

## Supporting Information

### **Exploring the Molecular Electronic Device Applications of Synthetically Versatile Silicon Pincer Complexes as Charge Transport and Electroluminescent Layers**

Margaret Kocherga, Kevin M. Boyle, Jon Merkert, Thomas A. Schmedake, and Michael G. Walter\*

[\*] Prof. M. G. Walter, Corresponding Author

Department of Chemistry

University of North Carolina at Charlotte

214-216 Burson Chemical Laboratory

Charlotte, NC 28223 (USA)

#### **S1. Synthesis and Characterization of bzimpy ligands and complexes 1-4**

Pincer ligands **2,6-bis(2-benzimidazolyl)pyridine** and **2,6-bis[2-(5,6-dimethylbenzimidazolyl)]pyridine** were synthesized following published methods.<sup>1-2</sup> The hydroxylated precursor to **2,6-bis(2-benzimidazolyl)-4-methoxypyridine** was also synthesized following a previously published method.<sup>3</sup> All other reagents were purchased and used without further purification.

##### **Synthesis of 2,6-bis(2-benzimidazolyl)-4-methoxypyridine**

Dry 2,6-bis(2-benzimidazolyl)-4-hydroxypyridine (3.0 g, 9.2 mmol) and anhydrous K<sub>2</sub>CO<sub>3</sub> (1.27 g, 9.2 mmol) were placed in a 100 mL round bottom flask with a stir bar. A condenser was attached and the flask was charged with nitrogen. DMF (50 mL) and MeI (0.57 mL, 9.2 mmol) were added. The flask was left to stir overnight at room temperature. The resulting mixture was then poured into 200 mL DI water. The precipitate was recovered and rinsed with DI water and left to dry. The ligand was recrystallized from hot methanol to yield 1.3 g (3.8 mmol, 41% yield). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 500 MHz): δ 4.06 [s, 3 H], 7.33 [m, 4 H], 7.76 [m, 4 H], 7.84 [s, 2 H], 12.96 [s, 2 H]. <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, 125 MHz): δ 56.1, 107.1, 111.8, 119.7, 122.2, 123.7, 134.3, 144.1, 149.4, 150.4, 167.3.

##### **Synthesis of 2,6-bis[2-(5,6-dimethylbenzimidazol-2-yl)]-4-hydroxypyridine**

Chelidamic acid (5.0 g, 27 mmol) was combined with 4,5-dimethyl-1,2-phenylenediamine (8.2 g, 60 mmol) in a 500 mL round bottom flask with a stir bar. 200 mL of polyphosphoric acid was heated on a hotplate and poured into the flask. The reaction was heated to 240 °C for 6 h, then poured into 1 L of cold DI water with rapid stirring. The precipitate was collected with vacuum filtration and rinsed twice with 25 mL of DI water. The precipitate was slowly added to 1 L of a 10% Na<sub>2</sub>CO<sub>3</sub>(aq) solution in under constant stirring. The resulting suspension was filtered and the precipitate was rinsed twice with 25 mL of DI water and dried overnight in an oven at 120 °C. The crude product was dissolved in a minimum amount of hot DMSO (about 10 mL/g) and filtered hot. DI water was added to precipitate out the product as a white powder. The resulting

powder was resuspended in boiling water (50 mL) and filtered to yield 3.2 g (31% yield) of 2,6-bis[2-(5,6-dimethylbenzimidazol-2-yl)]-4-hydroxypyridine, HO-L4. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 300 MHz): δ 2.37 [s, 12 H], 7.48 [s, 4 H], 7.64 [s, 2 H], 11.4 [s broad, 1H], 12.7 [s broad, 2 H].

#### **Synthesis of 2,6-bis[2-(5,6-dimethylbenzimidazol-2-yl)]-4-methoxypyridine, L4**

Dry HO-L4 (3.0 g, 7.8 mmol) and K<sub>2</sub>CO<sub>3</sub> (1.1 g, 7.8 mmol) were combined with DMF and MeI (0.49 mL, 7.8 mmol) as described in the procedure above to yield 1.6 g (41% yield) of L4. <sup>1</sup>H NMR(DMSO-d<sub>6</sub>, 500 MHz): δ 2.34 [s, 6 H], 2.39 [s, 6 H], 4.03 [s, 3 H], 7.43 [s, 2 H], 7.52 [s, 2 H], 7.74 [s, 2 H], 12.69 [s, 2H]. <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, 125 MHz): δ 20.1, 20.3, 56.0, 106.4, 111.6, 119.5, 130.7, 132.6, 132.9, 142.8, 149.6, 149.6.

#### **Synthesis of Si(bzimpy)<sub>2</sub> – Complex 1**

**Complex 1** was synthesized according to previously reported procedures.<sup>4</sup>

#### **Synthesis of Si(MeObzimpy)<sub>2</sub> – Complex 2**

Under a nitrogen atmosphere, 2,6-bis(2-benzimidazolyl)-4-methoxypyridine (1.380 g, 4.07 mmol) in chloroform (50 mL) was stirred at 0 °C, and triethylamine was added to a stirring suspension (1.13 mL, 8.10 mmol). Upon addition of silicon tetrachloride (0.23 mL, 2.00 mmol) the mixture instantly turned pale yellow color and was allowed to stir for 10 min at 0 °C. The resulting greenish-yellow suspension was warmed to room temperature, and the reaction allowed to proceed for 20 h with stirring. The light-yellow solid obtained was separated by removing the solvent via vacuum. The product was then dissolved in dichloromethane (150 mL), and washed with DI water (3 x 50 mL), then obtained solution was brought to dryness. Light yellow powder was then dissolved in 50:50% methanol:dichloromethane mixture of total volume 90 mL, and was purified via silica gel column (mobile phase 50:50% methanol:dichloromethane mixture). Obtained solution was dried to yield a bright light yellowish green solid, and dried *in vacuo* for 12 h at 110 °C (0.424 g, 30.0%). X-ray quality single crystals of Si(MeObzimpy)<sub>2</sub> were obtained via slow evaporation from CHCl<sub>3</sub>. Elemental analysis (%) calcd for C<sub>40</sub>H<sub>26</sub>N<sub>10</sub>O<sub>2</sub>Si: C, 67.97; H, 3.71; N, 19.82. Found: C, 67.38; H, 3.57; N, 19.62. <sup>1</sup>H NMR(CDCl<sub>3</sub>, 500 MHz): δ 4.44 [s, 6 H], 5.89 [d, J<sub>H-H</sub> = 9.5, 4 H], 6.93 [m, 4 H], 7.01 [m, , 4 H], 7.56 [d, J<sub>H-H</sub> = 8.0, 4 H], 8.07 s, 2 H]. <sup>13</sup>C NMR(CDCl<sub>2</sub>/CD<sub>3</sub>OD, 40/60 mixture, 125 MHz): δ 59.3 (2 C), 106.3 (4 C), 121.1 (4 C), 121.2 (4 C), 124.0 (4 C), 126.1 (4 C), 136.0 (4 C), 148.0 (4 C), 148.2 (4 C), 148.7 (4 C), 176.5 (s, 2 C). <sup>29</sup>Si NMR(CDCl<sub>3</sub>/CD<sub>3</sub>OD, Cr(acac)<sub>3</sub> added, 40/60 mixture, 99 MHz): δ -187.4. MS (MALDI-TOF): m/z = 706.9

### Synthesis of Si(Me<sub>2</sub>bzimpy)<sub>2</sub> – Complex 3

Under a nitrogen atmosphere, 2,6-bis[2-(5,6-dimethylbenzimidazolyl)]pyridine (1.00 g, 2.74 mmol) in chloroform (60 mL) was stirred at 0 °C, and triethylamine was added to a stirring suspension (0.76 mL, 5.45 mmol). Upon addition of silicon tetrachloride (0.16 mL, 1.39 mmol) the mixture instantly turned orange and was allowed to stir for 5 min at 0 °C. The resulting brownish-orange suspension was warmed to room temperature, and the reaction allowed to proceed for 18 h with stirring. The orange solid obtained was separated by removing the solvent via vacuum. The product was then dissolved in dichloromethane (100 mL), and washed with DI water (3 x 50 mL), then obtained solution was brought to dryness. Orange powder was then dissolved in 50:50 vol % acetonitrile:dichloromethane mixture of total volume 50 mL, and was purified via silica gel column (mobile phase 50:50 acetonitrile:dichloromethane mixture). Obtained solution was dried to yield a bright orange powder, and dried *in vacuo* for 12 h at 110 °C (0.454 g, 42.9%). X-ray quality single crystals of Si(Me<sub>2</sub>bzimpy)<sub>2</sub> were grown by evaporation from CHCl<sub>3</sub>. The structure revealed 8 water molecules included within the lattice. Elemental analysis (%) calcd for C<sub>46</sub>H<sub>38</sub>N<sub>10</sub>Si·2.25(H<sub>2</sub>O): C, 69.11; H, 5.36; N, 17.52. Found: C, 69.2; H, 5.38; N, 17.37. <sup>1</sup>H NMR(CD<sub>2</sub>Cl<sub>2</sub>, 500 MHz): δ 2.03 [s, 12 H], 2.13 [s, 12 H], 5.55 [s, 4 H], 7.28 [s, 4 H], 8.60 [d, J<sub>H-H</sub> = 7.9, 4 H], 8.84 [t, J<sub>H-H</sub> = 7.9, 2 H]. <sup>13</sup>C NMR(CD<sub>2</sub>Cl<sub>2</sub>, 125 MHz): δ 20.2 (4 C), 21.3 (4 C), 111.7 (8 C), 119.1 (4 C), 120.9 (4 C), 133.0 (4 C), 134.7 (4 C), 135.4 (4 C), 147.1 (4 C), 147.7 (4 C), 148.3 (2 C). <sup>29</sup>Si NMR(CD<sub>2</sub>Cl<sub>2</sub>, Cr(acac)<sub>3</sub> added, 99 MHz): δ -185.9. MS (MALDI-TOF): m/z = 758.5

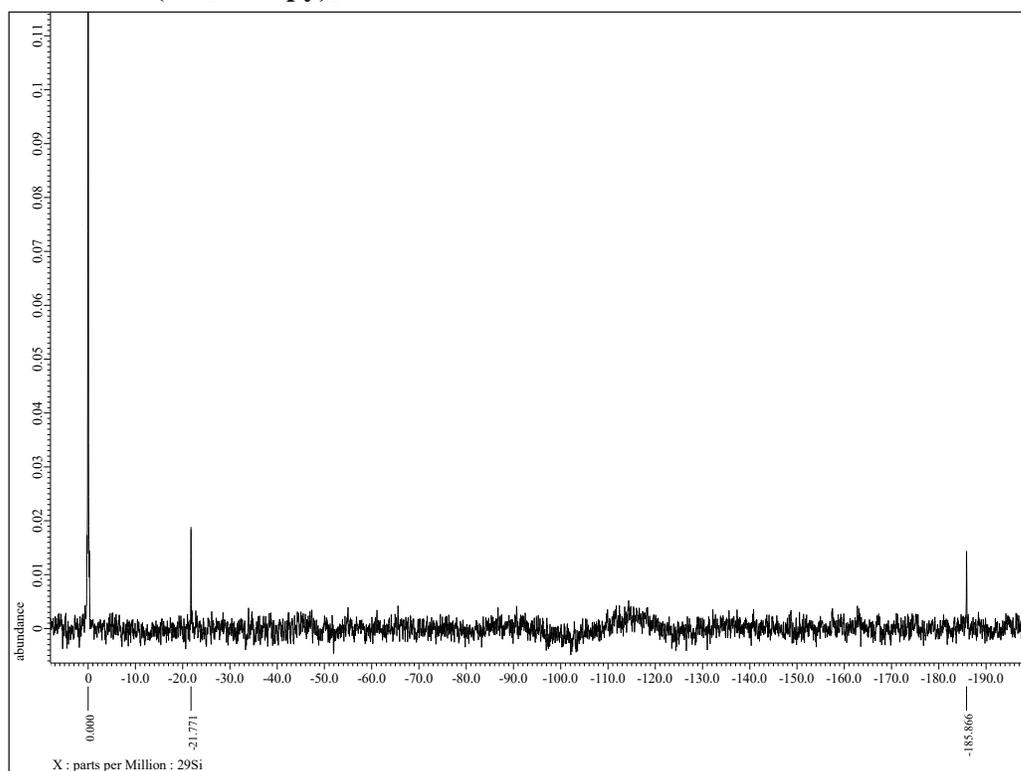
### Synthesis of Si(MeOMe<sub>2</sub>bzimpy)<sub>2</sub> – Complex 4

Under a nitrogen atmosphere, 2,6-bis[2-(5,6-dimethylbenzimidazolyl)]-4-methoxypyridine (1.00 g, 2.52 mmol) in chloroform (60 mL) was stirred at RT, and triethylamine was added to a stirring suspension (0.70 mL, 5.02 mmol). Upon addition of silicon tetrachloride (0.14 mL, 1.22 mmol) the mixture instantly turned yellow and the reaction allowed to proceed for 20 h with stirring. The yellow solid obtained was separated by removing the solvent via vacuum, the product was then dissolved in dichloromethane (120 mL), and washed with DI water (3 x 50 mL), then obtained solution was brought to dryness. Orange powder was then dissolved in 50:50% acetonitrile:dichloromethane mixture of total volume 100 mL, and was purified via silica gel column (mobile phase 50:50% acetonitrile:dichloromethane mixture). Obtained solution was dried to yield a bright yellow powder, and dried *in vacuo* for 14 h at 110 °C (0.497 g, 49.8%). X-ray quality single crystals were grown via slow evaporation from CHCl<sub>3</sub>. Structural analysis identified approximately 9 equivalents of water molecules trapped in the lattice. Elemental analysis (%) calcd for C<sub>48</sub>H<sub>42</sub>N<sub>10</sub>O<sub>2</sub>Si·3.6(H<sub>2</sub>O): C,

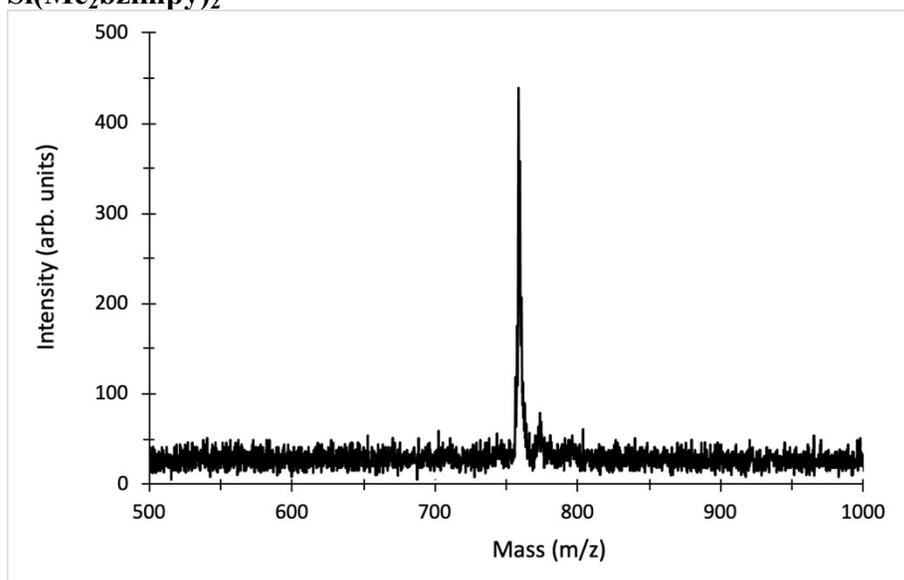




$^{29}\text{Si}$  NMR  $\text{Si}(\text{Me}_2\text{bzimpy})_2$

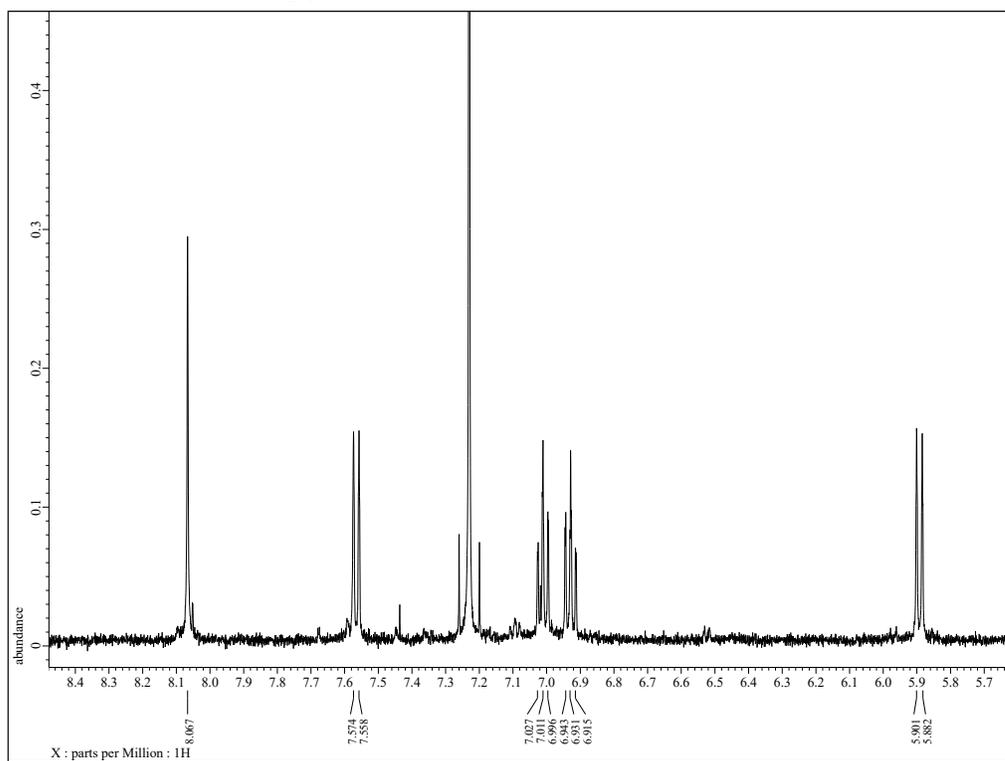


MALDI-MS  
 $\text{Si}(\text{Me}_2\text{bzimpy})_2$

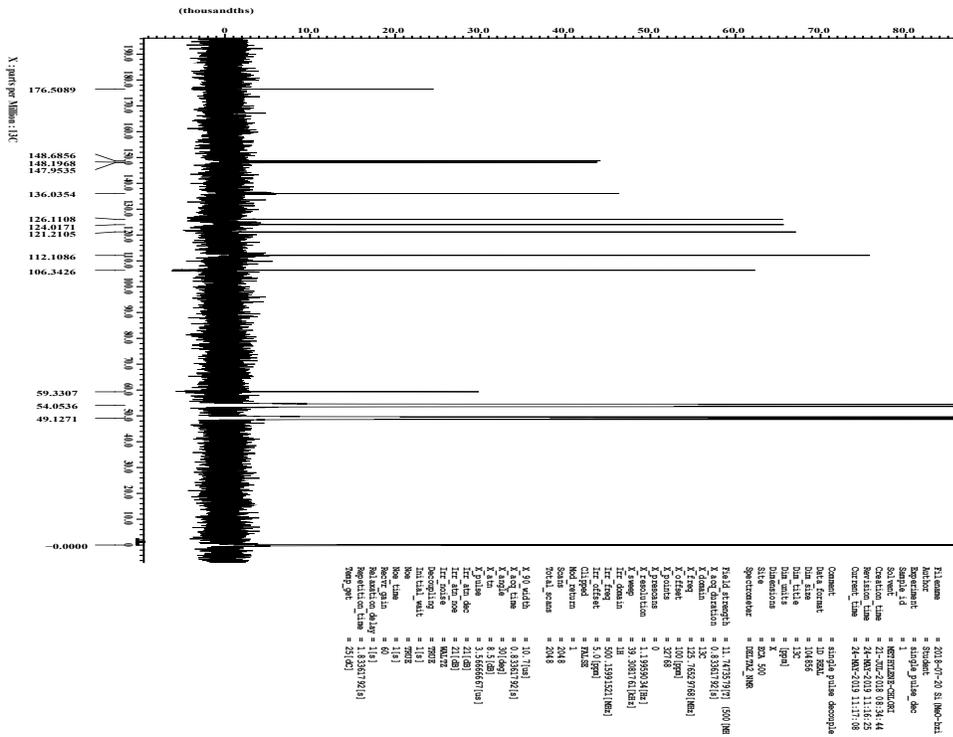


$\text{Si}(\text{MeObzimpy})_2$

$^1\text{H}$  NMR  $\text{Si}(\text{MeObzimpy})_2$

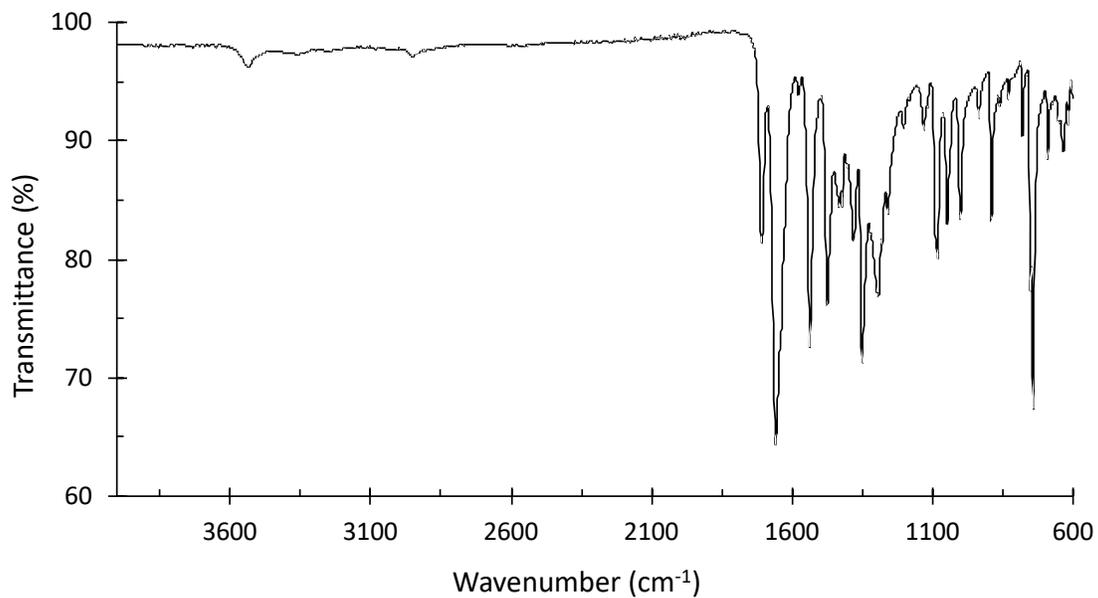


$^{13}\text{C}$  NMR  $\text{Si}(\text{MeObzimpy})_2$

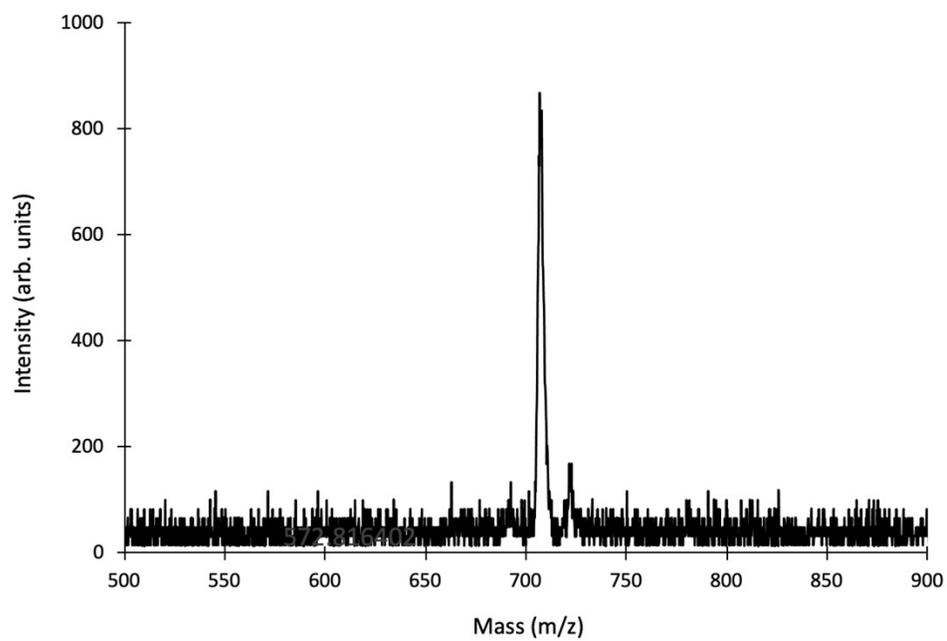






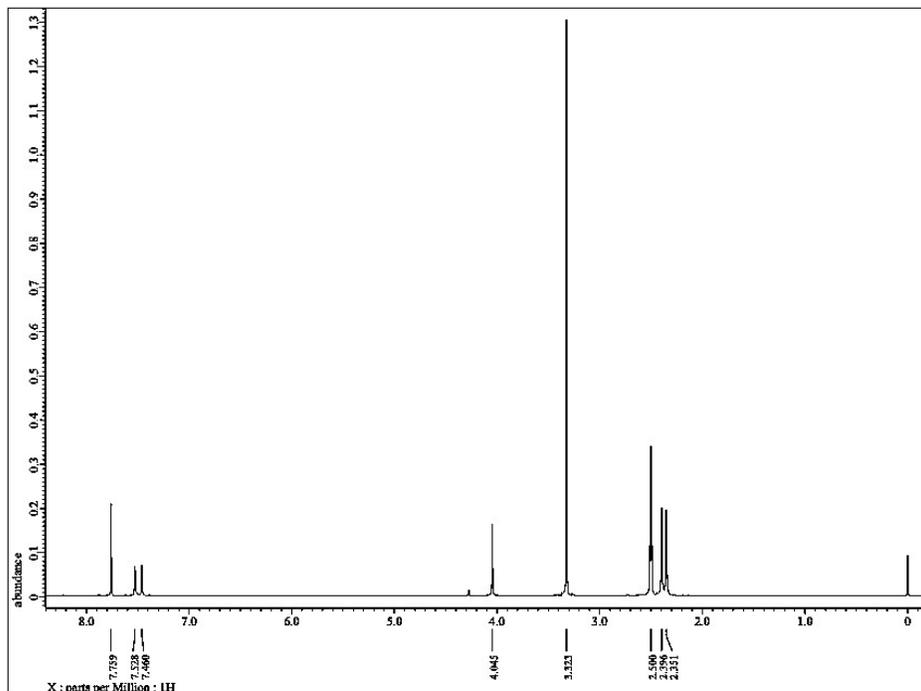


**MALDI-MS  $\text{Si}(\text{MeObzimpy})_2$**

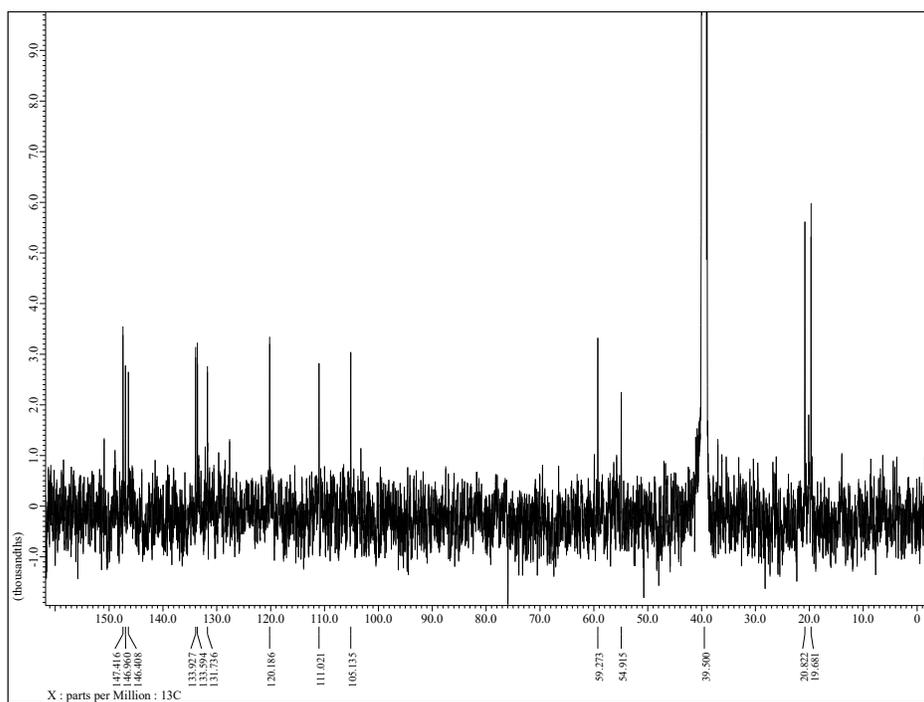


**$\text{Si}(\text{MeOMe}_2\text{bzimpy})_2$**

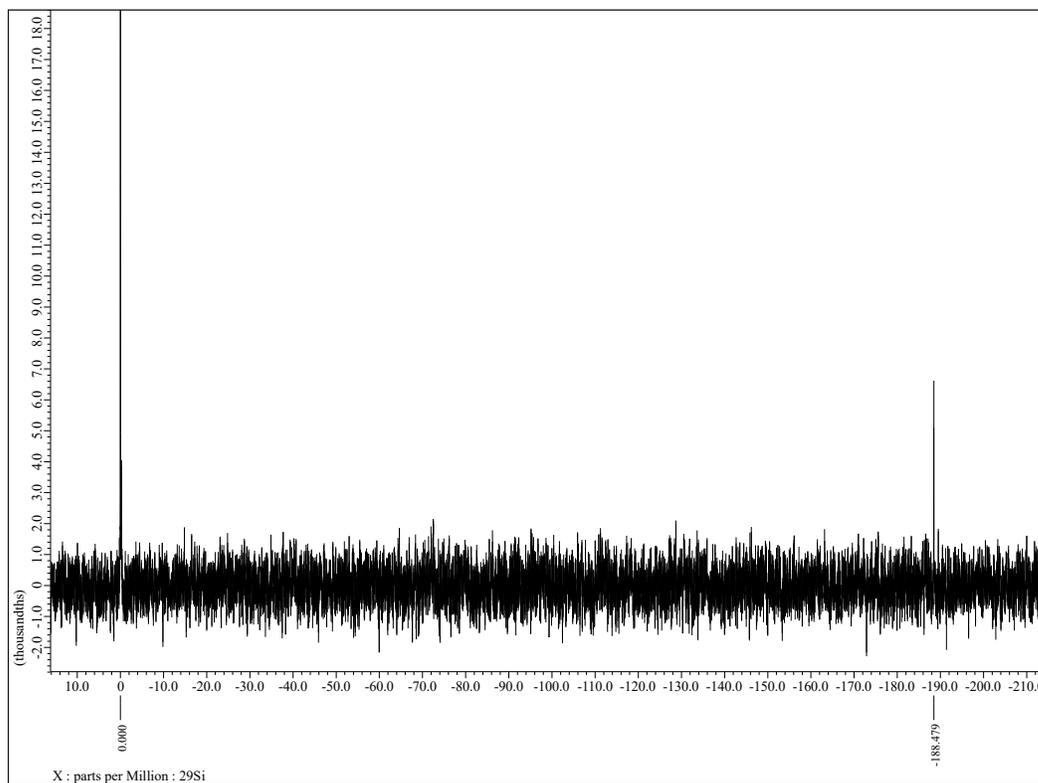
**$^1\text{H}$  NMR  $\text{Si}(\text{MeOMe}_2\text{bzimpy})_2$**



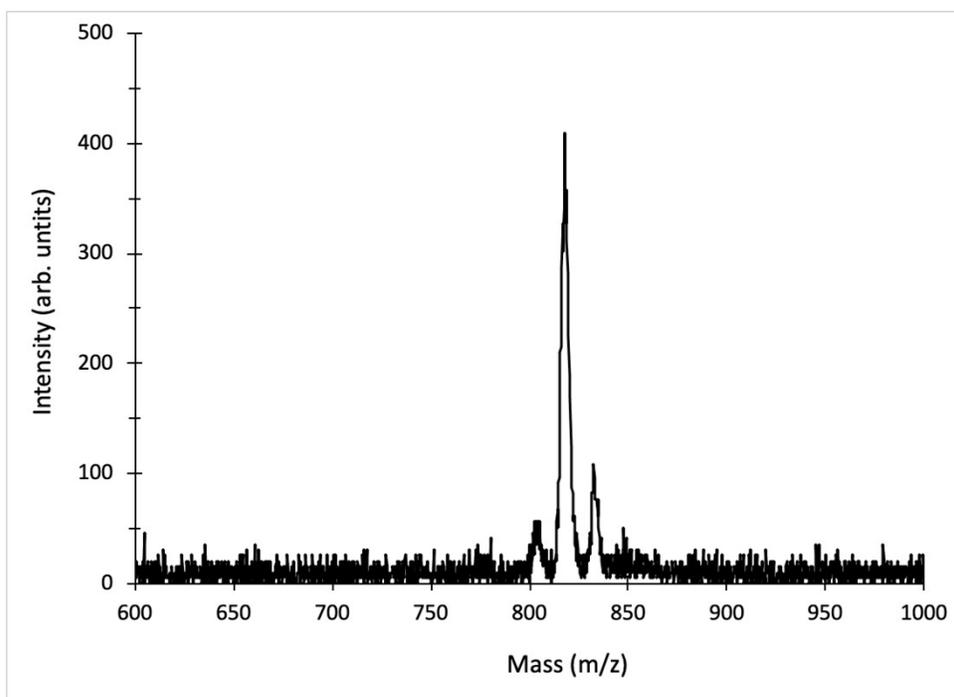
$^{13}\text{C}$  NMR  $\text{Si}(\text{MeOMe}_2\text{bzimpy})_2$

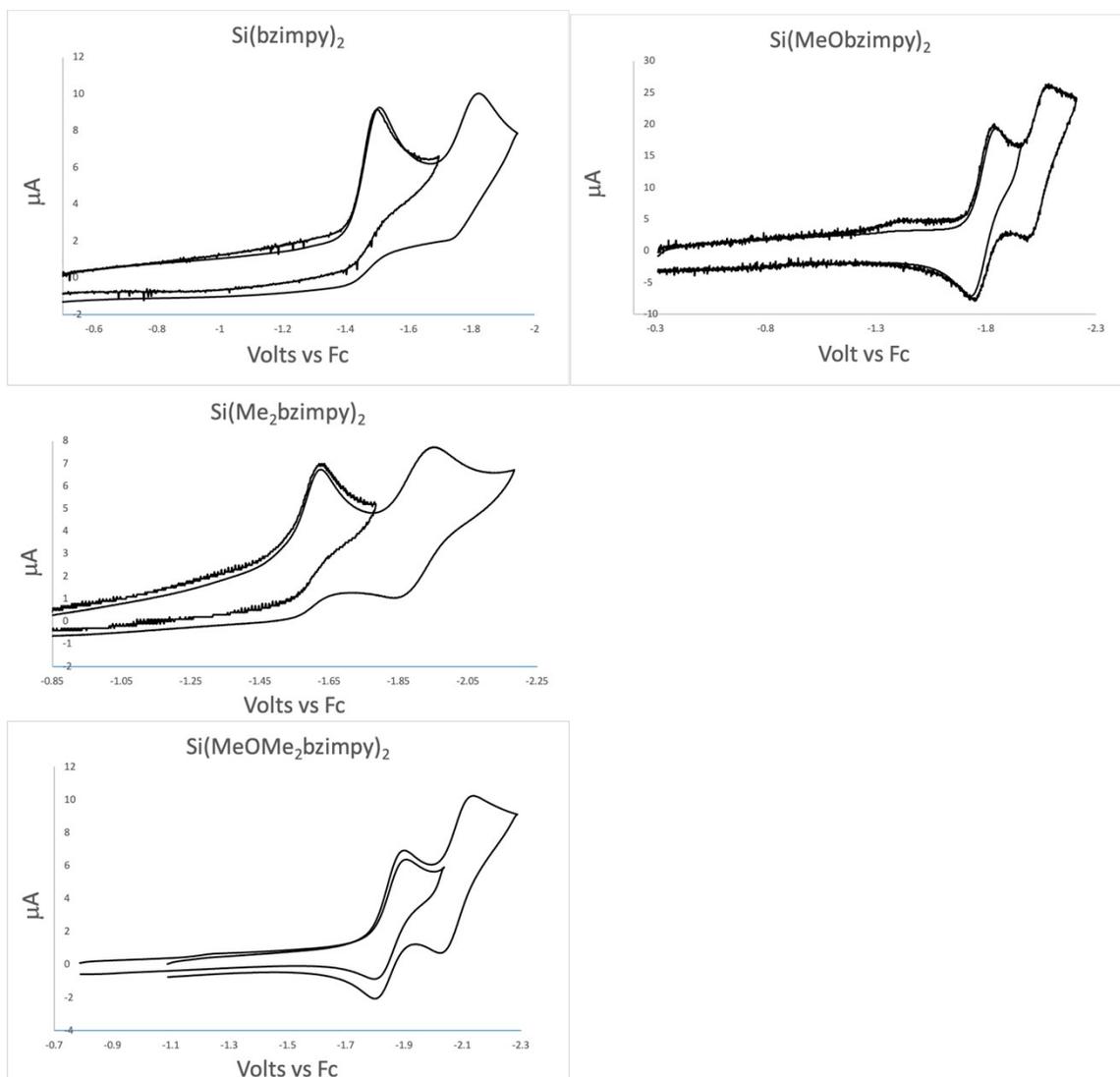


$^{29}\text{Si}$  NMR  $\text{Si}(\text{MeOMe}_2\text{bzimpy})_2$

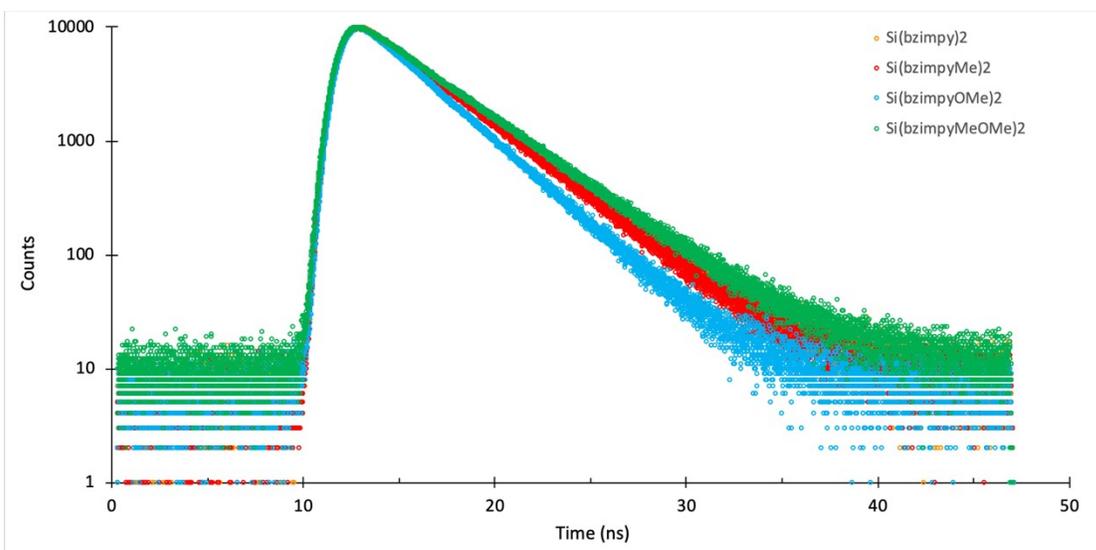


MALDI  $\text{Si}(\text{MeOMe}_2\text{bzimpy})_2$





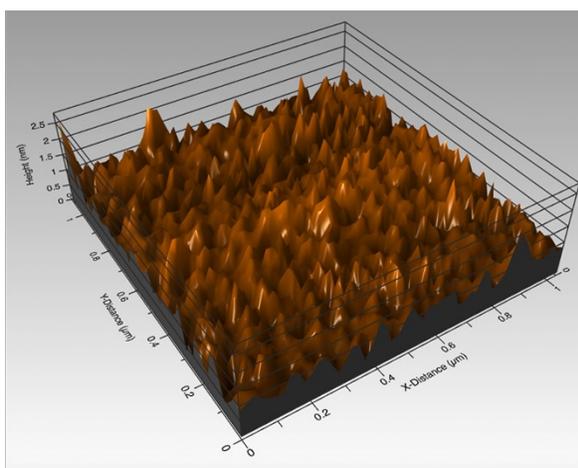
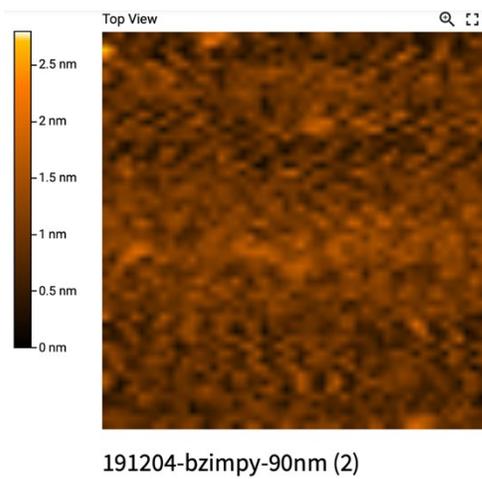
**Figure S1.** Cyclic voltammetry of Si complexes in dichloromethane using a Pt electrode and a scan rate of  $200 \text{ mV s}^{-1}$ . Potentials are referenced to ferrocene/ferrocenium.



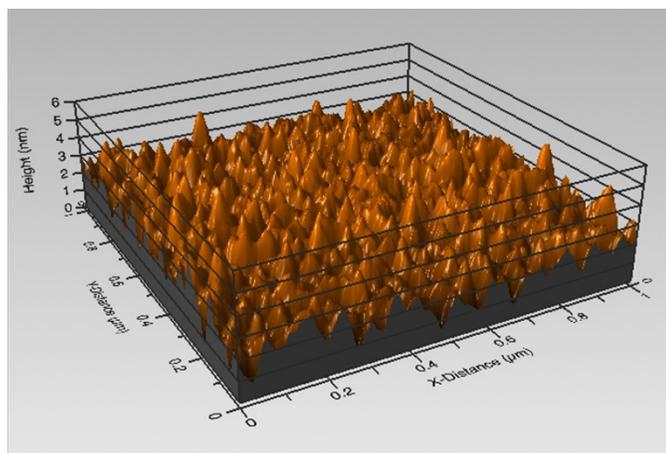
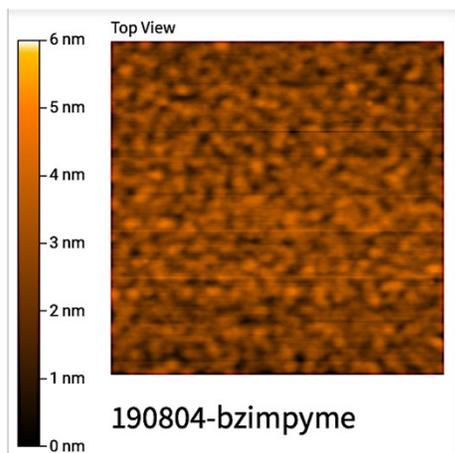
**Figure S2.** Singlet fluorescence lifetime plots (time-correlated single photon counting) of complexes 1-4 in dichloromethane solutions.

### S3. AFM images and surface roughness measurements of thermally evaporated $\text{Si}(\text{bzimpy})_2$ films.

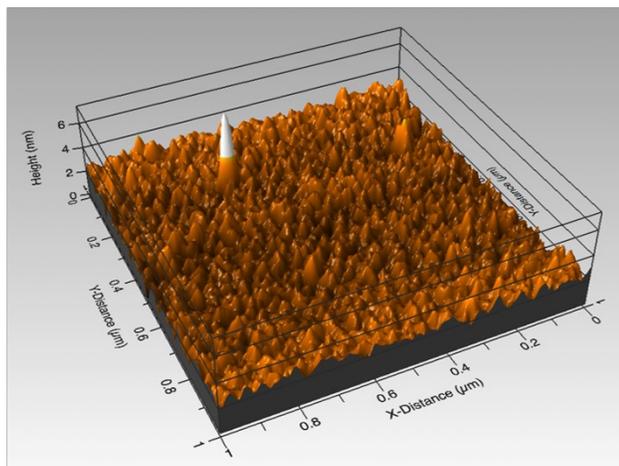
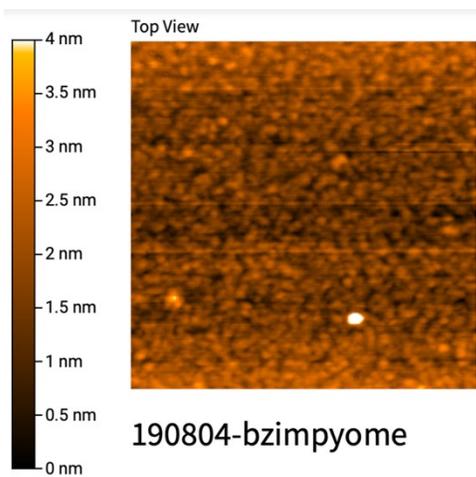
$\text{Si}(\text{bzimpy})_2$  90 nm film with 0.3 nm surface roughness



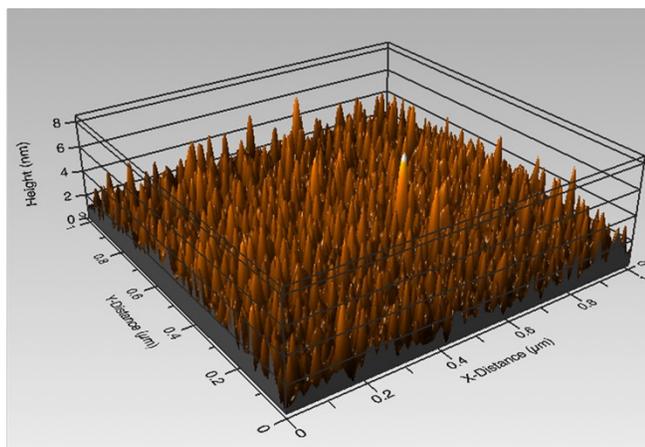
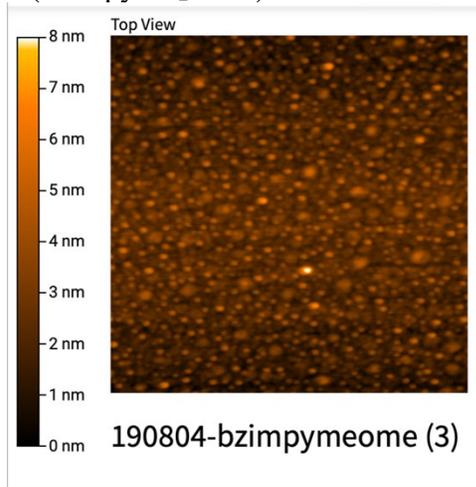
$\text{Si}(\text{bzimpyMe}_2)_2$  118 nm film with 0.6 nm surface roughness



Si(bzimpyme)<sub>2</sub> 18 nm film with 0.5 nm surface roughness



Si(bzimpymeMe<sub>2</sub>OMe)<sub>2</sub> 27 nm film with 0.5 nm surface roughness



### S3. Construction and preparation for SCLC, OLED, and OPV Devices

Patterned ITO glass substrates (Ossila) were sonicated in acetone for 10 min, followed by sonication in isopropyl alcohol for 10 min. ITO glass was blown dry with N<sub>2</sub> gas and treated with UV ozone etch for 20 min. All thermally evaporated materials were deposited at 10<sup>-6</sup> mbar pressure using tungsten evaporation boats. Devices to test **electron mobility** were constructed by depositing the Si(bzimpy)<sub>2</sub> derivatives directly onto the ITO electrodes followed by Al thermal evaporation using the following rates and resulting thicknesses: Si(bzimpy)<sub>2</sub> – 90 nm at 0.2 Å s<sup>-1</sup>, Si(Me<sub>2</sub>bmzimpy)<sub>2</sub> – 115 nm at 0.3 – 0.4 Å s<sup>-1</sup>, Si(MeObzimpy)<sub>2</sub> – 21 nm at 0.01-0.1 Å s<sup>-1</sup>, Si(MeOMebzimpy)<sub>2</sub> – 27 nm at 0.01-0.10 Å s<sup>-1</sup>, and Al – 20 nm at 0.2 Å s<sup>-1</sup> and 130 nm at 2.0 Å s<sup>-1</sup>. Devices to test **hole mobility** were constructed by depositing the Si(bzimpy)<sub>2</sub> derivatives onto PEDOT:PSS-coated ITO electrodes (preparation described below) followed by Au thermal evaporation using the following rates and resulting thicknesses: Si(bzimpy)<sub>2</sub> – 91 nm at 0.2 Å s<sup>-1</sup>, Si(Me<sub>2</sub>bmzimpy)<sub>2</sub> – 115 nm at 0.3 – 0.4 Å s<sup>-1</sup>, Si(MeObzimpy)<sub>2</sub> – 21 nm at 0.01-0.1 Å s<sup>-1</sup>, Si(MeOMebzimpy)<sub>2</sub> – 5 nm at 0.01-0.10 Å s<sup>-1</sup>, and Au – 51 nm at 0.2-0.25 Å s<sup>-1</sup> and 130 nm at 2.0 Å s<sup>-1</sup>. **OLEDs** MoO<sub>3</sub>/NPB/Si(bzimpy)<sub>2</sub>/LiF/Al were constructed using the following rates and resulting thicknesses: MoO<sub>3</sub> – 10 nm at 0.12 Å s<sup>-1</sup>, NPB – 32 nm at 0.12 Å s<sup>-1</sup>, Si(bzimpy)<sub>2</sub> – 91 nm at 0.2 Å s<sup>-1</sup>, Si(Me<sub>2</sub>bmzimpy)<sub>2</sub> – 77 nm at 0.3 – 0.4 Å s<sup>-1</sup>, Si(MeObzimpy)<sub>2</sub> – 81 nm at 0.01-0.1 Å s<sup>-1</sup>, Si(MeOMebzimpy)<sub>2</sub> – 53 nm at 0.01-0.10 Å s<sup>-1</sup>, LiF – 7.6 nm at 0.2 Å s<sup>-1</sup>, and Al – 20 nm at 0.2 Å s<sup>-1</sup> and 130 nm at 2.0 Å s<sup>-1</sup>. **Solar cells** were constructed using PEDOT:PSS hole conductor layer and P3HT:PCBM active layers. PEDOT:PSS solution was filtered through a 0.45 μm PES filter. This solution and the ITO glass were placed on a hot plate and heated to 55 °C prior to spin coating. The ITO glass was spun at 2000 rpm for 40 s, while 90 μL of PEDOT:PSS solution was deposited onto the slide. The film was allowed to dry for 3 min at room temperature. A second layer of PEDOT:PSS was added by spin coating 90 μL onto the substrate at 2000 rpm for 40 s. Slides were placed onto a hot plate for three min at 55 °C. The wide conductive strips of the ITO glass were wiped with a cotton swab dipped in water. The films were annealed at 140 °C for 10 min on a hot plate inside an N<sub>2</sub> filled glove box. A P3HT:PCBM solution (15 mg P3HT and 12 mg PCBM in 1 mL 1,2-dichlorobenzene) was heated to 50 °C on a hot plate inside an N<sub>2</sub> filled glove box for at least 2 h before use. The ITO glass was spun at 1900 rpm for 22 s in a spin coater, while 90 μL of P3HT:PCBM solution was deposited onto the substrate. The film was allowed to dry for 5 min at room temperature. Films were annealed at 110 °C on a hot plate, inside an N<sub>2</sub> filled glove box for 10 min. Si(bzimpy)<sub>2</sub> electron transport layers were deposited on the active layer at 10<sup>-6</sup> mbar pressure at the following rates and resulting thicknesses: Si(bzimpy)<sub>2</sub> – 3.5 nm at 0.2 Å s<sup>-1</sup>, Si(Me<sub>2</sub>bmzimpy)<sub>2</sub> – 4.0 nm at 0.3 – 0.4 Å s<sup>-1</sup>, Si(MeObzimpy)<sub>2</sub> – 6.0 nm at 0.01-0.1 Å s<sup>-1</sup>, and Si(MeOMebzimpy)<sub>2</sub> – 7.0 nm at 0.01-0.15 Å s<sup>-1</sup>. Al was deposited as a top electrode for the **solar cell** and **OLED** devices using the same conditions used for the electron mobility device measurements.

## S4 Crystallographic Information

X-ray crystallography data were acquired with an Agilent (now Rigaku) Gemini A Ultra diffractometer. Crystals of suitable size were coated with a thin layer of paratone-N oil, mounted on the diffractometer, and flash cooled to 100 K in the cold stream of the Cryojet XL liquid nitrogen cooling device (Oxford Instruments) attached to the diffractometer. The diffractometer was equipped with sealed-tube long fine focus X-ray sources with Mo target ( $\lambda = 0.71073 \text{ \AA}$ ) and Cu target ( $\lambda = 1.5418 \text{ \AA}$ ), four-circle kappa goniometer, and CCD detector. CrysAlisPro<sup>5</sup> software was used to control the diffractometer and perform data reduction. The crystal structure was solved with SHELXS.<sup>6</sup> All non-hydrogen atoms appeared in the E-map of the correct solution. Alternate cycles of model-building in Olex2<sup>7</sup> and refinement in SHELXL<sup>6</sup> followed. All non-hydrogen atoms were refined anisotropically. All hydrogen atom positions were calculated based on idealized geometry and recalculated after each cycle of least squares. During refinement, hydrogen atom – parent atom vectors were held fixed (riding motion constraint).

Solvent disorder modeling: Solvent disorder in **4** was modeled using idealized water molecules (DFIX) with partial occupancy in two separate partitions. For two pairs of water molecules (nearly overlapping but in separate partitions) the oxygen atom anisotropic displacement parameters were further constrained with EADP. Solvent disorder in **3** prevented the identification of all hydrogen atom locations associated with water molecules. One idealized water molecule and seven idealized OH fragments (all restrained with DFIX) were optimized with full occupancy without partitioning.

All structures and crystallographic data have been deposited with CCSD, and a summary of the structure and refinement parameters are provided in the following tables.

**Table 1. Crystal data and structure refinement for 2 (CCSD #2049551).**

Identification code	Si(MeObzimpy) <sub>2</sub>
Empirical formula	C <sub>40</sub> H <sub>26</sub> N <sub>10</sub> O <sub>2</sub> Si
Formula weight	706.804
Temperature/K	99.98(10)
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /c
a/Å	9.5059(3)
b/Å	30.4222(7)
c/Å	11.8486(4)
α/°	90
β/°	103.699(3)
γ/°	90
Volume/Å <sup>3</sup>	3329.03(17)
Z	4
ρ <sub>calc</sub> /g/cm <sup>3</sup>	1.410
μ/mm <sup>-1</sup>	1.072
F(000)	1469.5
Crystal size/mm <sup>3</sup>	0.64 × 0.072 × 0.0396
Radiation	Cu Kα (λ = 1.54184)
2θ range for data collection/°	8.22 to 133.46
Index ranges	-8 ≤ h ≤ 11, -36 ≤ k ≤ 35, -14 ≤ l ≤ 13
Reflections collected	22280
Independent reflections	5884 [R <sub>int</sub> = 0.0480, R <sub>sigma</sub> = 0.0365]
Data/restraints/parameters	5884/0/582
Goodness-of-fit on F <sup>2</sup>	1.077
Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.0433, wR <sub>2</sub> = 0.1000
Final R indexes [all data]	R <sub>1</sub> = 0.0536, wR <sub>2</sub> = 0.1075
Largest diff. peak/hole / e Å <sup>-3</sup>	0.32/-0.46

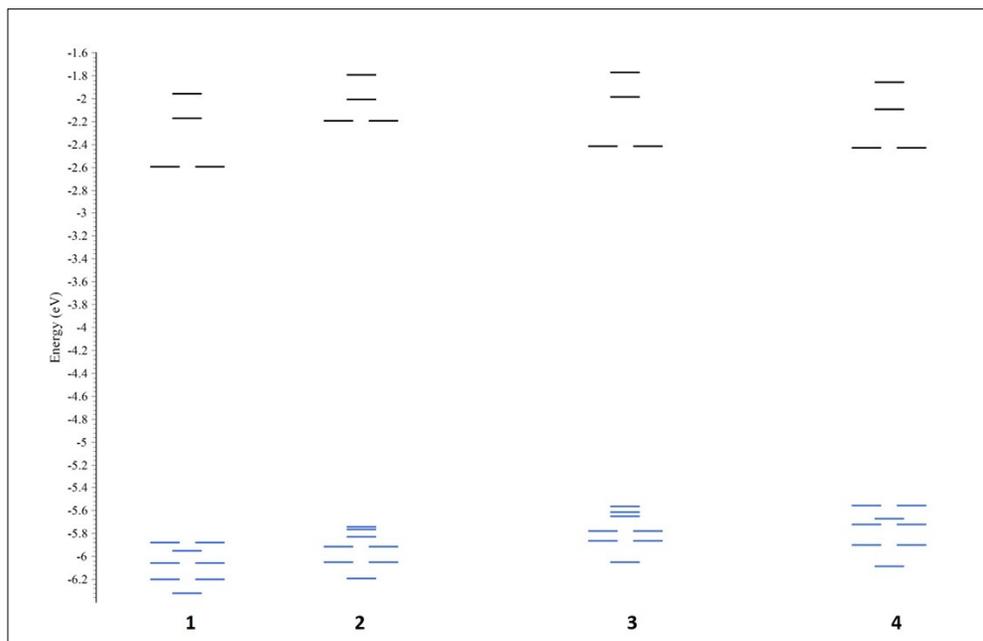
**Table 2. Crystal data and structure refinement for 3 (CCSD #2056293).**

Identification code	Si(Me <sub>4</sub> bzimpy) <sub>2</sub>
Empirical formula	C <sub>46</sub> H <sub>38</sub> N <sub>10</sub> Si•8(H <sub>2</sub> O)
Formula weight	896.034
Temperature/K	90(4)
Crystal system	orthorhombic
Space group	Pca2 <sub>1</sub>
a/Å	22.1141(15)
b/Å	10.9744(4)
c/Å	19.8058(8)
α/°	90
β/°	90
γ/°	90
Volume/Å <sup>3</sup>	4806.6(4)
Z	4
ρ <sub>calc</sub> /g/cm <sup>3</sup>	1.238
μ/mm <sup>-1</sup>	0.110
F(000)	1885.2
Crystal size/mm <sup>3</sup>	0.376 × 0.308 × 0.056
Radiation	Mo Kα (λ = 0.71073)
2θ range for data collection/°	6.66 to 57.42
Index ranges	-19 ≤ h ≤ 27, -14 ≤ k ≤ 14, -26 ≤ l ≤ 18
Reflections collected	15306
Independent reflections	7865 [R <sub>int</sub> = 0.0342, R <sub>sigma</sub> = 0.0483]
Data/restraints/parameters	7865/8/624
Goodness-of-fit on F <sup>2</sup>	1.051
Final R indexes [I >= 2σ (I)]	R <sub>1</sub> = 0.0482, wR <sub>2</sub> = 0.1185
Final R indexes [all data]	R <sub>1</sub> = 0.0622, wR <sub>2</sub> = 0.1288
Largest diff. peak/hole / e Å <sup>-3</sup>	0.42/-0.29
Flack parameter	-0.13(14)

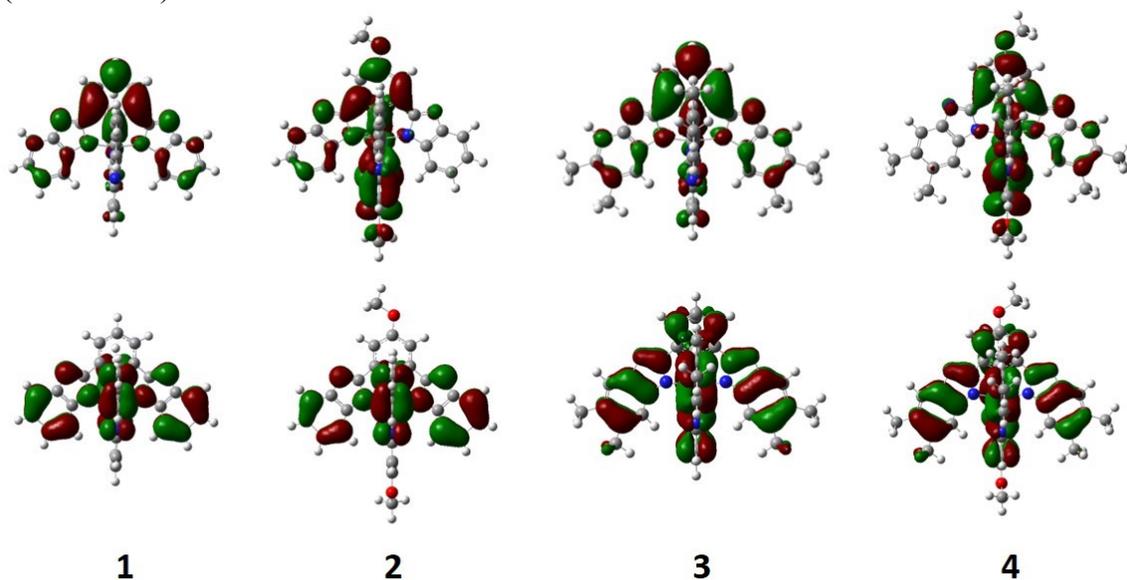
**Table 3. Crystal data and structure refinement for 4 (CCSD #2049366).**

Identification code	Si(Me <sub>4</sub> MeObzimpy) <sub>2</sub>
Empirical formula	C <sub>48</sub> H <sub>56.59</sub> N <sub>10</sub> O <sub>9.29</sub> Si
Formula weight	950.444
Temperature/K	100.01(10)
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /c
a/Å	10.78042(19)
b/Å	23.4583(4)
c/Å	20.0208(4)
α/°	90
β/°	95.6050(17)
γ/°	90
Volume/Å <sup>3</sup>	5038.87(16)
Z	4
ρ <sub>calc</sub> /g/cm <sup>3</sup>	1.253
μ/mm <sup>-1</sup>	0.943
F(000)	2019.4
Crystal size/mm <sup>3</sup>	0.11736 × 0.06262 × 0.06228
Radiation	Cu Kα (λ = 1.54184)
2θ range for data collection/°	7.54 to 133.5
Index ranges	-12 ≤ h ≤ 12, -27 ≤ k ≤ 27, -21 ≤ l ≤ 23
Reflections collected	37658
Independent reflections	8909 [R <sub>int</sub> = 0.0438, R <sub>sigma</sub> = 0.0350]
Data/restraints/parameters	8909/6/756
Goodness-of-fit on F <sup>2</sup>	1.052
Final R indexes [I >= 2σ (I)]	R <sub>1</sub> = 0.0532, wR <sub>2</sub> = 0.1387
Final R indexes [all data]	R <sub>1</sub> = 0.0692, wR <sub>2</sub> = 0.1540
Largest diff. peak/hole / e Å <sup>-3</sup>	0.68/-0.46

## S5. Computational Results



Molecular orbital diagram of frontier orbitals of **1-4**. MOs calculated using DFT (B3LYP/6-31G\*). Calculations were performed using Gaussian 16W with GaussView 6.1, and MO diagram was created using Chemissian (degeneracy threshold 15 meV) with occupied energy levels indicated as blue and unoccupied orbitals labeled black. A visual representation of the HOMO and LUMO of each species is also included (isovalue = 0.02). Note the greater emphasis of pyridine orbitals in the LUMO orbitals (top row) and greater emphasis on benzamidazolyl moiety in the HOMO representations (bottom row).



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