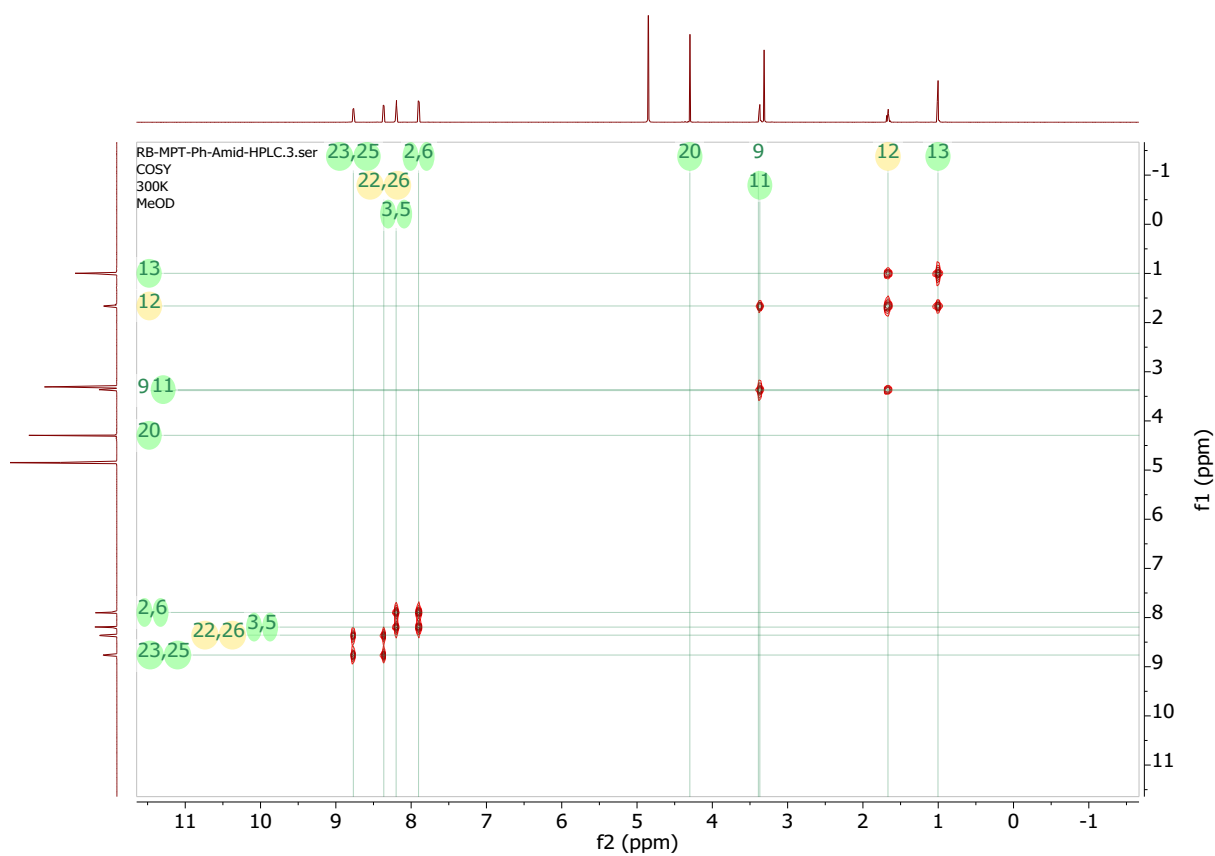
### Characterization Data for MPT-Ph-Amide (Compound 3)



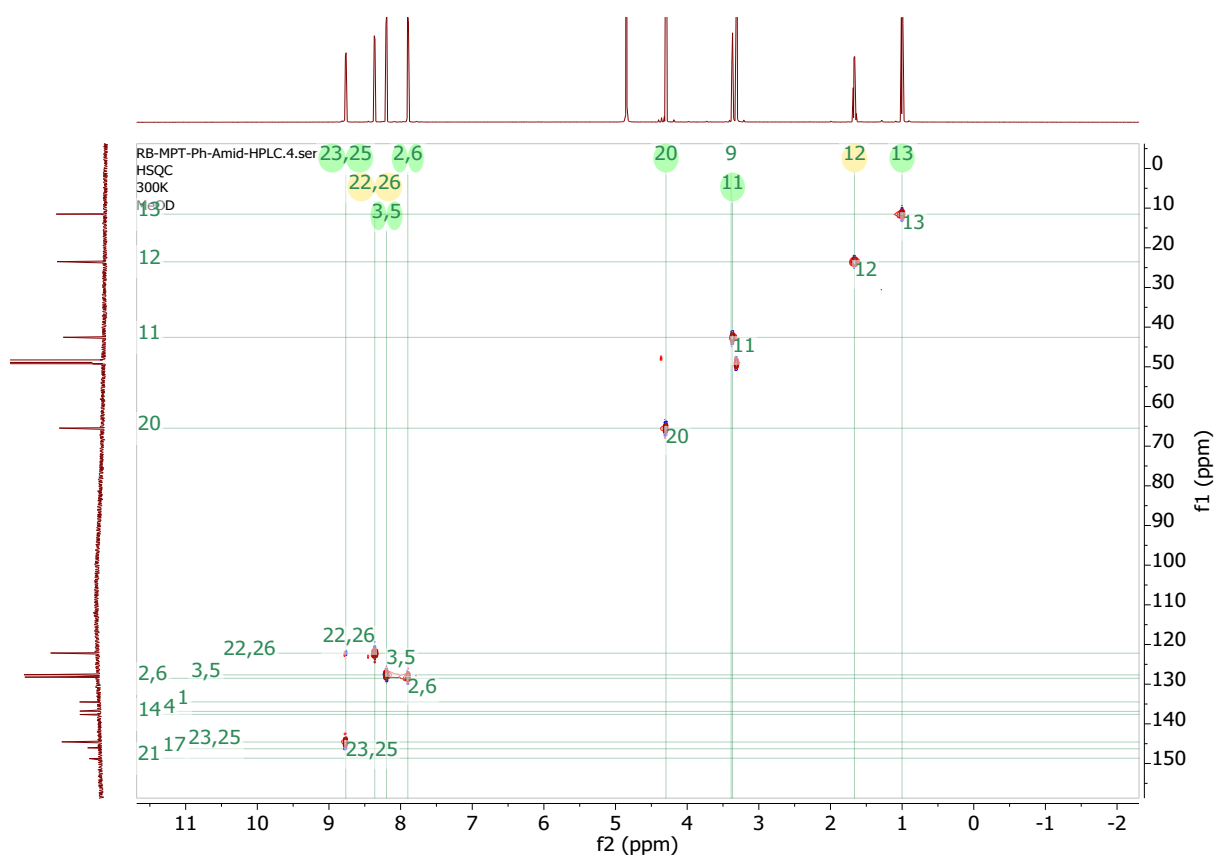
**Figure S3.** Chemical structure (top) and <sup>1</sup>H-NMR (bottom) of compound 3 MPT-Ph-Amide.



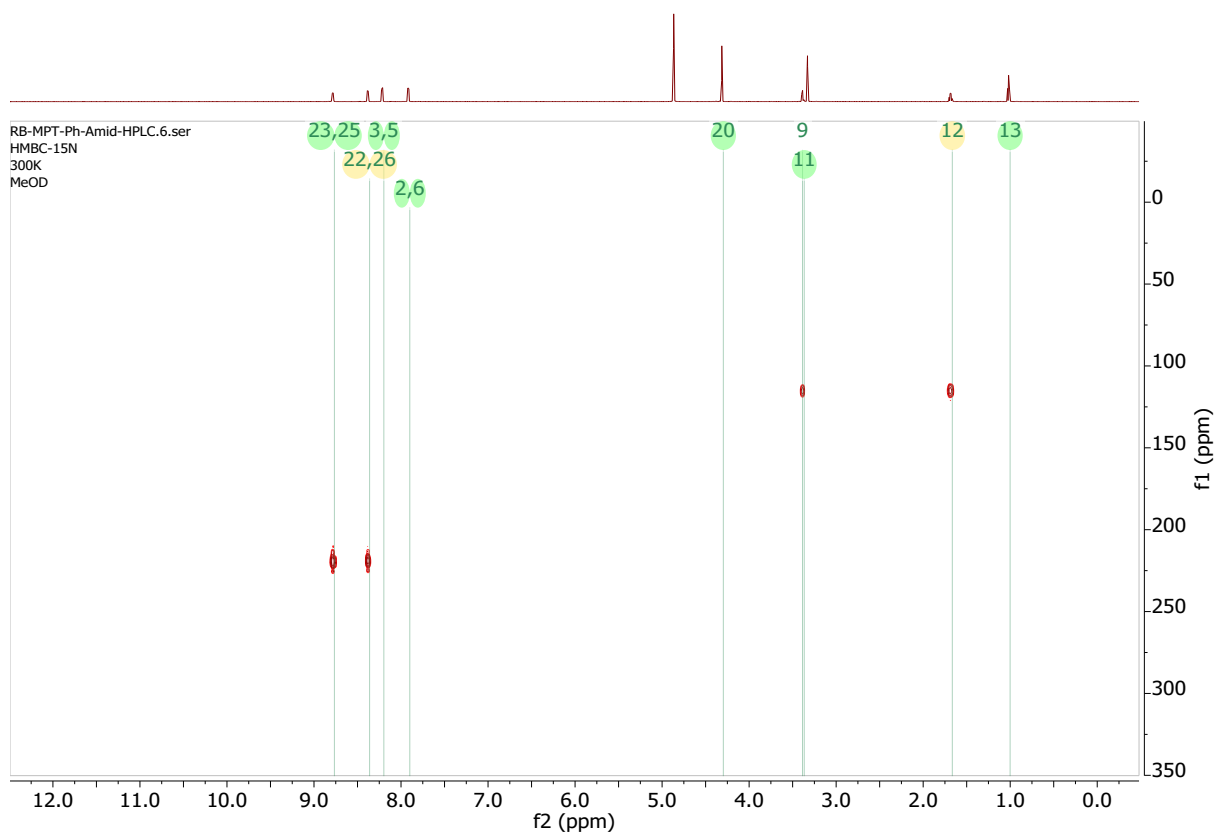
**Figure S4.**  $^{13}\text{C}$ -NMR spectrum of compound 3 MPT-Ph-Amide.



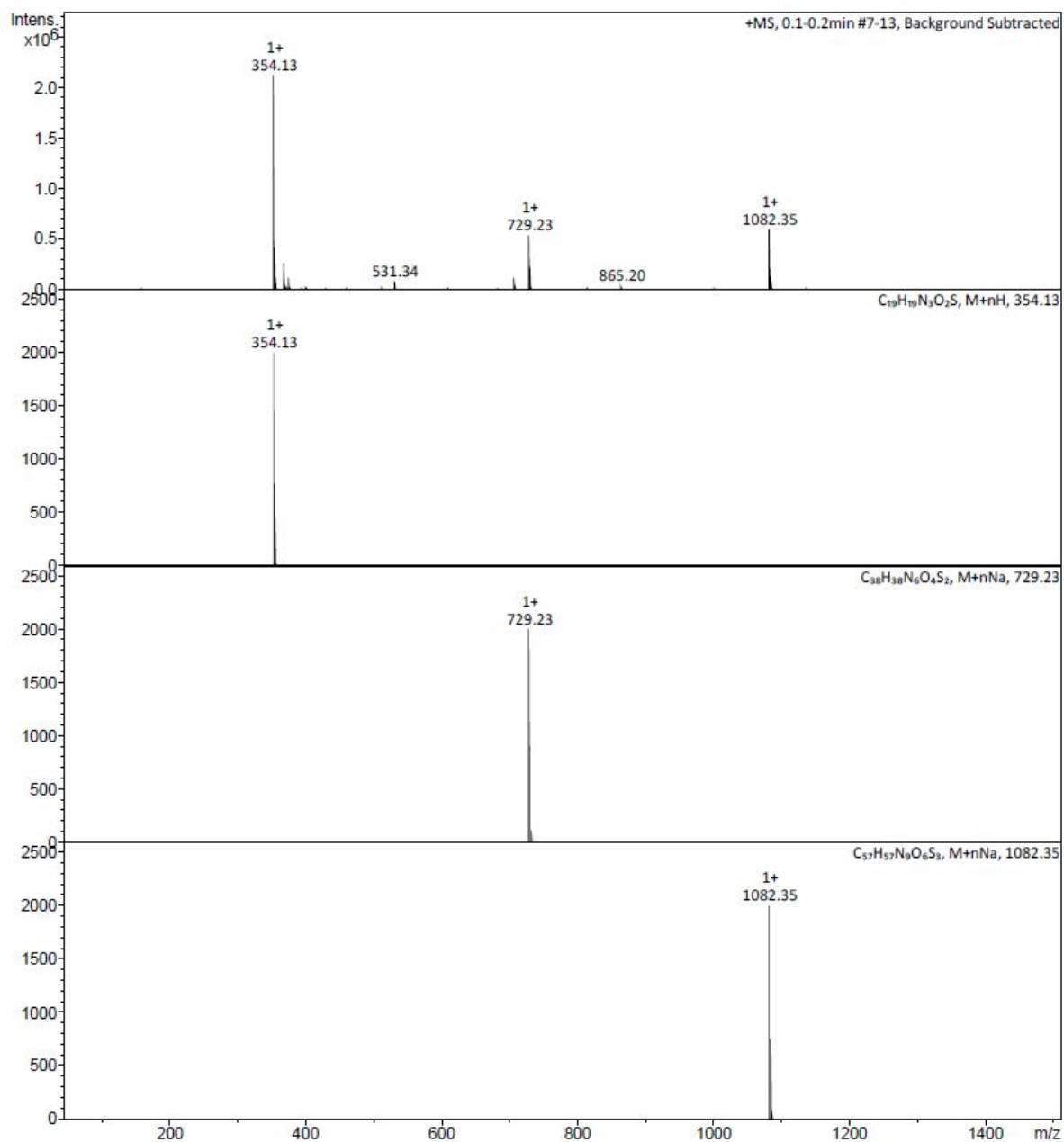
**Figure S5.**  $^1\text{H}$ -COSY-NMR spectrum of compound 3 MPT-Ph-Amide.



**Figure S6.**  $^1\text{H}$ - $^{13}\text{C}$ -HSQC-NMR spectrum of compound 3 MPT-Ph-Amide.

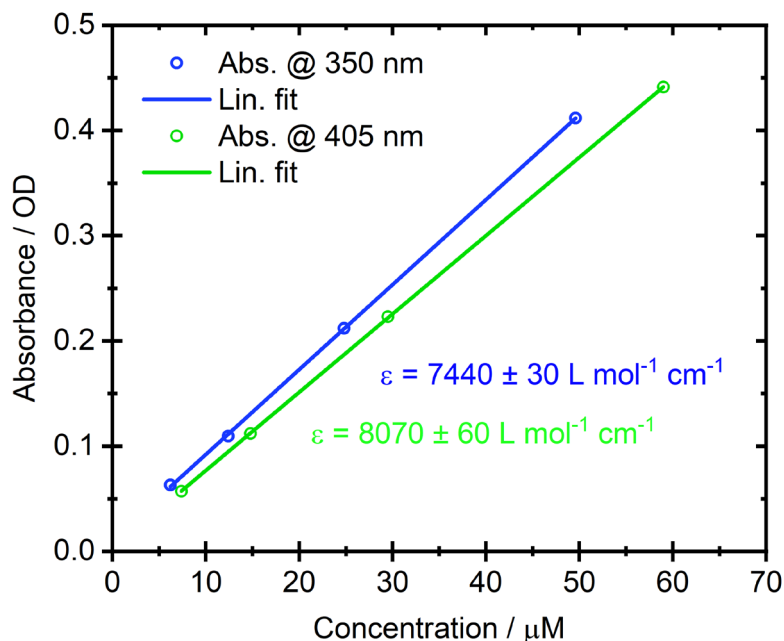


**Figure S7.**  $^1\text{H}$ - $^{15}\text{N}$ -HMBC-NMR spectrum of compound 3 MPT-Ph-Amide.



**Figure S8.** ESI-MS spectrum of compound 3 MPT-Ph-Amide.

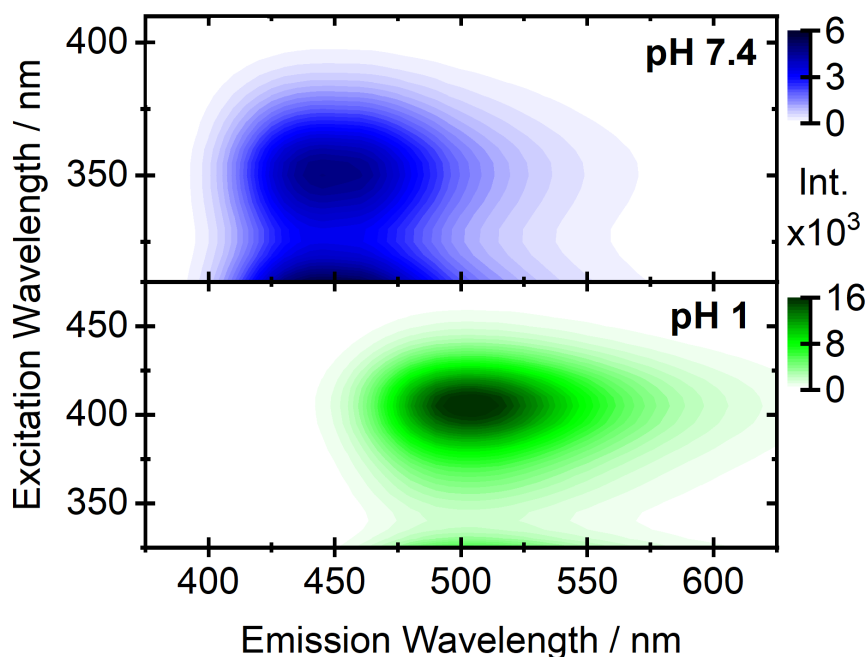
## Optical Properties of MPT-Ph (Compound 2)



**Figure S9.** Plot of the absorbance values at the maximum of the UV/vis absorption band of a dilution series depending on the respective concentrations at pH 7.4 (MPT-Ph, blue) and at pH 1 (MPT-Ph- $\text{H}^+$ , green). Datapoints (circles) were fit linearly (solid lines) and the molar extinction coefficients were determined from the slope of the fits.

To determine the molar extinction coefficients of the deprotonated (pH 7.4) and the protonated (pH 1) form of MPT-Ph, UV/vis absorbance spectra of a dilution series with known concentrations were recorded. The maximum absorbance of the sample solution was kept below 0.5 OD. According to Lambert-Beer's law, the extinction of a sample correlates linearly to its concentration, with the path length of the cuvette and the molar extinction coefficients as proportionality factors. Hence, the extinction coefficient can be derived from the linear regression of the absorbance values plotted against the corresponding concentrations.



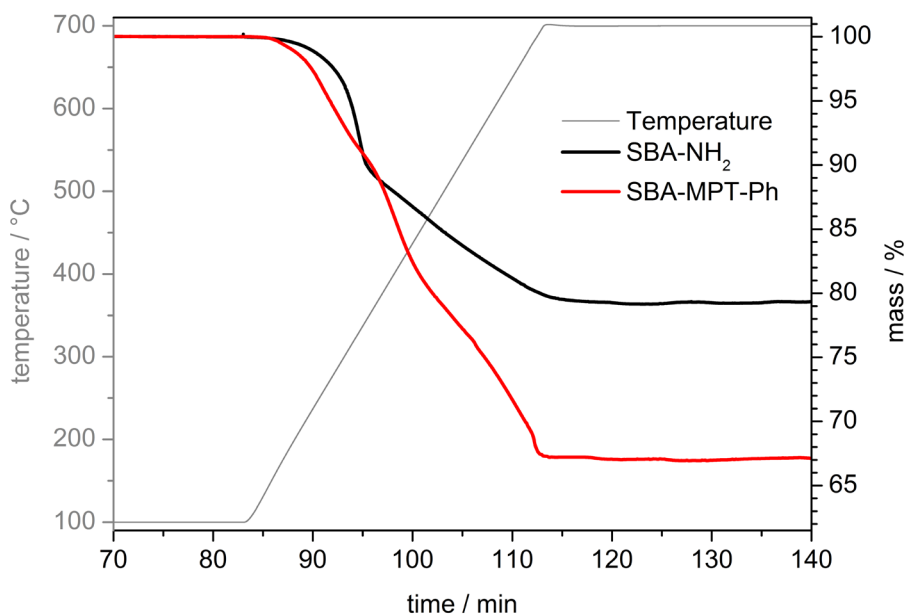


**Figure S10.** Excitation-wavelength dependent emission contour plots of MPH-Ph at pH 7.4 (upper panel, blue) and at pH 1 (lower panel, green).

To determine the fluorescence quantum yields, emission spectra of MPH-Ph at pH 7.4 and 1 were recorded and also spectra of the respective solvents to obtain the scattering light peak. The quantum yield  $\Phi$  is defined as the quotient  $\frac{n_{em}}{n_{abs}}$ , where  $n_{em}$  is the number of emitted photons and  $n_{abs}$  the number of absorbed photon. The number  $n_{em}$  is obtained by integrating the emission signal of the sample and  $n_{abs}$  corresponds to the difference of the scattering light peak intensity of the solvent and the sample measurement.

### Thermogravimetric analysis (TGA)

Thermo gravimetric analysis (TGA) was performed using a TG 209 F3 Tarsus from NETZSCH Thermal Analysis. Synthetic air was used as purge gas. The heating/cooling rates in all experiments were set to 20 K/min for all non-isothermal steps. To dry the samples, they were heated to 100°C and held at 100°C for 75 min. For organic decomposition the samples were heated to 700°C and held at this temperature for another 30 min to guarantee total decomposition.



**Figure S11.** Comparison of the TGA curves of the NH<sub>2</sub>-functionalized SBA-15 (black) and the MPT-Ph dye functionalized SBA-15 (red) (right axis). The temperature profile for the measurement is shown in grey (left axis).

**Table S1.** Weight fractions and its change ( $\Delta$ ) after MPT-Ph dye coupling obtained by thermogravimetric analysis.

Sample	organic content [wt%]	SiO <sub>2</sub> content [wt%]
SBA-NH <sub>2</sub>	20.8 ± 0.2	79.2 ± 0.2
SBA-MPT-Ph	32.5 ± 0.5	67.5 ± 0.5
$\Delta$	11.7 ± 0.7	11.7 ± 0.7

The organic content of the sample changes from 20.8% to 32.5% after MPT-Ph dye coupling. Assuming the mass change is only influenced by the introduced dye with a molecular mass of 353.44 g/mol the dye loading can be calculated as 0.33 mmol/g ± 0.02 by thermogravimetric analysis.

### Elemental analysis (EA)

Elemental analysis was performed with a VarioEL III CHN from Elementar. 2-3 mg of the samples were combusted under O<sub>2</sub> atmosphere. This results in the formation of CO<sub>2</sub>, NO<sub>x</sub>, H<sub>2</sub> and H<sub>2</sub>O. The NO<sub>x</sub> compounds were reduced to N<sub>2</sub> using elemental copper. The gases were separated by gas chromatography and detected quantitatively by a thermal conductivity detector (TCD). Acetanilide was used for calibration.

**Table S2.** Weight fractions of the samples obtained by elemental analysis.

Sample	N content [wt%]	C content [wt%]	H content [wt%]	Si + O content [wt%]
SBA-NH <sub>2</sub>	2.9 ± 0.0	8.9 ± 0.1	3.7 ± 0.1	84.5 ± 0.2
SBA-MPT-Ph	4.4 ± 0.1	19.5 ± 0.2	3.1 ± 0.1	72.9 ± 0.3

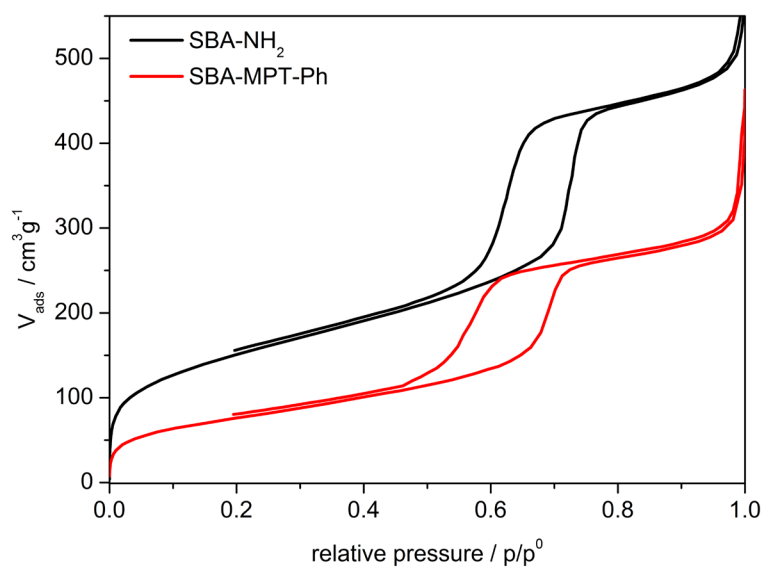
**Table S3.** Molar nitrogen and carbon content of the samples and its change ( $\Delta$ ) after MPT-Ph dye coupling obtained by elemental analysis.

Sample	Nitrogen content [mmol/g]	Carbon content [mmol/g]
SBA-NH <sub>2</sub>	2.1 ± 0.0	7.4 ± 0.1
SBA-MPT-Ph	3.2 ± 0.1	16.3 ± 0.2
$\Delta$	1.1 ± 0.1	8.8 ± 0.3

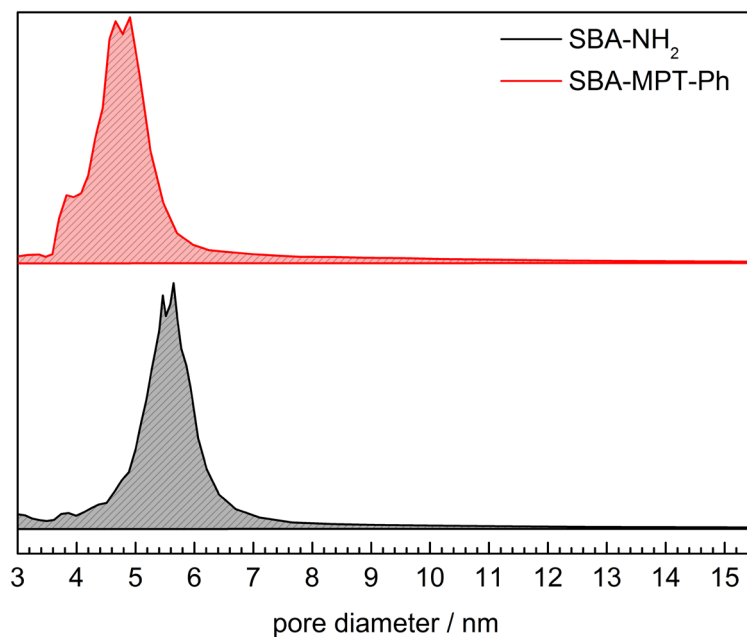
Considering the amount of nitrogen (2) and carbon (16) atoms introduced by the MPT-Ph dye this results in a dye loading of  $0.54 \pm 0.05$  mmol/g or  $0.55 \pm 0.02$  mmol/g respectively obtained by elemental analysis.

### Brunauer–Emmett–Teller (BET)

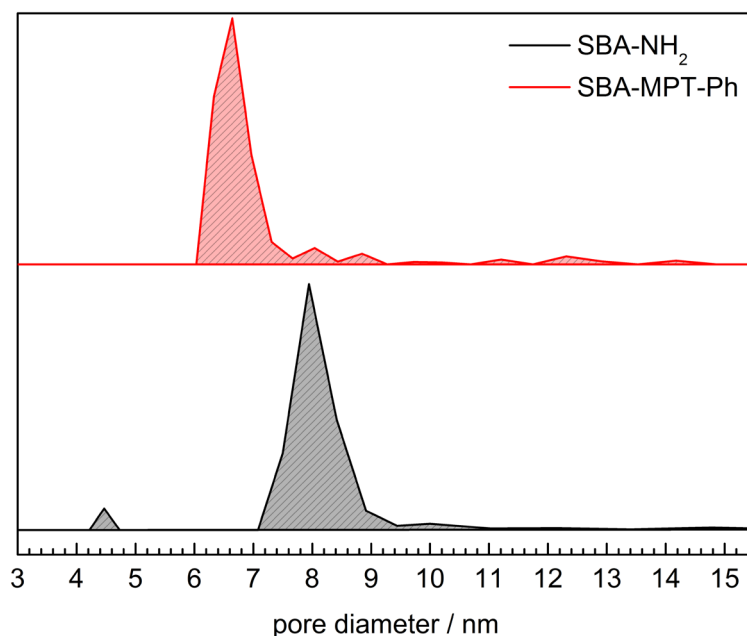
The porosity and specific surfaces area of the materials were characterized by nitrogen adsorption at 77 K, employing a Thermo Fisher Scientific Surfer BET analyzer using N<sub>2</sub> gas as adsorbent. The specific surface was obtained by the Brunauer Emmett Teller (BET) method analyzing the curve in the  $p/p^0$  range between 0.03 and 0.3. The pore volume was obtained by the Gurvich method and the  $p/p^0$  value at 0.95 was used. Pore size distributions were obtained by applying the Barrett-Joyner-Halenda (BJH) analyzing the adsorption-desorption isotherms in the  $p/p^0$  range between 0.3 and 0.95 and nonlocal density functional theory (NLDFT) method.



**Figure S12.** N<sub>2</sub> adsorption–desorption isotherms of the NH<sub>2</sub>-functionalized SBA-15 (black) and the MPT-Ph dye functionalized SBA-15 (red).



**Figure S13.** Normalized BJH curves calculated from the nitrogen adsorption-desorption isotherms of the NH<sub>2</sub>-functionalized SBA-15 (black) and the MPT-Ph dye functionalized SBA-15 (red). For clarity, results for different samples are vertically shifted.



**Figure S14.** Normalized NLDFT curves calculated from the nitrogen adsorption-desorption of the NH<sub>2</sub>-functionalized SBA-15 (black) and the MPT-Ph dye functionalized SBA-15 (red). For clarity, results for different samples are vertically shifted.

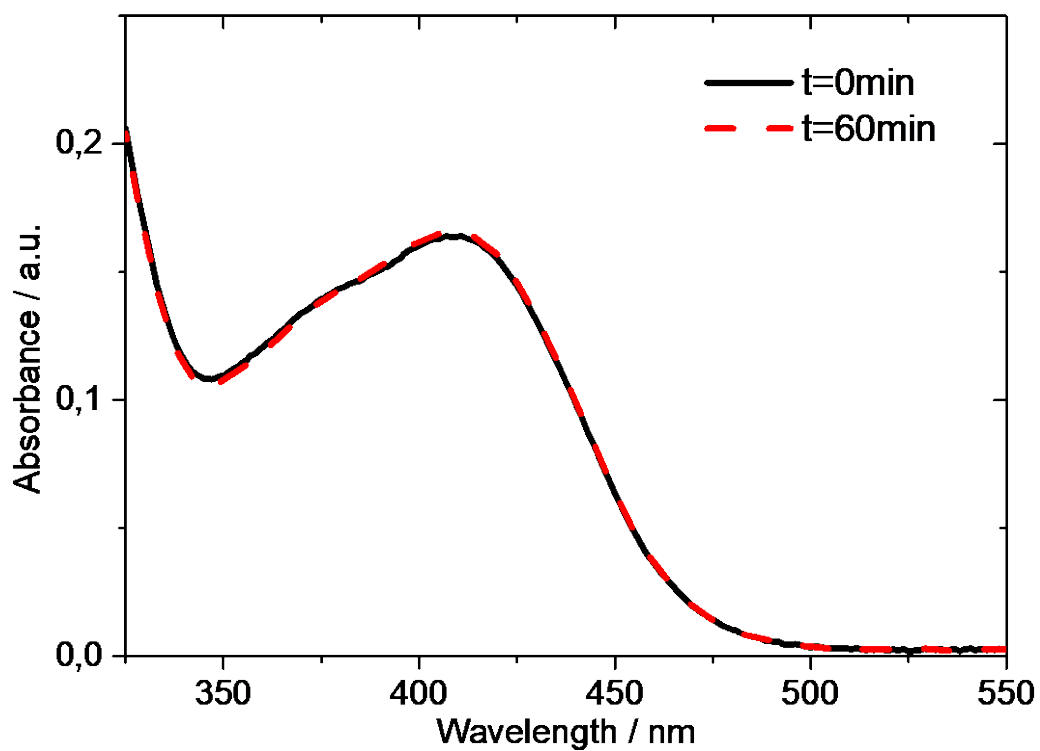
**Table S4.** Pore volume (Gurvich at  $p/p^0$  0.95), specific surface area (BET) and median pore diameters calculated by the BJH (left) and NLDFIT (right) method as obtained from BET analysis.

Sample	Pore volume [cm <sup>3</sup> /g]	Surface Area [m <sup>2</sup> /g]	Pore diameter by BJH (nm)	Pore diameter by NLDFIT (nm)
SBA-NH <sub>2</sub>	0.74 ± 0.02	545 ± 16	5.6 ± 0.2	7.9 ± 0.2
SBA-MPT-Ph	0.45 ± 0.01	271 ± 7	4.9 ± 0.3	6.6 ± 0.3

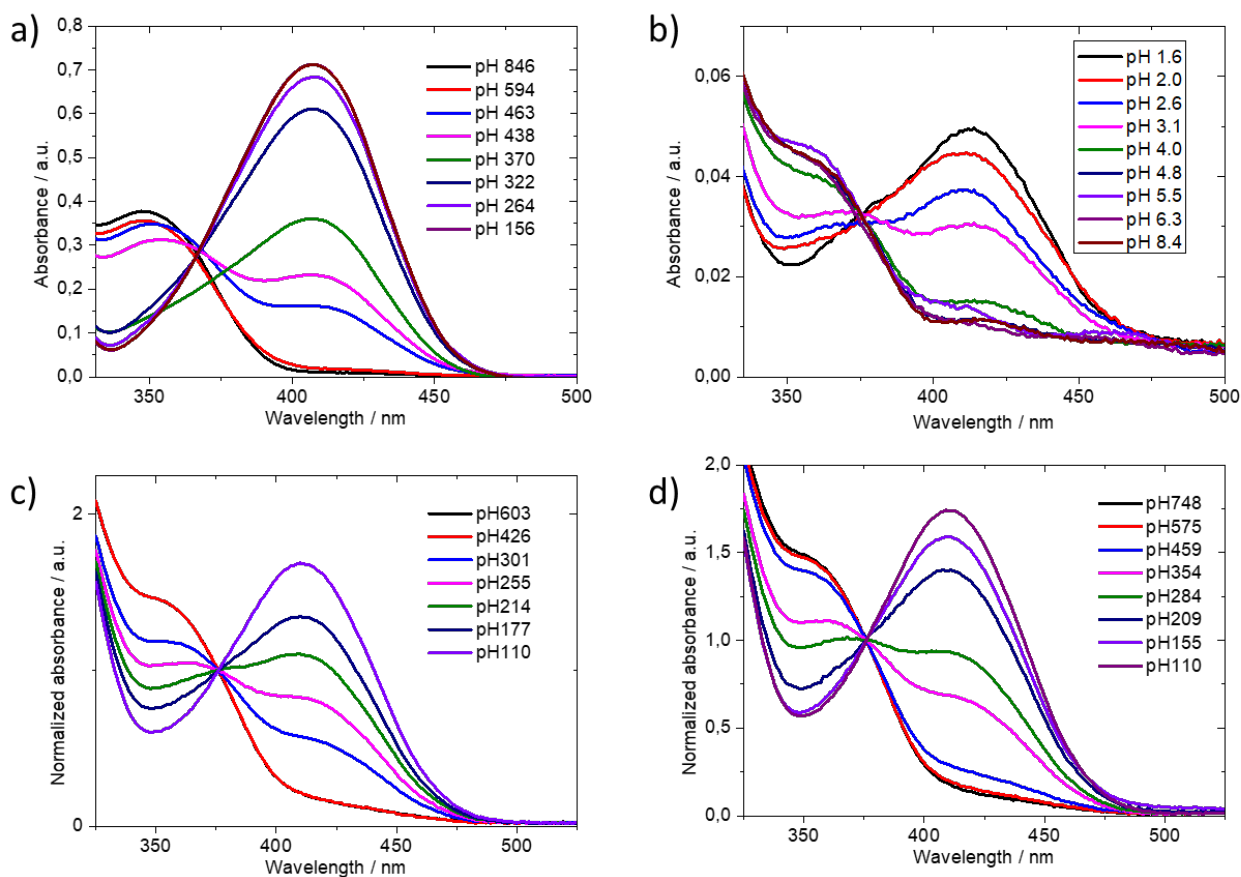
Taking into account the obtained BET surface for the functionalized SBA-15 support of 271 m<sup>2</sup>/g, and the obtained MPT-Ph dye loading obtained by elemental analysis (~0.55 mmol/g) and thermogravimetric analysis (~0.33 mmol/g), the surface grafting density can be calculated by

$$\text{Molecules/nm}^2 = \frac{\text{dye loading [mol/g]}}{\text{specific surface area [m}^2\text{/g]}} \times N_a \quad (1)$$

This results in a MPT-Ph dye surface grafting density between 0.7 and 1.2 dye molecules/nm<sup>2</sup>.

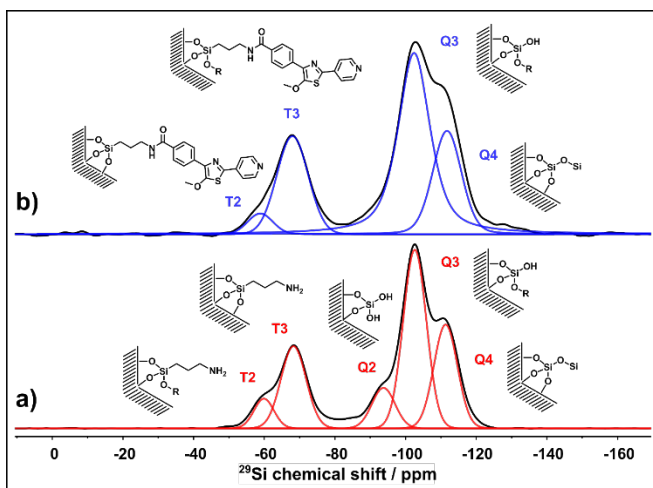


**Figure S15.** UV-vis measurements of a MPT-Ph functionalized mesoporous silica film that was kept in the measurement solution for 60 minutes. Measurements were taken at t t=0 minutes (black solid line) and t=60 minutes (red dashed line).



**Figure S16.** Measured UV-vis spectrums of MPT-Ph-Amide and MPT-Ph functionalized mesoporous silica films at different pH values. Measurements shown leads to the data shown in Figure 6 in the main manuscript. a) corresponds to Figure 5a MPT-Ph-Amide (black spheres); b) corresponds to Figure 5a MPT-Ph-Surface on a 700 nm big pore film (red spheres); c) corresponds to Figure 5b MPT-Ph grafted on a mesoporous silica thin film with big pores and a film thickness of  $\sim 500$  nm. Measurements conducted at an ionic strength of 0.1xPBS (15 mM) (blue spheres); d) corresponds to Figure 5b MPT-Ph grafted on a mesoporous silica thin film. Measurements conducted at an ionic strength of 1xPBS (150 mM) (black spheres).





**Figure S17.** Comparison of the  $^{29}\text{Si}$  CP MAS spectra of the functionalized SBA-15 at 5 kHz spinning. From bottom to the top spectra of the APTES functionalized SBA-15 (a), and MPT-Ph dye functionalized SBA-15 (b).

The  $^{29}\text{Si}$  CP MAS spectrum of the APTES functionalized SBA-15 (Figure S17 a) shows signals between -120 ppm and -85 ppm, which are assigned to the Q-groups of the bulk silica material. Additional signals are present between -80 ppm and -50 ppm, which are attributed to T-groups that represent the covalent binding of the APTES linker to the silica surface.<sup>[1]</sup> Since the APTES functionalized SBA-15 is synthesized by a co-condensation route Q- and T-groups are both present. After functionalization with the MPT-Ph dye (Figure S17 b) two sets of signals between -125 ppm and -85 ppm and -80 ppm and -55 ppm are present. Again, these can be attributed to the Q- and T-groups. Comparing the two spectra the signal of the Q2-group drastically decrease after the MPT-Ph dye functionalization step. Furthermore, the signal of the T2-group seems to decrease in intensity in favor of the signal of the T3-group. Both observations hint a condensation of some surface silica species due to MPT-Ph dye functionalization. The presence of T-groups in both spectra proof covalent binding of the APTES linker carbons to the surface silicon atoms.

## References

- [1] M. Brodrecht, H. Breitzke, T. Gutmann, G. Buntkowsky, *Chemistry* **2018**, *24*, 17814-17822.