

Supporting Information

Probing the Molecular Character of Periodic Mesoporous Organosilicates via Photoluminescence of Lewis Acid-Base Adducts

*Indre Thiel,^[a] Alexey Fedorov,^[a] Rene Verel,^[a] Sergii Yakunin,^[a]
Maksym V. Kovalenko^[a] and Christophe Copéret*^[a]*

^[a] Department of Chemistry and Applied Biosciences, ETH Zürich, Vladimir-Prelog-Weg 1–5,
CH-8093 Zürich (Switzerland)

E-mail: ccoperet@ethz.ch

Table of Contents

GENERAL INFORMATION	3
EXPERIMENTAL PROCEDURES	4
3-BROMO-2-METHYL-6-(4-(TRIMETHYLSILYL)PHENYL)PYRIDINE (A, SCHEME S1)	4
3-IODO-2-METHYL-6-(4-(TRIMETHYLSILYL)PHENYL)PYRIDINE (B, SCHEME S1).....	6
3-IODO-2-METHYL-6-(4-IODOPHENYL)PYRIDINE (C, SCHEME S1)	8
3-TRIETHOXSILYL-2-METHYL-6-(4-TRIETHOXSILYLPHENYL)PYRIDINE (D, SCHEME 1)	9
MATERIAL SYNTHESIS	11
SYNTHESIS OF PPY ^{Me} -PMO	11
SYNTHESIS OF PPY-PMO AND BIPH-PMO	14
PASSIVATION OF MATERIALS	15
IMPREGNATION OF MATERIALS.....	15
¹¹ B ssNMR AND MQMAS DATA	19
PHOTOLUMINESCENCE DATA	20
SAMPLE PREPARATION FOR PL MEASUREMENTS	20
REFERENCES	23

CHARACTERISATION DATA

Figure S1. ¹ H NMR spectrum of 3-bromo-2-methyl-6-(4-(trimethylsilyl)phenyl)pyridine.....	5
Figure S2. ¹³ C NMR spectrum of 3-bromo-2-methyl-6-(4-(trimethylsilyl)phenyl)pyridine	6
Figure S3. ¹ H NMR spectrum of 3-iodo-2-methyl-6-(4-(trimethylsilyl)phenyl)pyridine	7
Figure S4. ¹³ C NMR spectrum of 3-iodo-2-methyl-6-(4-(trimethylsilyl)phenyl)pyridine	7
Figure S5. ¹ H NMR spectrum of 3-iodo-2-methyl-6-(4-iodophenyl)pyridine	8
Figure S6. ¹³ C NMR spectrum of 3-iodo-2-methyl-6-(4-iodophenyl)pyridine	9
Figure S7. ¹ H NMR spectrum of 3-triethoxysilyl-2-methyl-6-(4-triethoxysilylphenyl)pyridine.....	10
Figure S8. ¹³ C NMR spectrum of 3-triethoxysilyl-2-methyl-6-(4-triethoxysilylphenyl)pyridine	10
Figure S9. N ₂ Adsorption/Desorption isotherm for ppy ^{Me} -PMO	11
Figure S10. Powder-XRD spectrum of ppy ^{Me} -PMO	11
Figure S11. Transition electron micrograph images of ppy ^{Me} -PMO	12
Figure S12. ¹ H MAS NMR spectrum of ppy ^{Me} -PMO (spinning rate 10 kHz)	13
Figure S13. ¹³ C CP MAS NMR spectrum of ppy ^{Me} -PMO (spinning rate 10 kHz, contact time 600 μs).....	13
Figure S14. ²⁹ Si CP MAS spectrum NMR of ppy ^{Me} -PMO (spinning rate 10 kHz, contact time 5 ms)	14
Figure S15. DRIFT-IR spectra of ppy ^{Me} -PMO (A), ppy ^{Me} -PMO _{pas} (B) and B-ppy ^{Me} -PMO _{pas} (C)	17
Figure S16. DRIFT-IR spectra of B-ppy ^{Me} -PMO _{pas} (A), B-biph-PMO _{pas} (B) and B(C ₆ F ₅) ₃ (C).....	18
Figure S18. ¹¹ B ssNMR of B(C ₆ F ₅) ₃ (spinning rate 20kHz).....	19
Figure S19. Zoomed in overlay of ¹¹ B MQMAS of B-ppy-PMO _{pas} (red) and B(C ₆ F ₅) ₃ + ppy adduct (blue) (128 MHz, spinning rate 20kHz).	19
Figure S20. Photograph of samples for PL measurements irradiated at 366 nm.....	20
Figure S21. DRIFT UV-VIS spectra (A) and overlay of PL spectra of ppy ^{Me} -derivatives (B), ppy ^{Me} -derivatives (C) and biph-derivatives (D).	21
Figure S22. PL decay of ppy ^{Me} + B(C ₆ F ₅) ₃	22
Figure S23. PL decay of ppy + B(C ₆ F ₅) ₃	22
Figure S24. PL decay of B-ppy ^{Me} -PMO _{pas}	23
Figure S25. PL decay of B-ppy-PMO _{pas}	23

General Information

All reactions were carried out under an inert gas atmosphere using standard Schlenk and glove box techniques. DCM, Et₂O and toluene were purified by passage through double solvent purification alumina columns (MBraun) and degassed prior to utilization. THF was dried over and vacuum transferred from purple sodium/benzophenone ketyl. NEt₃ was dried over CaH₂. Dry DMF was purchased from Sigma Aldrich.

All liquid phase NMR measurements were done on a Bruker DPX-300 MHz instrument using CDCl₃ as a solvent, if not stated otherwise. The ¹H and ¹³C chemical shifts are referred to TMS and calibrated with the residual solvent peak. High-resolution mass spectra were measured by the MS-service of the Laboratorium für Organische Chemie, ETH Zürich. Values are given as m/z and the intensity (I) is % of the base peak. Elemental analysis was performed by the microelemental analysis service of the Laboratorium für Organische Chemie, ETH Zürich. Melting points were determined on a Büchi Melting Point B-540 apparatus in open capillaries and are uncorrected. All infrared (IR) spectra were recorded using a Bruker FT-IR Alpha spectrometer placed in the glovebox, equipped with OPUS software, and using spectral range 275-7500, resolution < 2 cm⁻¹, RockSolid interferometer, DTGS (triglycine sulphate) detector and SiC globar source. Solid samples were investigated in a magnetic pellet holder. A typical DRIFT-IR experiment consisted of measuring 32 scans in the region from 4000 to 400 cm⁻¹. DRIFT UV-Vis spectra were recorded on a Cary 5000 UV-Vis-NIR spectrophotometer from Agilent Technologies. Solid-state NMR spectra were recorded under MAS conditions on Bruker Advance III 400 or 700 spectrometers with conventional triple resonance 2.5 and 4 mm CP-MAS probe. Samples were introduced in zirconia rotors in the glove box. Electron microscopy was done using the ScopeM facilities, ETH Zürich.

Steady-state photoluminescence spectra were acquired with a Fluorolog iHR 320 Horiba Jobin Yvon spectrofluorimeter, equipped with Xe-lamp and a PMT detector. PL lifetime measurements were performed using a time-correlated single photon counting (TCSPC) setup, equipped with SPC-130-EM counting module (Becker & Hickl GmbH) and an IDQ-ID-100-20-ULN avalanche photodiode (Quantic) for recording the decay traces. The emission of the mesoporous organosilicates in form of powder was excited by a 355 nm (frequency-tripled to 355 nm from fundamental wavelength of Nd:YAG laser Duetto Time-Bandwidth Products) 10 ps laser pulses with a repetition of 72 kHz synchronized to TCSPC counting module through an electronic delay generator (DG535 from Stanford Research Systems). The pump wavelength was filtered by long-pass filter FEL400 from Thorlabs.

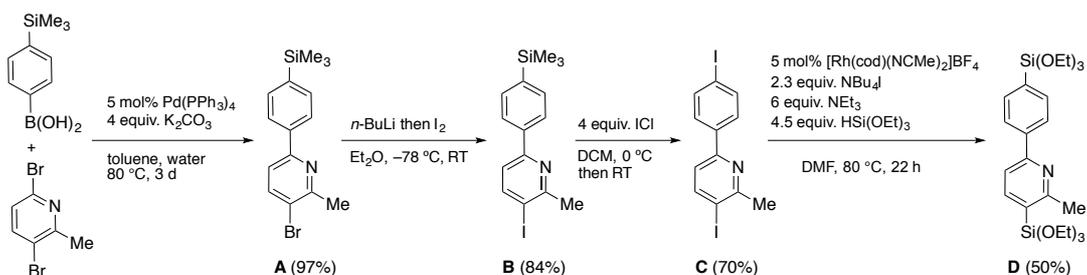
2,5-Dibromo-6-methyl pyridine (AK Scientific), trimethylstearylammonium chloride (TCI), trimethylsilyl bromide (Sigma Aldrich), tris(perfluorophenyl)borane (TCI), tetrakis(triphenylphosphine)palladium (Sigma Aldrich), bis(acetonitrile)(1,5-cyclooctadiene)-rhodium(I) tetrafluoroborate (Strem), iodine monochloride (VWR), *n*-butyl lithium (1.6 M in hexane, Sigma Aldrich), triethoxysilane (Sigma Aldrich), triethylamine (Sigma Aldrich) were

purchased from the respective vendor. Tris(perfluorophenyl)borane was sublimed immediately before use. 4-Trimethylsilylphenylboronic acid was synthesized according to published procedures.^[1]

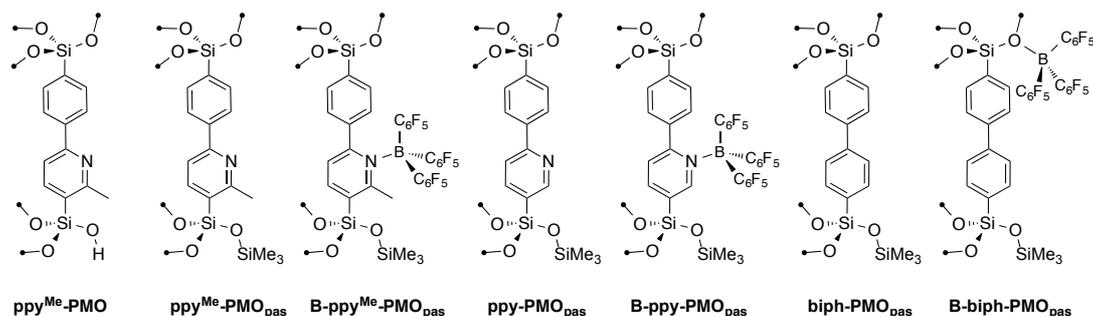
Experimental Procedures

Scheme S1. Synthesis of molecular precursors and PMO materials

Synthesis of molecular precursors



PMO materials



Materials **ppy-PMO_{pas}** and **biph-PMO_{pas}** as well as respective molecular precursors were prepared following literature procedures.^{[1],[2]} Note that boron-impregnated materials **B-ppy-PMO_{pas}** and **B-ppy^{Me}-PMO_{pas}** (Scheme S1) feature both B–O and B–N interactions, as discussed in details in the Manuscript.

3-Bromo-2-methyl-6-(4-(trimethylsilyl)phenyl)pyridine (**A**, Scheme S1)

A 2 L three neck flask was charged with toluene (700 mL) and water (90 mL) and the solvent mixture saturated with N₂ (30 min of purging). 2,5-Dibromo-6-methyl pyridine (12.5 g, 50 mmol) and 4-trimethylsilylphenylboronic acid (9.7 g, 50 mmol, 1 equiv.) were added, followed by Pd(PPh₃)₄ (2.5 g, 4.3 mol%) and K₂CO₃ (27.6 g, 200 mmol, 4 equiv.). The solution was heated to 80 °C and stirred for 3 days before it was cooled down to room temperature. The phases were separated and the organic phase washed with water (2 × 200 ml) and subsequently dried over MgSO₄. Evaporation of the solvent gave yellow oil. Purification by column chromatography on silica (eluent: cyclohexane – dichloromethane, v/v 2:1) yielded **A** as a colorless oil, which solidified upon standing at room temperature (15.5 g, 97%).

¹H NMR δ = 0.30 (s, 9H), 2.74 (s, 3H), 7.42 (d, *J* = 8.6 Hz, 1H), 7.62 (d, *J* = 8.2 Hz, 2H), 7.84 (d, *J* = 8.6 Hz, 1H), 7.94 (d, *J* = 8.2 Hz, 2H)

^{13}C NMR $\delta = -1.0, 25.4, 119.3, 120.1, 126.1, 128.6, 133.9, 139.1, 140.4, 155.8, 157.2$

EI m/z 319.04 [M^+], 304.02 [$\text{M}^+ - \text{CH}_3$]

mp $78\text{ }^\circ\text{C}$

Figure S1. ^1H NMR spectrum of 3-bromo-2-methyl-6-(4-(trimethylsilyl)phenyl)pyridine

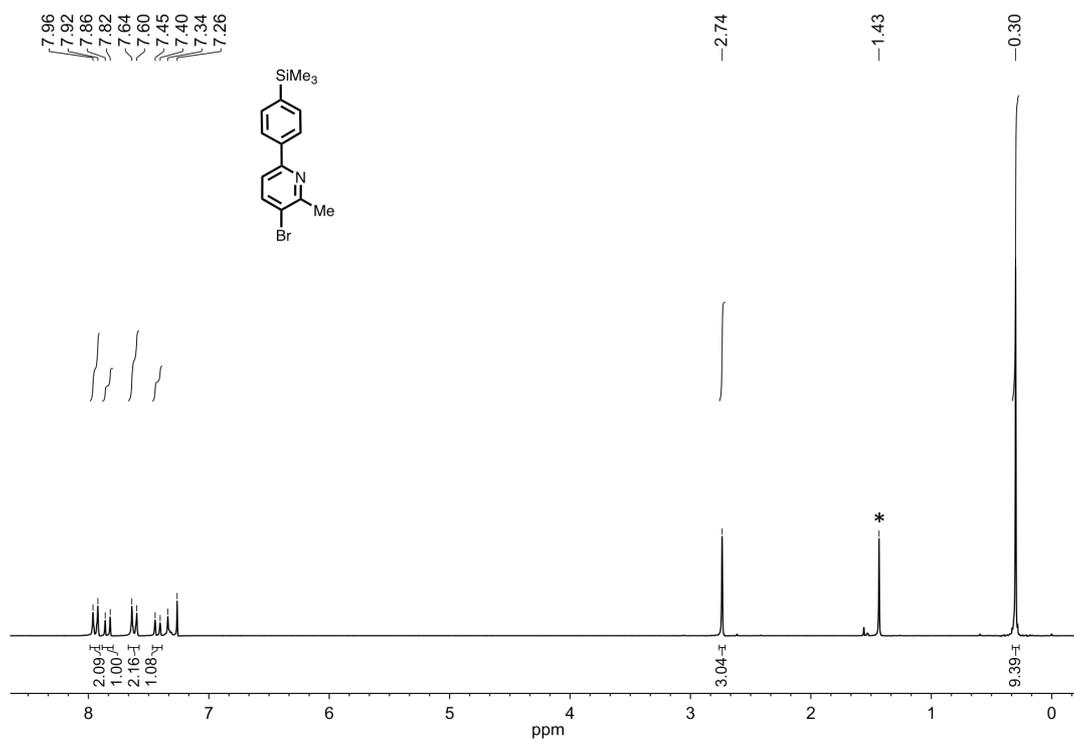
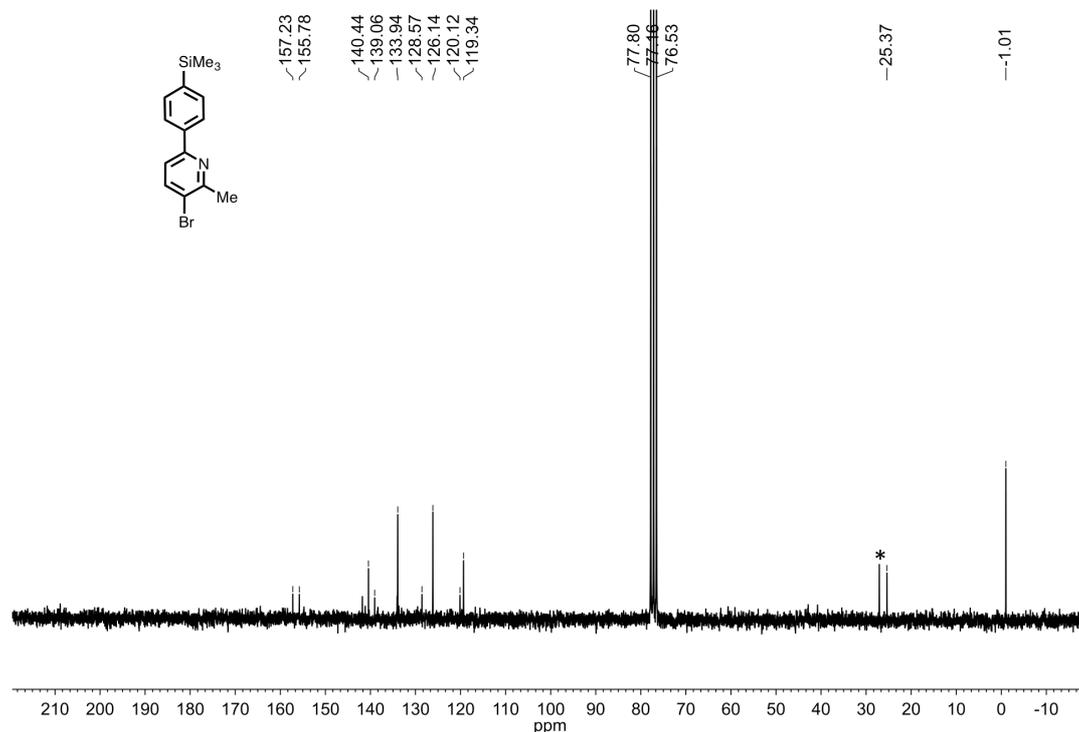


Figure S2. ^{13}C NMR spectrum of 3-bromo-2-methyl-6-(4-(trimethylsilyl)phenyl)pyridine

In **Figures S1** and **S2**, *denotes cyclohexane solvent residue.

3-Iodo-2-methyl-6-(4-(trimethylsilyl)phenyl)pyridine (**B**, Scheme S1)

3-Bromo-2-methyl-6-(4-(trimethylsilyl)phenyl)pyridine (**A**, 14 g, 44 mmol) was dissolved in diethyl ether (300 mL) and cooled down to $-78\text{ }^{\circ}\text{C}$. *n*-BuLi (1.6 M in hexane, 27.5 mL, 44 mmol, 1 equiv.) was added dropwise to the ether solution, which was then stirred for 2.5 h before a solution of iodine (13.4 g, 53 mmol, 1.2 equiv.) in diethyl ether (150 mL) was slowly added. The reaction mixture was allowed to reach room temperature over night. Water (400 mL) and an aqueous solution of $\text{Na}_2\text{S}_2\text{O}_5$ (1.5 g in 100 mL) were added and the reaction mixture vigorously stirred for 10 min. The organic phase was separated and washed with water ($2 \times 200\text{ ml}$) and the aqueous phase with extracted with dichloromethane ($2 \times 200\text{ ml}$). The combined organic phases were dried over MgSO_4 , filtered and the solvent removed under reduced pressure. Purification via column chromatography on silica (eluent: cyclohexane – ethyl acetate, v/v 10:1) gave **B** as a colorless oil (13.57 g, 84%).

^1H NMR $\delta = 0.29$ (s), 2.81 (s), 7.25, (d, $J = 7.4\text{ Hz}$, 1H), 7.61 (d, $J = 8.1\text{ Hz}$, 2H), 7.94 (d, $J = 7.4\text{ Hz}$, 2H), 8.08 (d, $J = 8.1\text{ Hz}$, 1H)

^{13}C NMR $\delta = -1.0, 29.3, 94.6, 119.3, 126.1, 133.9, 139.1, 141.9, 156.6, 160.1$

EI m/z 367.03 [M^+], 352.00 [$\text{M}^+ - \text{CH}_3$]

Figure S3. ^1H NMR spectrum of 3-iodo-2-methyl-6-(4-(trimethylsilyl)phenyl)pyridine

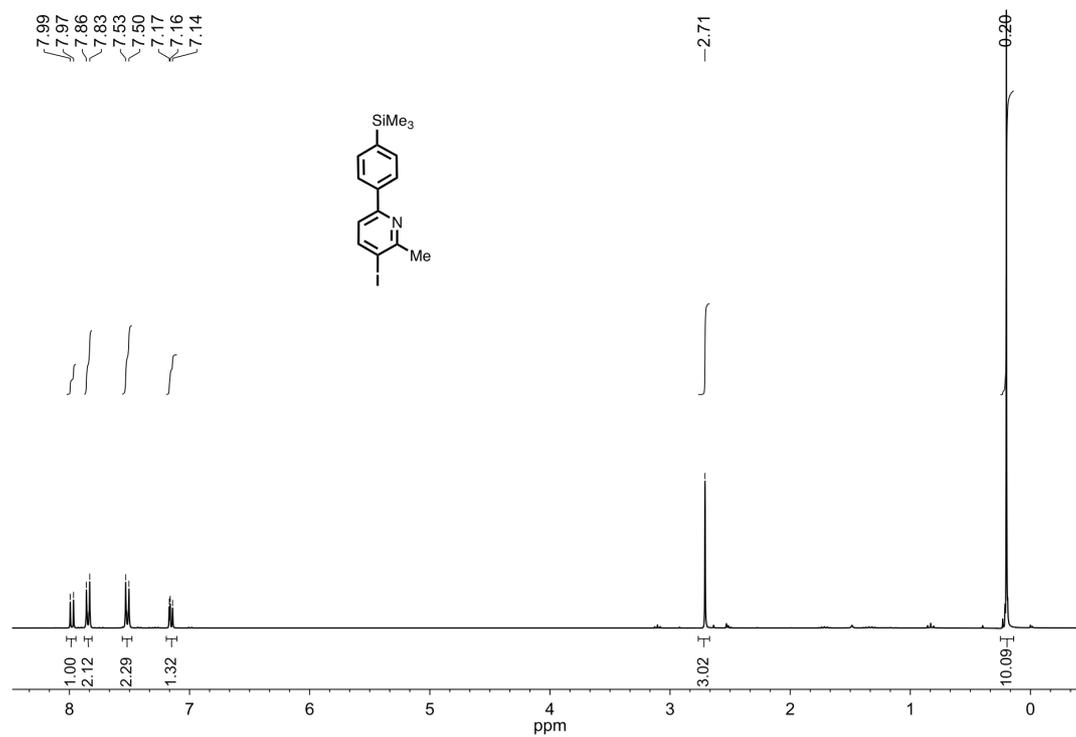
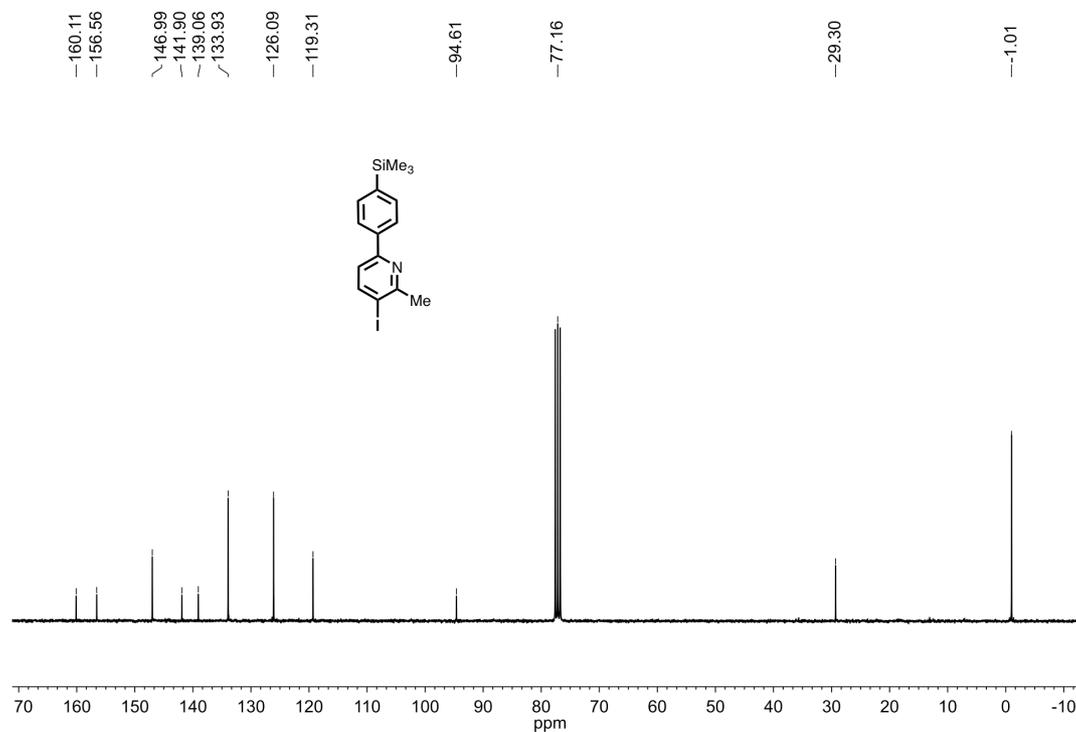


Figure S4. ^{13}C NMR spectrum of 3-iodo-2-methyl-6-(4-(trimethylsilyl)phenyl)pyridine



3-Iodo-2-methyl-6-(4-iodophenyl)pyridine (C, Scheme S1)

3-Iodo-2-methyl-6-(4-(trimethylsilyl)phenyl)pyridine (**B**, 15 g, 41 mmol) was dissolved in dichloromethane (300 mL) and cooled down to 0 °C. A solution of ICl (8.6 mL, 164 mmol, 4 equiv.) in dichloromethane (150 mL) was added dropwise and the reaction mixture slowly allowed warming to room temperature. The solution was stirred for further 16 h before NaOH (8M, 600 mL) and Na₂S₂O₅ (12 g in 100 mL) were added. The phases were separated and the aqueous phase extracted with dichloromethane (2 × 200 ml). The combined organic phase was dried over MgSO₄. After filtration, the solvent was removed under reduced pressure giving a pale beige solid, which was recrystallized from dichloromethane at 4 °C to give **C** as beige needles (12.0 g, 70%).

¹H NMR δ = 2.79 (s, 3H), 7.22 (d, *J* = 8.2 Hz, 1H), 7.73 (m, 4H), 8.08 (d, *J* = 8.2 Hz, 1H)

¹³C NMR δ = 29.3, 95.0, 95.7, 118.9, 128.6, 138.0, 138.1, 147.2, 155.3, 160.3

EI m/z 420.88 [M⁺], 293.98 [M⁺-I], 167.07 [M⁺-I₂]

mp 152 °C

Figure S5. ¹H NMR spectrum of 3-iodo-2-methyl-6-(4-iodophenyl)pyridine

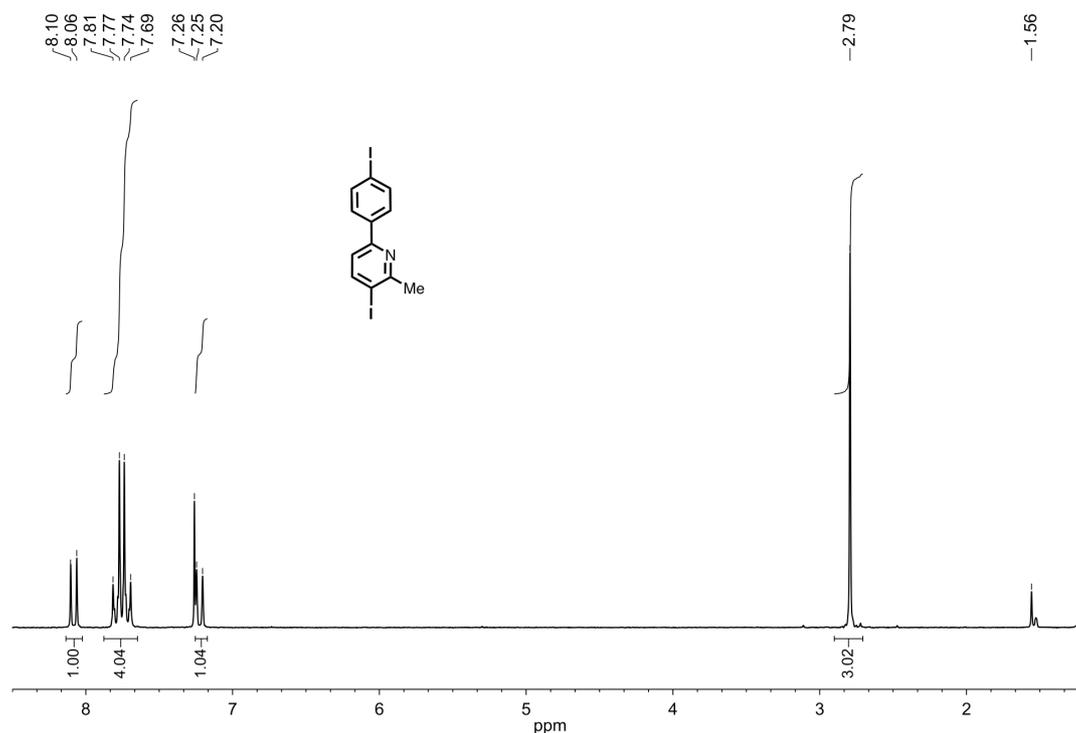
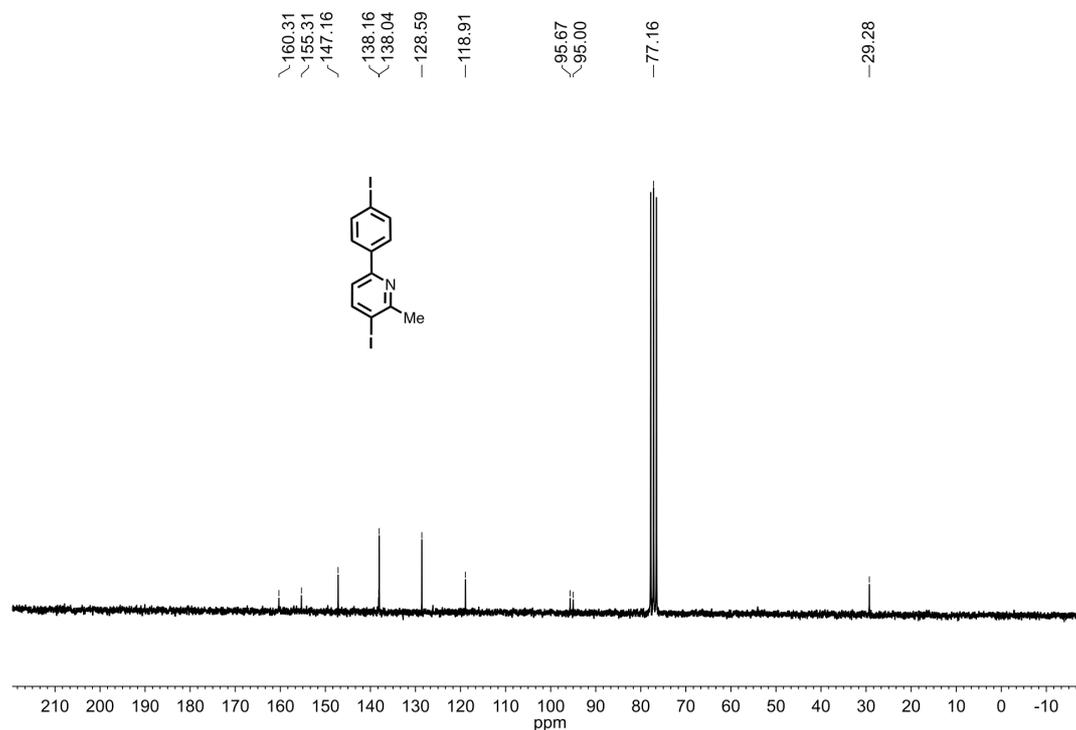


Figure S6. ^{13}C NMR spectrum of 3-iodo-2-methyl-6-(4-iodophenyl)pyridine**3-triethoxysilyl-2-methyl-6-(4-triethoxysilylphenyl)pyridine (D, Scheme 1)**

3-Iodo-2-methyl-6-(4-iodophenyl)pyridine (12.6 g, 30 mmol), tetrabutylammonium iodide (25.5 g, 68.9 mmol, 2.3 equiv.) and $[\text{Rh}(\text{cod})(\text{NCMe})_2]\text{BF}_4$ (0.5 g, 1.3 mmol, 4.3 mol%) were placed in a 1 L two neck flask under argon and dry DMF (500 mL) was added. Triethylamine (25 mL, 180 mmol, 6 equiv.) and triethoxysilane (25 mL, 135 mmol, 4.5 equiv.) were added to the reaction mixture, which was then stirred at 80 °C for 22 h. After this time, the solvent was removed under reduced pressure and the resulting slurry taken up in diethyl ether (300 mL). The suspension was filtered over Celite and activated charcoal before the solvent removal. *Kugelrohr* distillation at 250 °C and 10^{-3} mbar gave **D** as a slightly yellow oil (7.49 g, 50%).

^1H NMR δ = 1.21-1.30 (m, 18H), 2.78 (s, 3H), 3.84-3.94 (m, 12H), 7.53 (d, J = 8.1 Hz, 1H), 7.77 (d, J = 8.1 Hz, 2H), 8.02 (d, J = 8.1 Hz, 2H), 8.06 (d, J = 8.1 Hz, 1H)

^{13}C NMR δ = 18.2, 25.9, 58.8, 117.0, 123.2, 126.4, 131.6, 135.3, 141.3, 145.5, 157.9, 164.0

^{29}Si NMR δ = -58.1, -57.7

EI m/z 493.23 [M^+], 478.21 [$\text{M}^+ - \text{CH}_3$], 448.20 [$\text{M}^+ - \text{OEt}$]

Figure S7. ^1H NMR spectrum of 3-triethoxysilyl-2-methyl-6-(4-triethoxysilylphenyl)pyridine

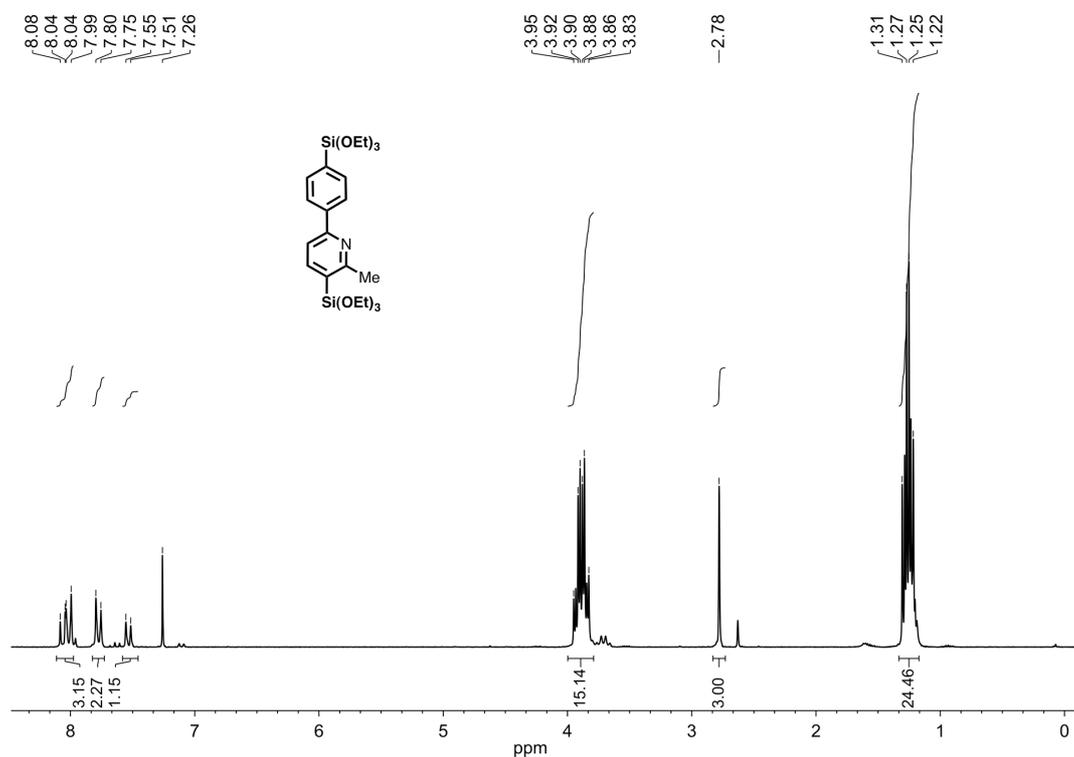
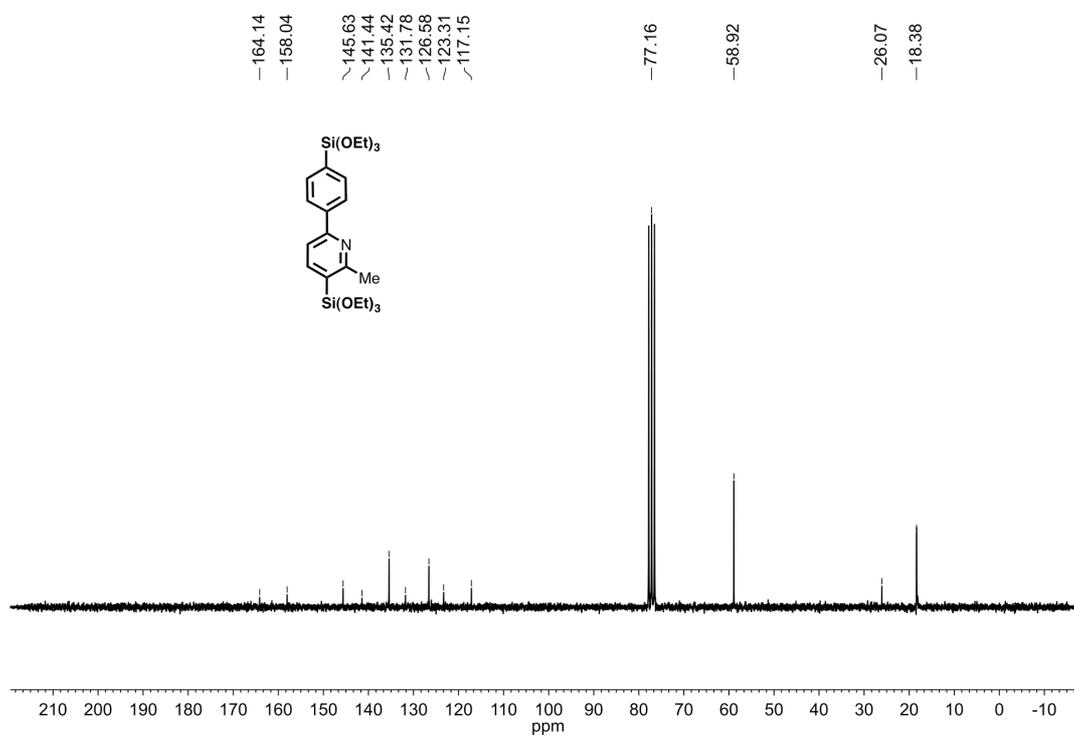


Figure S8. ^{13}C NMR spectrum of 3-triethoxysilyl-2-methyl-6-(4-triethoxysilylphenyl)pyridine



Material Synthesis

Synthesis of $\text{ppy}^{\text{Me}}\text{-PMO}$

Trimethylstearylammonium chloride (1.25 g, 3.6 mmol) was dissolved in water (78 mL) and an aqueous NaOH solution (6 M, 1.3 mL) was added. The resulted solution was stirred for 20 min before 3-triethoxysilyl-2-methyl-6-(4-triethoxysilylphenyl)pyridine (**D**, 1.4 g, 2.8 mmol) was added under vigorous stirring. The resulting suspension was stirred at room temperature for 24 h followed by heating to 97 °C under static conditions for 24 h. Filtration and washing with water (3×35 mL) and acetone (2×75 mL) afforded a white solid which was dried at 85 °C under vacuum (10^{-2} mbar) overnight. The white solid was suspended in a solution of 2 M HCl, pyridine and water (50 mL : 50 mL : 17 mL) and stirred at 65 °C for 16 h. The product was filtered and washed with deionized water (3×100 mL), methanol (1×100 mL) and acetone (3×100 mL). Drying under high vacuum (10^{-5} mbar) at 135 °C for 16 h yielded $\text{ppy}^{\text{Me}}\text{-PMO}$ as a white powder (249 mg).

EA found: C, 50.75%; H, 3.71%; N, 4.58%

BET surface area (N_2 , 77K) $976 \text{ m}^2 \text{ g}^{-1}$; BJH pore size: < 2.4 nm

Figure S9. N_2 Adsorption/Desorption isotherm for $\text{ppy}^{\text{Me}}\text{-PMO}$

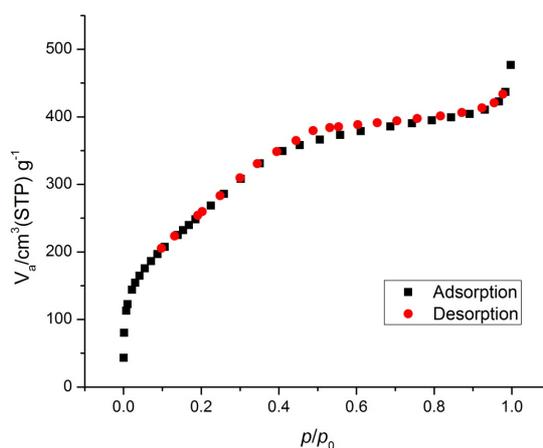


Figure S10. Powder-XRD spectrum of $\text{ppy}^{\text{Me}}\text{-PMO}$

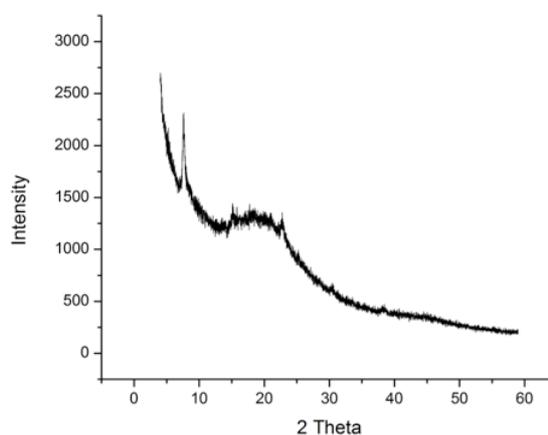


Figure S11. Transition electron micrograph images of **ppy^{Me}-PMO**

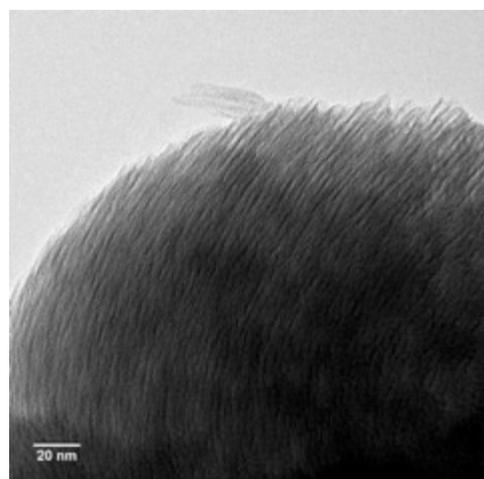
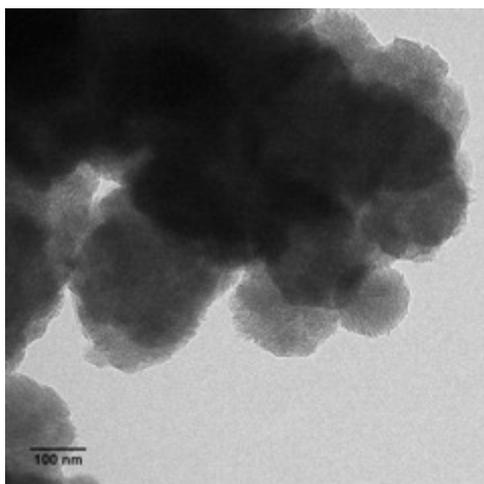


Figure S12. ^1H MAS NMR spectrum of $\text{ppy}^{\text{Me}}\text{-PMO}$ (spinning rate 10 kHz)

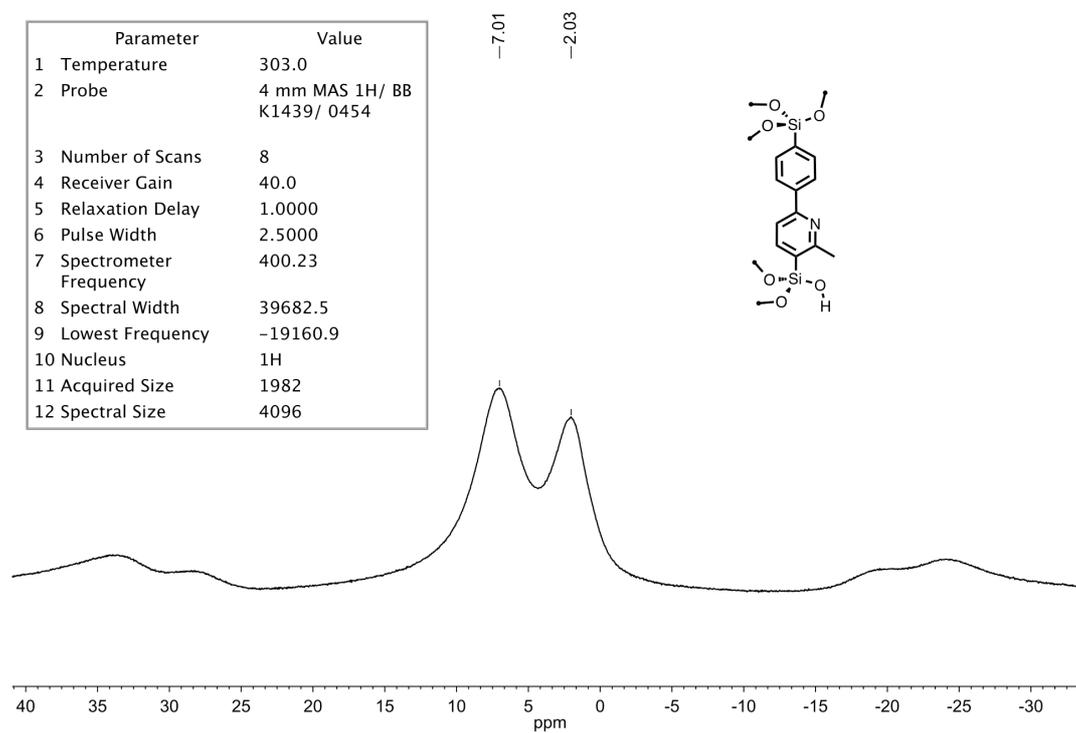


Figure S13. ^{13}C CP MAS NMR spectrum of $\text{ppy}^{\text{Me}}\text{-PMO}$ (spinning rate 10 kHz, contact time 600 μs)

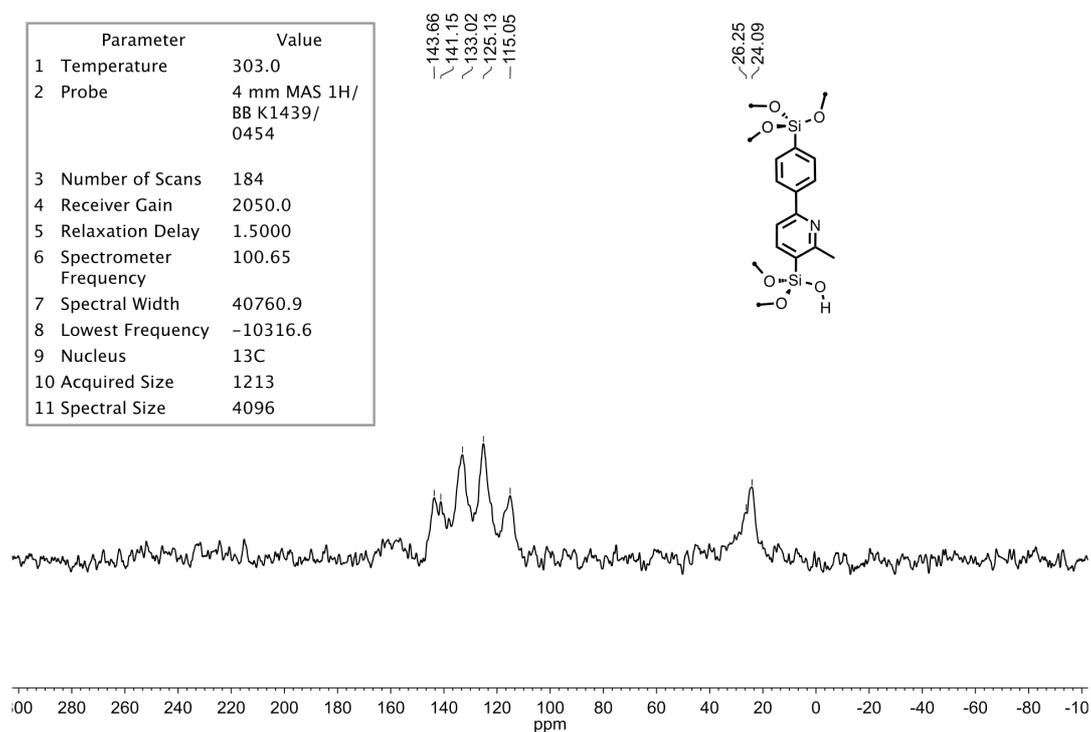
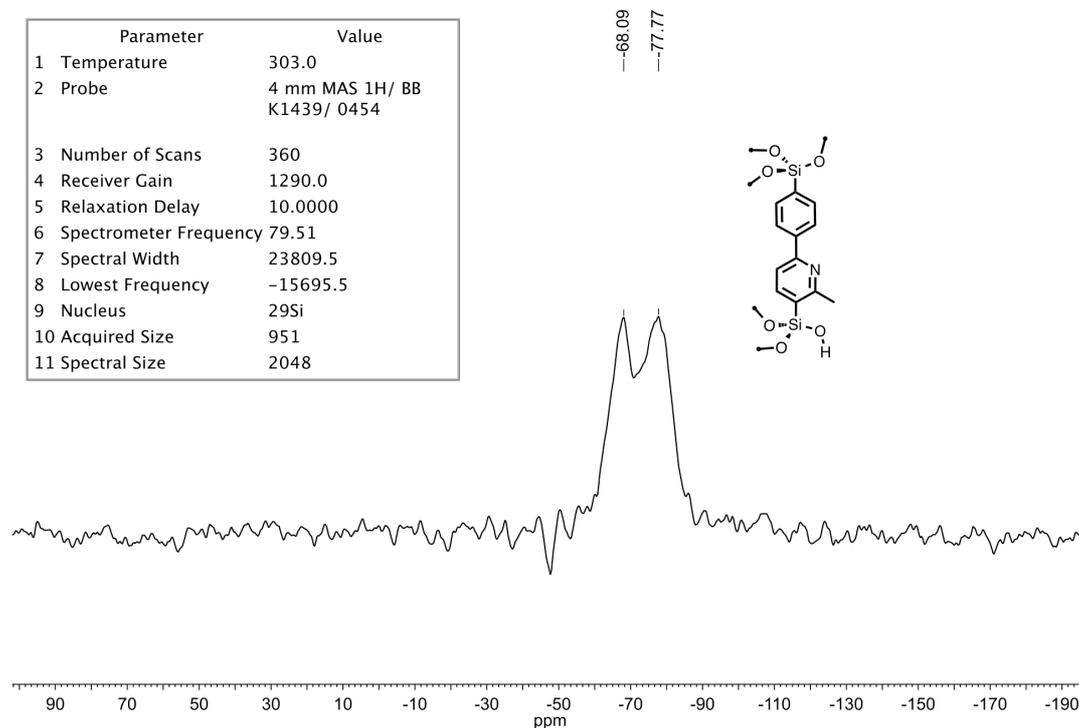


Figure S14. ^{29}Si CP MAS spectrum NMR of **ppy^{Me}-PMO** (spinning rate 10 kHz, contact time 5 ms)

Synthesis of ppy-PMO and biph-PMO

ppy-PMO material was prepared according to literature.^[1] For convenience, the synthetic procedure is reproduced below.

Trimethylstearylammmonium chloride (1.25 g, 3.6 mmol) was dissolved in water (78 mL) and an aqueous NaOH solution (6 M, 1.3 mL) was added. The solution was stirred for 20 min before 3-triethoxysilyl-6-(4-triethoxysilylphenyl)pyridine (1.36 g, 2.8 mmol) was added under vigorously stirring. The resulting suspension was stirred at room temperature for 24 h followed by heating to 97 °C under static conditions for 24 h. Filtration and washing with water (3×35 mL) and acetone (2×75 mL) afforded a white solid. The white solid was suspended in a premixed mixture of 2 M HCl, pyridine and water (50 mL : 50 mL : 17 mL) and stirred at 65 °C for 16 h. The product was filtered and washed with deionized water (3 × 100 mL), methanol (1 × 100 mL) and acetone (3 × 100 mL). Drying under high vacuum (10^{-5} mbar) at 135 °C for 16 h yielded **ppy-PMO** as a white powder (488 mg).

EA found: C, 42.81%; H, 2.76%; N, 4.46%

BET surface area (N_2 , 77 K) $634 \text{ m}^2 \text{ g}^{-1}$; pore size: < 2.4 nm

biph-PMO material was prepared according to literature.^[2] For convenience, the synthetic procedure is reproduced below.

Trimethylstearylammmonium chloride (1.87 g, 5.4 mmol) was dissolved in water (117 mL) and an aqueous NaOH solution (6 M, 1.95 mL) was added. The solution was stirred for 20 min before 4,4'-bis(triethoxysilyl)-1,1'-biphenyl (2.01 g, 4.2 mmol) was added under vigorous stirring. The resulting suspension was stirred at room temperature for 24 h followed by heating to 97 °C under static conditions for 24 h. Filtration and washing with water (3 × 35 mL) and acetone (2 × 75 mL) afforded a white solid which The material was suspended in a premixed mixture of 2 M HCl, pyridine and water (50 mL : 50 mL : 17 mL) and stirred at 65 °C for 16 h. The product was filtered and washed with deionized water (3 × 100 mL), methanol (1 × 100 mL) and acetone (3 × 100 mL). Drying under high vacuum (10⁻⁵ mbar) at 135 °C for 16 h yielded **biph-PMO** as a white powder (512 mg).

EA found: C, 49.53%; H, 2.95%

BET surface area (N₂, 77 K) 776 m² g⁻¹; pore size: < 2.4 nm

Passivation of Materials

A typical procedure to prepare passivated PMOs is given below.

ppy^{Me}-PMO (182 mg) was suspended in dry THF (20 mL) and triethylamine (2.1 mL) added. The suspension was stirred for 20 min at room temperature before TMSBr (1.9 mL) was slowly added. The suspension was further stirred for 24 h at room temperature followed by quenching with ethanol. Filtration, washing with water (3 × 100 mL), ethanol (2 × 75 mL), methanol (3 × 50 mL) and acetone (3 × 75 mL) and drying at 10⁻⁵ mbar at 135 °C for 16 h yielded **ppy^{Me}-PMO_{pas}** as a fine white powder (166 mg).

ppy^{Me}-PMO_{pas}

EA found: C, 43.37%; H, 2.68%; N, 4.45%

BET surface area (N₂, 77K) 853 m² g⁻¹; pore size < 2.4 nm

ppy-PMO_{pas}

EA found: C, 49.38%; H, 4.21%; N, 4.23%

BET surface area (N₂, 77 K) 436 m² g⁻¹; pore size < 2.4 nm

biph-PMO_{pas}

EA found: C, 49.68%; H, 3.59%

BET surface area (N₂, 77K) 728 m² g⁻¹; pore size < 2.4 nm

Impregnation of Materials

A typical procedure to impregnate passivated PMOs with B(C₆F₅)₃ is given below.

A solution of freshly sublimed $\text{B}(\text{C}_6\text{F}_5)_3$ (32 mg, 0.2 equiv.) in 300 μL of toluene was added dropwise to **ppy^{Me}-PMO_{pas}** material (100 mg, 0.31 mmol N sites) and the material left at room temperature for 30 min. (The amount of solvent used corresponds to the total pore volume of **ppy^{Me}-PMO_{pas}**.) The material was then dried at 10^{-5} mbar at room temperature for 6 h yielding **B-ppy-PMO_{pas}** as a fine white powder (121 mg).

B-ppy-PMO_{pas}

EA found: C, 43.50%; H, 2.38%; N, 3.17%

BET surface area (N_2 , 77K) $175 \text{ m}^2 \text{ g}^{-1}$; pore size < 2.4 nm

B-ppy^{Me}-PMO_{pas}

EA found: C, 46.78%; H, 3.09%; N, 3.02%

BET surface area (N_2 , 77K) $372 \text{ m}^2 \text{ g}^{-1}$; pore size < 2.4 nm

B-biph-PMO_{pas}

EA found: C, 48.79%; H, 3.23%; N, 0.01%

BET surface area (N_2 , 77K) $176 \text{ m}^2 \text{ g}^{-1}$; pore size < 2.4 nm

Figure S15. DRIFT-IR spectra of **ppy^{Me}-PMO** (A), **ppy^{Me}-PMO_{pas}** (B) and **B-ppy^{Me}-PMO_{pas}** (C)

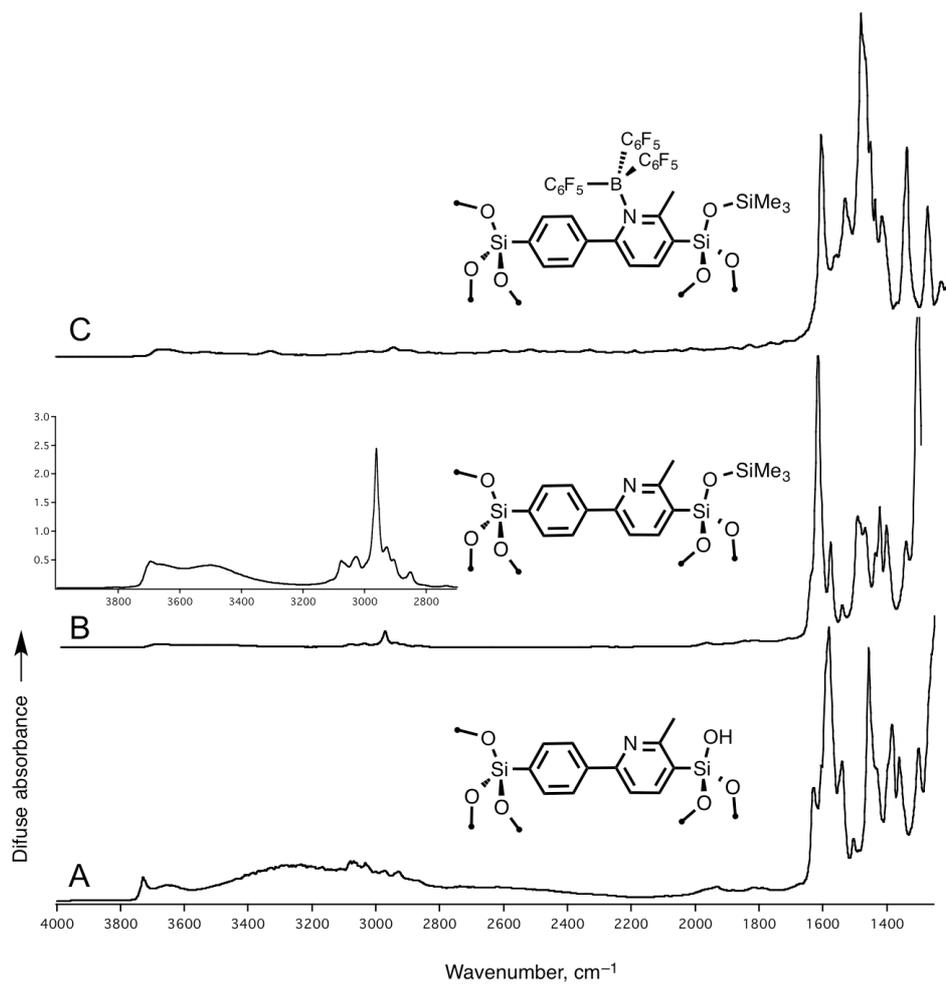
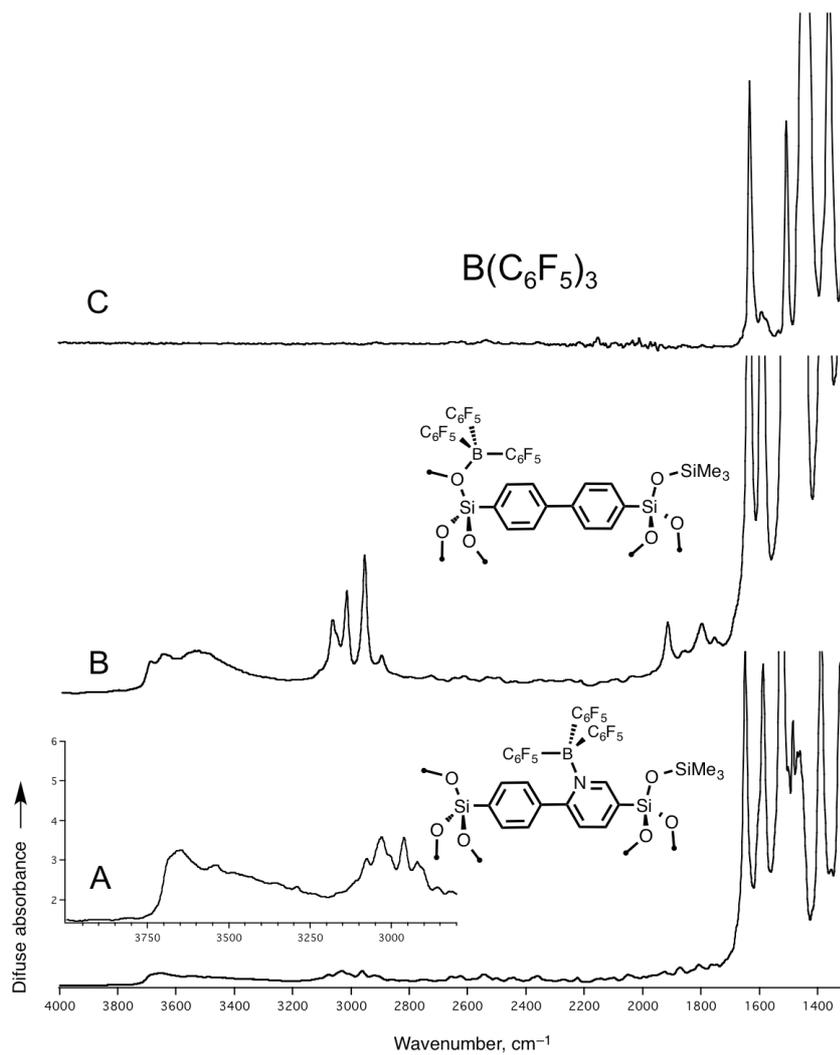


Figure S16. DRIFT-IR spectra of **B-ppy^{Me}-PMO_{pas}** (A), **B-biph-PMO_{pas}** (B) and **B(C₆F₅)₃** (C)



^{11}B ssNMR and MQMAS data

Figure S17. ^{11}B ssNMR of $\text{B}(\text{C}_6\text{F}_5)_3$ (spinning rate 20kHz)

Parameter	Value
1 Temperature	300.0
2 Probe	3.2 mm MAS BB/ 1H H13640/ 0005
3 Number of Scans	32
4 Receiver Gain	631.6
5 Relaxation Delay	3.8000
6 Spectrometer Frequency	128.41
7 Spectral Width	200000.0
8 Lowest Frequency	-100000.0
9 Nucleus	^{11}B
10 Acquired Size	2562
11 Spectral Size	8192

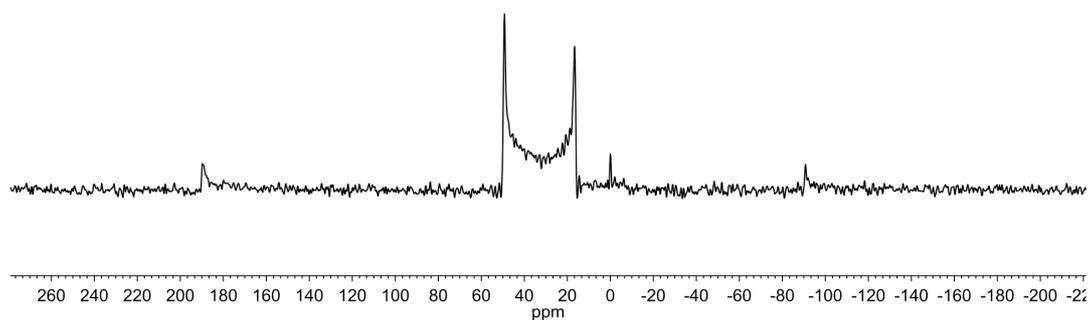
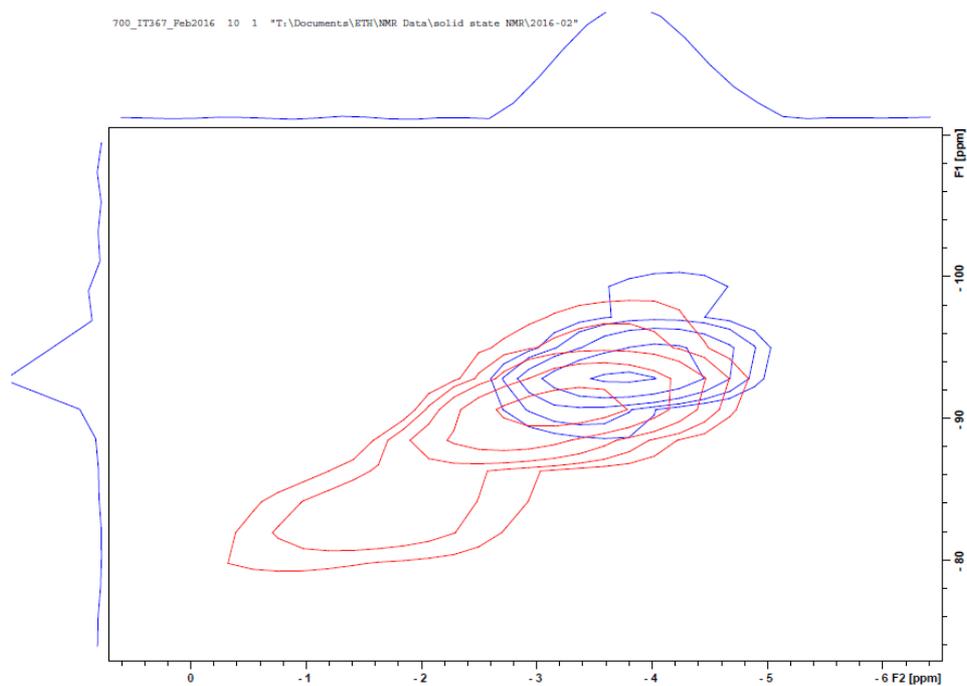


Figure S18. Zoomed in overlay of ^{11}B MQMAS of **B-ppy-PMO_{pas}** (red) and $\text{B}(\text{C}_6\text{F}_5)_3$ + ppy adduct (blue) (128 MHz, spinning rate 20kHz).



Photoluminescence Data

Sample preparation for PL measurements

In the case of the impregnated materials, a pentane suspension of the freshly prepared material was added dropwise to a glass slide inside a glovebox. Drying of the solvent gave an even coverage of the material on the glass surface.

Model molecular adducts were prepared by stirring equimolar amounts of $B(C_6F_5)_3$ with ppy, ppy^{Me} or biph in dichloromethane for 15 min. After removal of solvent in vacuo, the white solid was introduced onto the glass slides in a similar manner as described above for the impregnated materials.

Figure S19. Photograph of samples for PL measurements irradiated at 366 nm

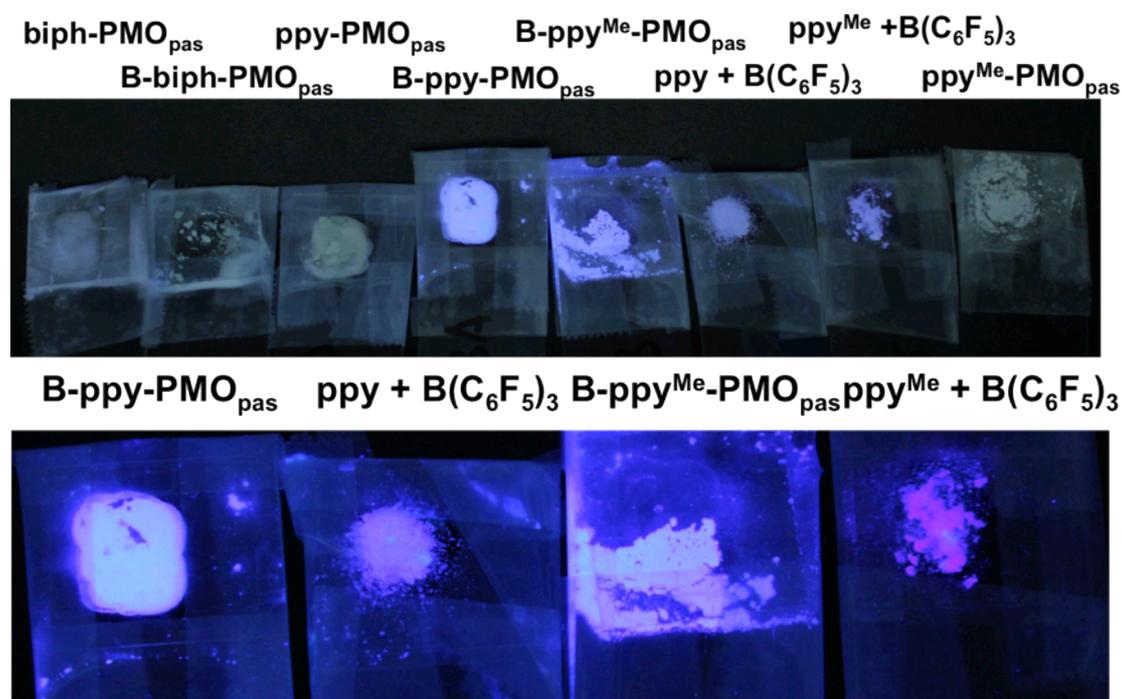


Figure S20. DRIFT UV-VIS spectra (A) and overlay of PL spectra of **ppy**-derivatives (B), **ppy^{Me}**-derivatives (C) and **biph**-derivatives (D).

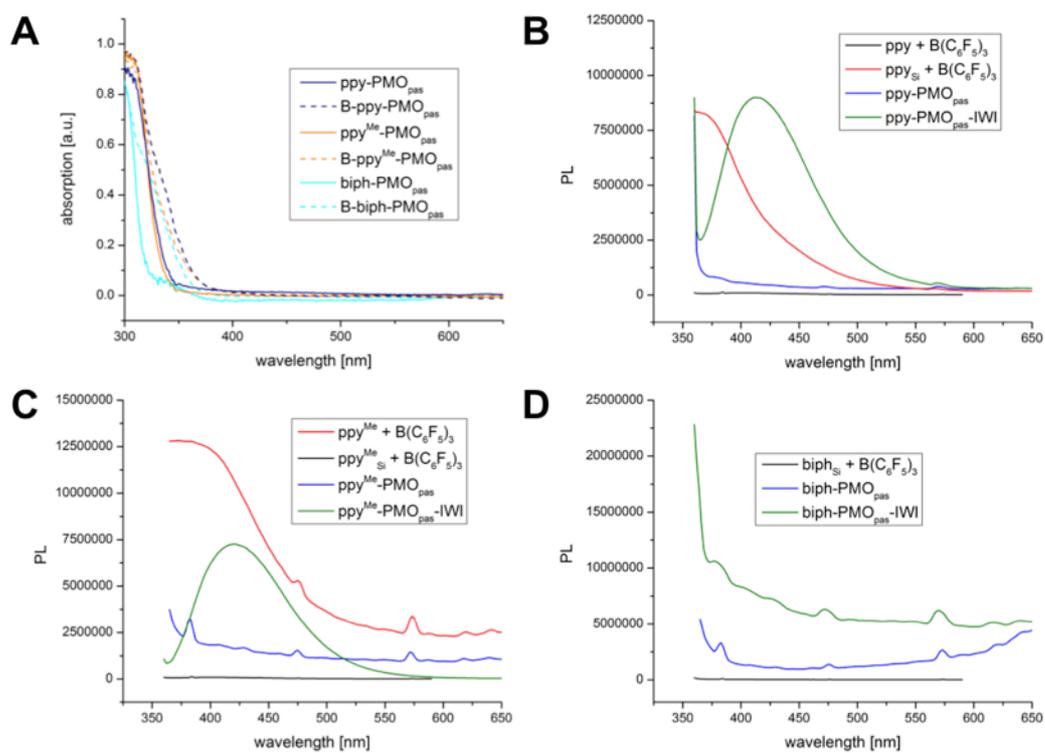


Figure S21. PL decay of $\text{ppy}^{\text{Me}} + \text{B}(\text{C}_6\text{F}_5)_3$

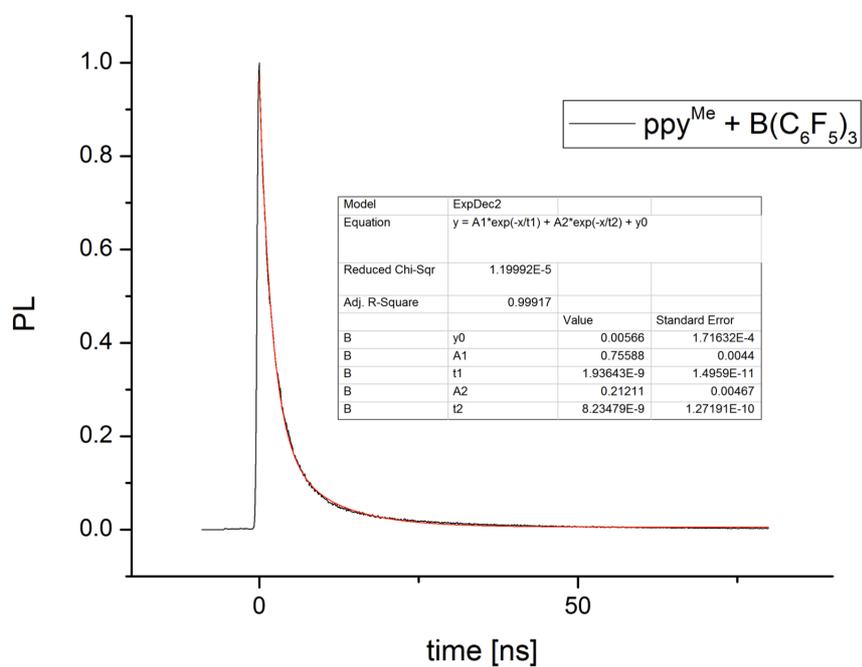


Figure S22. PL decay of $\text{ppy} + \text{B}(\text{C}_6\text{F}_5)_3$

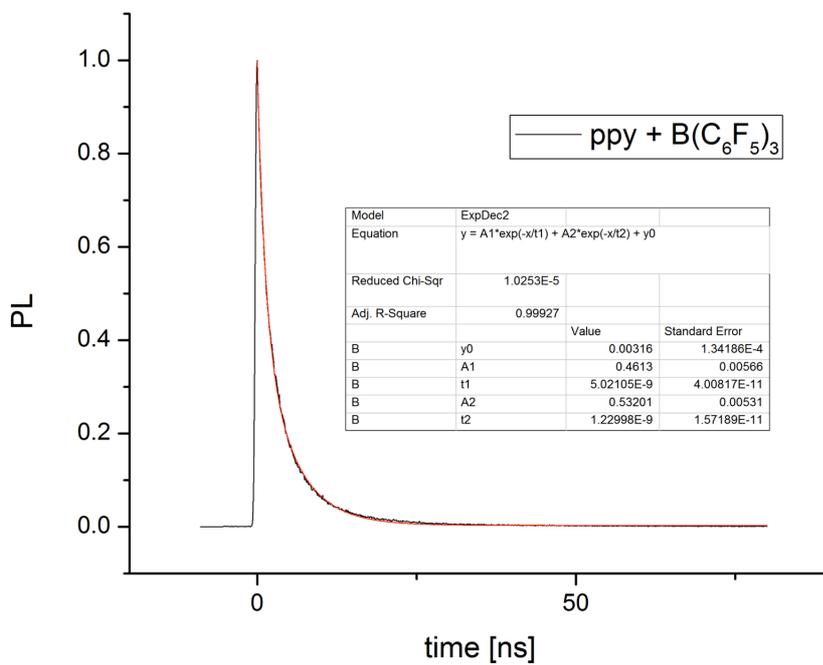
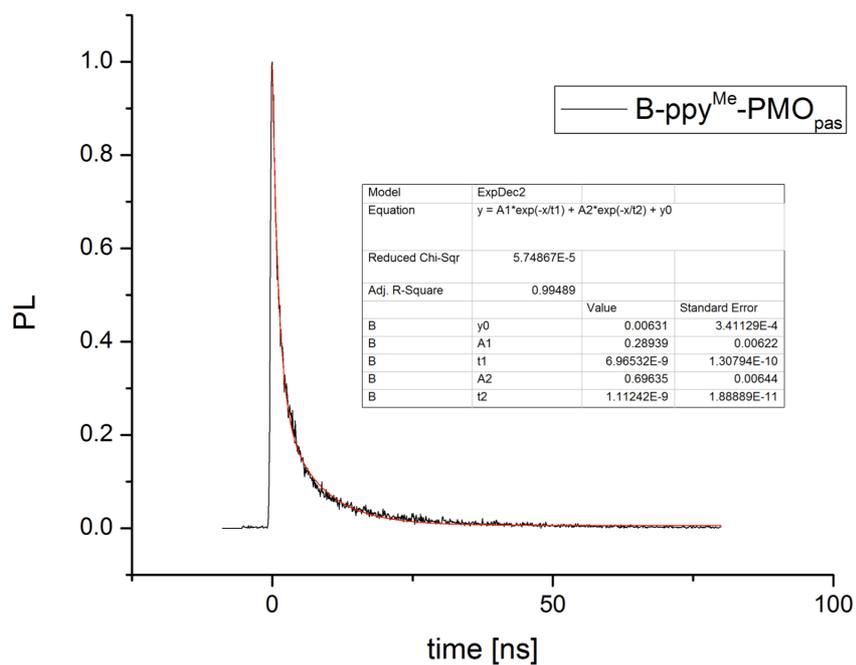
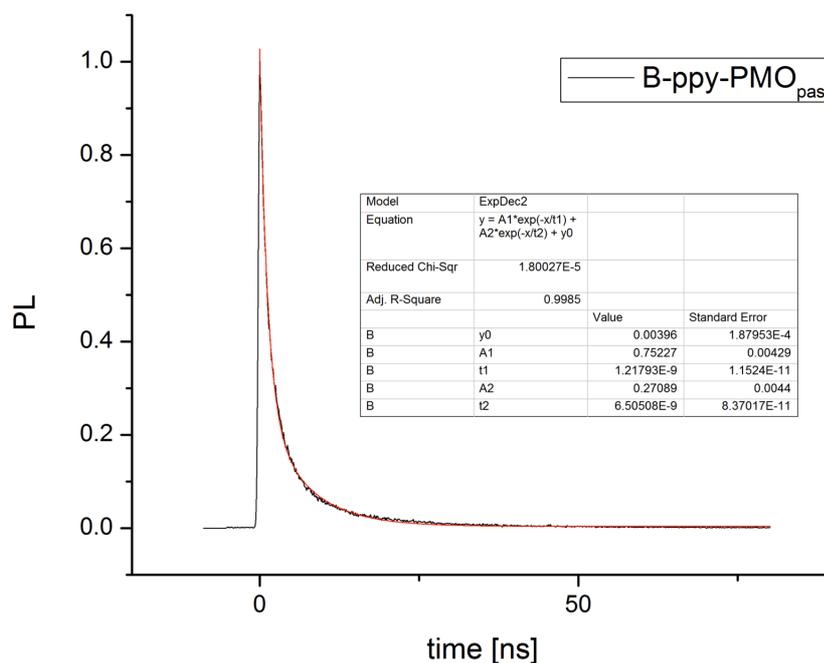


Figure S23. PL decay of **B-ppy^{Me}-PMO_{pas}****Figure S24.** PL decay of **B-ppy-PMO_{pas}****References:**

- [1] (a) W. R. Gruning, A. J. Rossini, A. Zagdoun, D. Gajan, A. Lesage, L. Emsley, C. Copéret, *Phys. Chem. Chem. Phys.* **2013**, *15*, 13270-13274. (b) M. Waki, N. Mizoshita, T. Tani and S. Inagaki, *Angew. Chem., Int. Ed.*, **2011**, *50*, 11667-11671.
- [2] M. P. Kapoor, Q. Yang, S. Inagaki, *J. Am. Chem. Soc.* **2002**, *124*, 15176-15177.