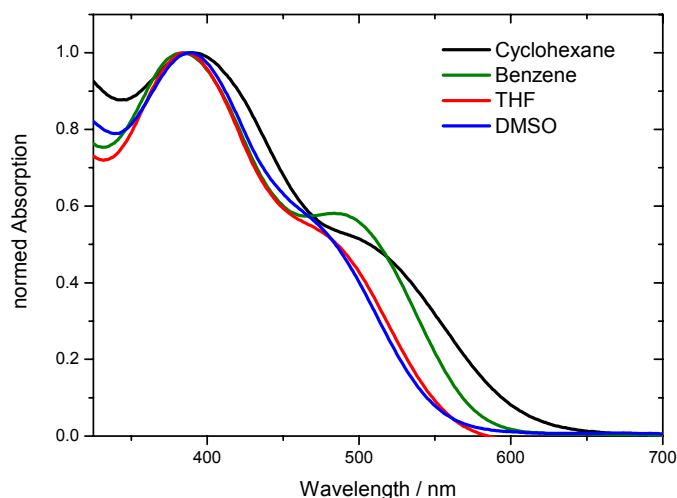


## Supporting Information



**Figure S1:** UV-vis absorption spectra of MePy<sup>+</sup>-9T **8** in solvents of different polarity.

### General procedures:

NMR spectra were recorded on a *Bruker* AMX 500 (<sup>1</sup>H NMR: 500 MHz, <sup>13</sup>C NMR: 125 MHz) or an Avance 400 spectrometer (<sup>1</sup>H NMR: 400 MHz, <sup>13</sup>C NMR: 100 MHz), normally at 25 °C. Chemical shift values ( $\delta$ ) are expressed in parts per million using residual solvent protons (<sup>1</sup>H NMR:  $\delta_{\text{H}} = 7.26$  for CDCl<sub>3</sub>,  $\delta_{\text{H}} = 2.50$  for [D<sub>6</sub>]DMSO,  $\delta_{\text{H}} = 3.57$  for [D<sub>8</sub>]THF; <sup>13</sup>C NMR:  $\delta_{\text{C}} = 77.0$  for CDCl<sub>3</sub>,  $\delta_{\text{C}} = 39.43$  for [D<sub>6</sub>]DMSO,  $\delta_{\text{C}} = 67.2$  for [D<sub>8</sub>]THF) as internal standard. Melting points were determined using a *Büchi* B-545 apparatus. Elemental analyses were performed on an *Elementar Vario* EL (University of Ulm) and a *Carlo Erba* 1104 (University of Stuttgart). Thin layer chromatography was carried out on aluminium plates, pre-coated with silica gel, *Merck* Si60 F<sub>254</sub>. Preparative column chromatography was performed on glass columns packed with silica gel, *Merck* Silica 60, particle size 40-43  $\mu\text{m}$ . EI and CI mass spectra were recorded on a *Finnigan* MAT SSQ-7000 or a *Varian* Saturn 2000 GC-MS, MALDI-TOF on a *Bruker* Daltonics Reflex III. Optical measurements were carried out in 1 cm cuvettes with *Merck* Uvasol grade solvents, absorption spectra recorded on a *Perkin Elmer* Lambda 19 spectrometer and fluorescence spectra on a *Perkin Elmer* LS 55 spectrometer. Cyclic voltammetry experiments were performed with a computer-controlled *EG&G* PAR 273 potentiostat in a three-electrode single-compartment cell with a platinum working electrode, a platinum wire counter

electrode, and an Ag/ AgCl reference electrode. All potentials were internally referenced to the ferrocene/ferricenium couple. Diffraction data were collected on a STOE-IPDS image-plate diffractometer ( $MO_{K\alpha}$  radiation, graphite monochromator) in the  $\Phi$ -rotation mode. The structure was solved by direct methods with the SHELXL93. Non-hydrogen atoms were refined anisotropically.

Tetrahydrofuran (Merck) and 1,4-dioxane (Merck) were dried under reflux over sodium/ benzophenone and dichloromethane (Merck) over calcium hydride. All synthetic steps were carried out under argon atmosphere (except TMS-deprotections). Iodine monochloride and trifluoroacetic acid were purchased from Merck, 4-iodopyridine from Apollo Scientific, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (ITDB) from Aldrich and was dried over molar sieve (4 Å) prior to use,  $Pd_2(dba)_3 \cdot CHCl_3$ ,  $HP(tBu)_3BF_4$ ,  $nBuLi$  (1.6 mol/L in hexane) and methyl trifluoromethane sulfonate from Acros.

Tetra-*n*-butylammonium fluoride solution (1 M) was prepared by dissolving  $nBu_4NF \cdot 3H_2O$  (Merck) in THF. The potassium phosphate solution was prepared by dissolving potassium phosphate monohydrate (Riedel-de Haën) in deionized water and was degassed prior to use. Synthesis of TMS-protected boronic acid ester B-3T-Si **7** and B-9T-Si **12** was already been described in ref<sup>24</sup>.

Photovoltaic devices were prepared by spin coating EL-grade PEDOT:PSS (Clevios P VPAI4083; H. C. Starck) onto cleaned, patterned indium tin oxide (ITO) substrates ( $14 \Omega \text{ cm}^{-2}$ ). The photoactive layer was deposited by spin-coating from a chlorobenzene solution with a total concentration of 25 mg / mL. Film thicknesses were determined by profilometry (Veeco Dektak 150). The counter electrode of LiF (1 nm) and aluminum (100 nm) was deposited by vacuum evaporation at approximately  $1 \times 10^{-6}$  mbar. The active area of the cells was  $0.167 \text{ cm}^2$ . Spectral response was measured with a Keithley 2400 source meter, using monochromatic light from a tungsten halogen lamp in combination with monochromator (Oriel, Cornerstone 130). A calibrated Si cell was used as reference. The device was kept behind a quartz window in a nitrogen filled container. *J-V* characteristics were measured under ca.  $100 \text{ mW cm}^{-2}$  simulated solar light from a tungsten-halogen lamp (Philips Brilliantline Pro) filtered by a Schott GG 385 and a Hoya LB 120 filter. The exact current density was calculated by convolution of the spectral response with the AM1.5G spectrum ( $100 \text{ mW cm}^{-2}$ ).

### Crystal data for silver complex 12:

All data of the single crystal X-ray analysis are deposited at the Cambridge Structural Database (CSD) with the deposition number CCDC 711680

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<b>12</b>	
Formula	C <sub>37</sub> H <sub>25</sub> Ag F <sub>3</sub> N <sub>3</sub> O <sub>3</sub> S <sub>7</sub>
Formula weight	907.84
Temperature [K]	293(2)
Wavelength [Å]	0.71073
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /c (IT no. 14)
Unit cell dimensions [Å]	a = 11.9979(12) b = 17.9901(16) c = 17.0699(19)
$\beta$ [°]	103.271(12)
Volume [Å <sup>3</sup> ]	3586.0(6)
Z	4
$\rho_{\text{calcd.}}$ [g cm <sup>-3</sup> ]	1.682
Absorption coefficient [mm <sup>-1</sup> ]	1.025
F(000)	1848
Crystal size [mm]	0.2 x 0.4 x 0.4
$\Theta$ range [°]	2.08 to 26.00
Limiting indices	-14 ≤ h ≤ 14, -22 ≤ k ≤ 22, -20 ≤ l ≤ 21
Reflections collected / unique	27919 / 6981 [R(int) = 0.0607]
Completeness to theta = 26.00	99.1 %
Refinement method	Full-matrix least squares on $F^2$
Data / restraints / parameters	6981 / 0 / 520
Goodness-of-fit on $F^2$	0.942
Final R indices [ $I > 2\sigma(I)$ ]	R <sub>1</sub> = 0.0546, wR <sub>2</sub> = 0.1508
R indices (all data)	R <sub>1</sub> = 0.0917, wR <sub>2</sub> = 0.1662
Largest diff. peak and hole [e Å <sup>-3</sup> ]	1.433 / -1.007

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