Supplementary data

Intermolecular Peripheral 2,5-Bipyridyl Interactions by Cyclization of 1,1'-Silanylene Unit of 2,3,4,5-Aryl Substituted Siloles: Enhanced Thermal Stability, High Charge Carrier Mobility, and Their Application to Electron Transporting Layers for OLEDs

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Contents

Experimental Procedures

All manipulations were carried out under a dry nitrogen (or an argon atmosphere) atmosphere using standard Schlenk techniques. THF was dried over sodium/benzophenone. Silacyclopentyl dichloride (**1-Cy5**) and silacyclohexyl dichloride (**1-Cy6**) were prepared using the method reported elsewhere.[1] The ^1H and ^{13}C spectra were recorded on a Varian Unity Inova AS600 spectrometer operating at 599.80 and 150.83 MHz, respectively. All proton and carbon chemical shifts were measured relative to the internal residual benzene from the lock solvent (99.9% $CDCl_3$) and then referenced to Me_4Si (0.00 ppm). The elemental analyses were performed with a Carlo Erba Instruments CHNS-O EA 1108 analyzer. High Resolution Tandem Mass Spectrometry (Jeol LTD JMS-700) was performed by the Korean Basic Science Institute (Seoul).

The absorption and photoluminescence spectra were recorded on a Shimadzu UV-3101PC UV-VIS-NIR scanning spectrophotometer and a Varian Cary Eclipse fluorescence spectrophotometer, respectively. The fluorescence quantum yields in chloroform using 9,10-diphenylanthracene as a standard were determined by the dilution method.

The temporal profiles of the fluorescence decay were measured using a time-correlated single photon counting method (TCSPC) with a self-mode-locked femtosecond Ti:sapphire laser (Coherent Co.) pumped by an Nd:YVO_4 laser used as the excitation source. The laser output can span the excitation wavelength over the range, 350−490 nm, using second harmonic generation and the standard electronics for TCSPC were obtained from Edinburgh Instruments. The instrumental response function was measured by detecting the scattered laser pulse with a quartz crystal. This TCSPC method allows a time resolution of approximately 50 ps after deconvolution.

The cyclic voltammetry (CV) experiments were performed using a BAS 100 electrochemical analyzer. Platinum, platinum wire, and $Ag/AgNO_3$ (0.10 M) were used as the working, counter, and reference electrodes, respectively. The CV experiments were performed using these three electrodes immersed in a 0.1 M tetrabutylammonium perchlorate (Bu_4NClO_4) solution in anhydrous CH_2Cl_2 at room temperature under argon with a scan rate of 0.1 V/s.

The hole mobility of **3-Cy5**, **3-Cy6**, and **PyPySPyPy** were measured with thick sandwiched samples (2.24, 3.70, and 3.26 μm, respectively) using ITO and Al electrodes. Devices with the structure ITO/siloles/Al (100 nm) were fabricated for the TOF measurements. The sample had a 2 mm × 2 mm square pattern. The sample was irradiated with a N_2 laser (Photon Technology International Inc. GL 3300) with a pulse width of 10 nm at a wavelength of 350 nm. A resistor was connected in series to the samples, an electric field was biased to the sample and the resistor, and the photocurrent was measured using a digital oscilloscope (Lecroy LC564A).

Preparation of 2,5-bipyridylsiloles

Synthesis of bis(phenylethynyl)silacyclopentylsilane (2-Cy5). A solution of 2.5 M *n*-BuLi/hexane (4.4 mL, 11 mmol) at –78 ºC was added to a stirred solution of phenylacetylene (1.02 g, 10 mmol) in THF (50 mL), and the resulting mixture was stirred at the same temperature for 1 h. Subsequently, 0.775 g (5 mmol) of silacyclopentyl dichloride (**1-Cy5**) was added and the mixture was stirred at room temperature for 6 h. After filtering the resulting mixture through a Celite pad, the volatile solvent was removed under reduced pressure and the residue was purified by flash chromatography over silica gel using hexane as the eluent. Recrystallization from hexane at 0 ºC afforded **2-Cy5** (1.22 g, 85%) as a white powder (Found: C, 83.75; H, 6.23. $C_{20}H_{18}Si$ requires C, 83.86; H, 6.33%); δ_H(599.80 MHz; $CDCl_3$; Me_4Si) 7.57 (4 H, dd, *J* 7.2 and 1.8, *Ph*), 7.34 (6 H, m, *Ph*), 1.81 (4 H, m, $SiCH_2CH_2$), 1.11 (4 H, t, *J* 7.2, $SiCH_2CH_2$); δ_C(150.83 MHz; $CDCl_3$; Me_4Si) 132.4, 129.3, 128.6, 122.9, 107.4, 89.7, 27.3, 14.7; HRMS(FAB) calcd. for $C_{20}H_{18}Si$: 286.1178. Found: 286.1186 $[M]^+$.

Synthesis of bis(phenylethynyl)silacyclohexylsilane (2-Cy6). This compound was prepared using a similar procedure to that used to synthesize **2-Cy5** but using silacyclohexyl dichloride (**1-**

Cy6) instead of silacyclopentyl dichloride (**1-Cy5**); the product (**2-Cy6**) was isolated as a colorless oil. Yield: 1.38 g (92%) (Found: C, 83.85; H, 6.69. $C_{21}H_{20}Si$ requires C, 83.94; H, 6.71%); δ_H(599.80 MHz; $CDCl_3$; Me_4Si) 7.51 (4 H, dd, *J* 7.8 and 1.2, *Ph*), 7.32 (6 H, m, *Ph*), 1.83 (4 H, m, $SiCH_2C\mathit{H}_2CH$), 1.47 (2 H, m, $SiCH_2CH_2C\mathit{H}$), 0.99 (4 H, t, *J* 7.2, $SiC\mathit{H}_2CH_2CH$); δ_C(150.83 MHz; $CDCl_3$; Me_4Si) 132.4, 129.1, 128.4, 122.9, 106.7, 89.4, 29.6, 24.0, 14.3; HRMS(FAB) calcd for $C_{21}H_{20}Si$: 300.1334. Found: 300.1341 $[M]^+$.

Synthesis of 1,1-silacyclopentyl-2,5-bipyridyl-3,4-diphenylsilole (3-Cy5). A mixture of lithium (0.17 g, 12 mmol) and naphthalene (1.54 g, 12 mmol) in 10 mL of THF was stirred at room temperature under nitrogen for 3 h to form a deep dark-green solution of lithium naphthaleneide. A solution of bis(phenylethynyl)silacyclopentylsilane (0.86 g, 3 mmol) in 8 mL of THF was added dropwise to the lithium naphthaleneide solution over 2 min at room temperature. After stirring for 15 min, the mixture was cooled to 0 ºC. $ZnCl_2$(tmeda) (3.0 g, 12 mmol) was added as a solid to the mixture at 0 ºC, followed by dilution with 15 mL of THF, to give a black suspension. After stirring for an additional hour at room temperature, a solution of 6-bromo-2,2′-bipyridyl (1.41 g, 6 mmol) and $Pd(PPh_3)_2Cl_2$ (0.1 g, 0.12 mmol) in 15 ml of THF was added. The mixture was heated under reflux for 14 h. The mixture was then hydrolyzed with water. The organic layer was extracted with CH_2Cl_2 and dried over magnesium sulfate. The solvent was removed under reduced pressure, and the residue was purified by silica gel column chromatography using ethyl acetate/hexane (1:10) as the eluent. **3-Cy5** was obtained as a green powder (1.146 g, 64%) (Found: C, 80.42; H, 5.36; N, 9.34. $C_{40}H_{32}N_4Si$ requires C, 80.50; H, 5.40; N, 9.39%); mp (DSC) 275 ºC; δ_H(599.80 MHz; $CDCl_3$; Me_4Si) 8.63 (2 H, m), 8.24 (2 H, d, *J* 7.8), 8.07 (2 H, dd, *J* 7.8 and 1.2), 7.75 (2 H, td, *J* 7.8 and 1.8), 7.38 (2 H, t, *J* 7.8), 7.24 (2 H, m), 7.09 (6 H, m), 6.92 (4 H, m), 6.59 (2 H, dd, *J* 8.4 and 1.2), 1.86 (4 H, m, $SiCH_2C\mathit{H}_2$), 1.32 (4 H, t, *J* 6.6, $SiC\mathit{H}_2CH_2$); δ_C(150.83 MHz; $CDCl_3$; Me_4Si) 158.2, 156.9, 156.8, 155.6, 149.2, 142.5, 139.2, 136.9, 136.4, 129.7, 128.1, 127.0, 123.9, 123.7, 121.4, 118.1, 28.0, 10.8; HRMS(FAB) calcd for $C_{40}H_{32}N_4Si$: 596.2396. Found: 596.2385 $[M]^+$.

Synthesis of 1,1-silacyclohexyl-2,5-bipyridyl-3,4-diphenylsilole (3-Cy6). This compound was prepared using a similar procedure to that used to synthesize **3-Cy5** but using silacyclohexyl dichloride (**2-Cy6**) instead of silacyclopentyl dichloride (**2-Cy5**); the product (**3-Cy6**) was isolated as a green powder. Yield: 1.246 g (68%) (Found: C, 80.58; H, 5.57; N, 9.15. $C_{41}H_{34}N_4Si$ requires C, 80.62; H, 5.61; N, 9.17%); mp (DSC): 247 °C; δ_H(599.80 MHz; $CDCl_3$; Me_4Si) 8.65 (2 H, m), 8.46 (2 H, d, *J* 7.2), 8.11 (2 H, d, *J* 7.8), 7.78 (2 H, t, *J* 7.8), 7.39 (2 H, td, *J* 7.8 and 1.2), 7.25 (2 H, m), 7.03 (6 H, m), 6.89 (4 H, m), 6.62 (2 H, d, *J* 8.4), 1.79 (4 H, m, $SiCH_2CH_2CH$), 1.50 (2 H, m, $SiCH_2CH_2CH$), 1.39 (4 H, t, *J* 6.0, $SiCH_2CH_2CH$); δ_C(150.83 MHz; $CDCl_3$; Me_4Si) 159.0, 156.8, 156.2, 155.5, 149.3, 144.2, 138.9, 136.9, 136.5, 129.8, 128.0, 126.9, 123.9, 123.7, 121.5, 117.9, 29.6, 24.6, 11.0; HRMS(FAB) calcd for $C_{41}H_{34}N_4Si$: 610.2553. Found: 610.2532 $[M]^+$.

Crystal structure determination

Crystals of **3-Cy5**, **3-Cy6**, and **PyPySPyPy** were obtained from CH_2Cl_2/hexane (*v*/*v* = 1/1) and mounted on the diffractometer. The preliminary examination and data collection were performed using a Bruker SMART CCD detector system single-crystal X-ray diffractometer equipped with a sealed-tube X-ray source (40 kV × 50 mA) using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The preliminary unit cell constants were determined from a set of 45 narrow-frame (0.3° in ω) scans. The double-pass method of scanning was used to exclude noise. The frames collected were integrated using an orientation matrix determined from the narrow-frame scans. The SMART software package was used for data collection, and SAINT was used for frame integration.[2a] The final cell constants were determined by a global refinement of the *xyz* centroids of the reflections harvested from the entire data set. Structure solution and refinement were carried out using the SHELXTL-PLUS software package.[2b]

Fabrication of OLED devices

ITO-coated glass (20 Ω/sq) was first cleaned using conventional procedures. Under an inert atmosphere in a fabrication chamber, the sample was exposed to an UV/ozone treatment. The organic and metal layers were deposited thermally onto an ITO surface at a rate of 1-2 Å/s at a pressure of ca. 4×10^{-6} Torr. Typical devices were fabricated with PEDOT·PSS as the hole-injection layer (70 nm), NPB as the hole-transporting layer (50 nm), Alq_3 as the emitting layer (50 nm), and the silole compounds (**3-Cy5**, **3-Cy6**, or **PyPySPyPy**) as the electron-transporting layer (45 nm). LiF (0.5 nm) and Al (100 nm) were deposited as the cathode. The deposited film thickness was measured using a Tencor P-2 long scan profiler. The characteristics of the OLED devices were determined using a Photoresearch PR650 spectrometer and Keithley 306 source measure unit.

References

1. S.-J. Kim, I. N. Jung, B. R. Yoo, S. Cho, J. Ko, S. H. Kim, D. Byun, S. O. Kang, *Organometallics* 2001, **20**, 2136.

2. (a) *SMART* and *SAINT*; Bruker Analytical X-Ray Division: Madison, WI, **2002**. (b) G. M. Sheldrick, *SHELXTL-PLUS* Software Package; Bruker Analytical X-Ray Division: Madison, WI, **2002**.

Table S1. Crystal data and structure refinement for **PyPySPyPy**, **3-Cy5**, and **3-Cy6**

	PyPySPyPy	**3-Cy5**	**3-Cy6**
Empirical formula	$C_{38}H_{30}N_4Si$	$C_{40}H_{32}N_4Si$	$C_{41}H_{34}N_4Si$
Formula weight	570.76	596.79	610.82
Temperature	293(2) K	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $C2/c$	Monoclinic, $C2/c$
Unit cell dimensions	a = 22.863(4) Å α = 90°	a = 23.862(5) Å α = 90°	a = 24.1053(18) Å α = 90°
	b = 10.3528(18) Å β = 90.721(4)°	b = 12.213(3) Å β = 96.596(5)°	b = 12.0672(9) Å β = 90.0750(10)°
	c = 26.024(4) Å γ = 90°	c = 10.898(2) Å γ = 90°	c = 11.2330(8) Å γ = 90°
Volume	6159.5(18) $Å^3$	3155.1(12) $Å^3$	3226.6(4) $Å^3$
Z, Calculated density	8, 1.231 Mg/m^3	4, 1.256 Mg/m^3	4, 1.257 Mg/m^3
μ	0.110 mm^{-1}	0.113 mm^{-1}	0.109 mm^{-1}
$F(000)$	2400	1256	1288
Crystal size	0.31 × 0.25 × 0.21 mm	0.41 × 0.35 × 0.22 mm	0.33 × 0.26 × 0.25 mm
θ range for data collection	1.57 to 28.42°	1.72 to 28.27°	1.71 to 28.33°
Limiting indices	$-30<=h<=30, -13<=k<=13, -34<=l<=34$	$-31<=h<=31, -16<=k<=16, -14<=l<=13$	$-32<=h<=32, -16<=k<=16, -14<=l<=14$
Reflections collected / unique	61832 / 15379 [R(int) = 0.0906]	15594 / 3915 [R(int) = 0.0559]	16323 / 4002 [R(int) = 0.0268]
Max. and min. transmission	0.9731 and 0.9626	0.9762 and 0.9563	0.9727 and 0.9652
Completeness to theta	99.3%, Completeness to theta = 28.42	99.9%, Completeness to theta = 28.27	99.8 %, Completeness to theta = 28.33
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	15379 / 0 / 780	3915 / 0 / 205	4002 / 0 / 209
Goodness-of-fit on F^2	0.996	1.003	0.968
Final R indices [$I>2\sigma(I)$]	$R_1 = 0.0567$, $wR_2 = 0.1318$	$R_1 = 0.0495$, $wR_2 = 0.1217$	$R_1 = 0.0594$, $wR_2 = 0.1695$
R indices (all data)	$R_1 = 0.1863$, $wR_2 = 0.2004$	$R_1 = 0.1107$, $wR_2 = 0.1536$	$R_1 = 0.0912$, $wR_2 = 0.2090$
Largest diff. peak and hole	0.259 and −0.279 e. $Å^{-3}$	0.397 and −0.282 e. $Å^{-3}$	0.504 and −0.543 e. $Å^{-3}$

[a] $R_1 = \Sigma||F_o| - |F_c||$ (based on reflections with $F_o^2 > 2\sigma F^2$. [b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.095P)^2]$; $P = [\max(F_o^2, 0) + 2F_c^2]/3$(also with $F_o^2 > 2\sigma F$).

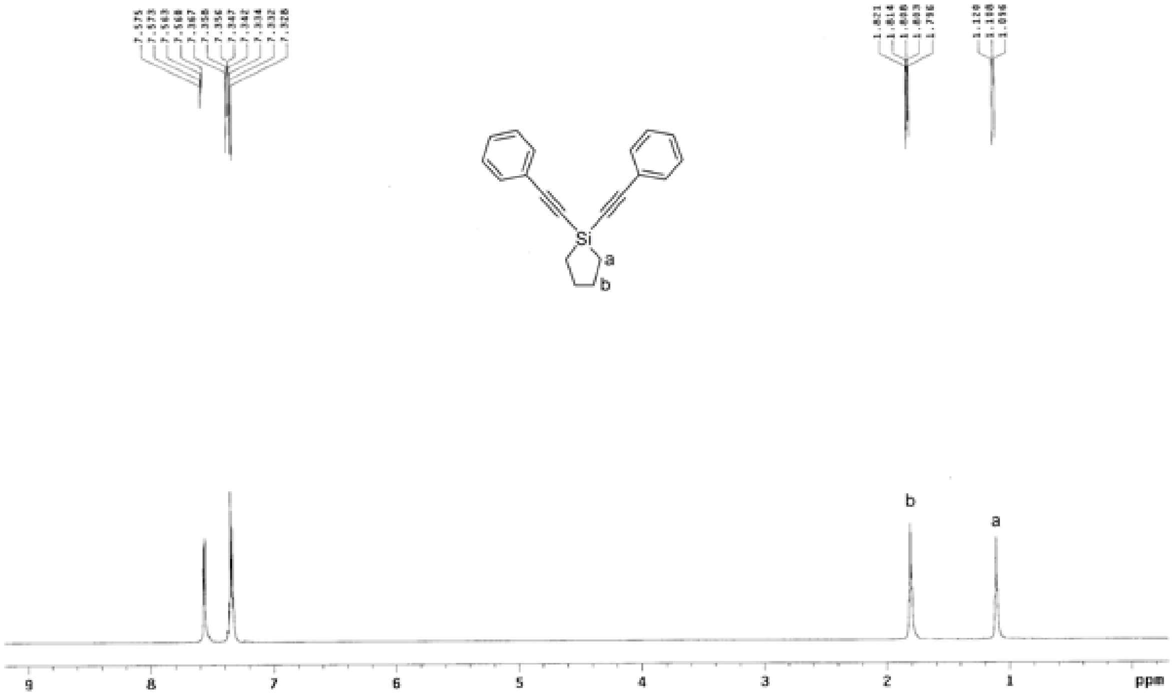

Figure S1 (a). ^{1}H-NMR spectroscopic view of **2-Cy5** in $CDCl_3$.

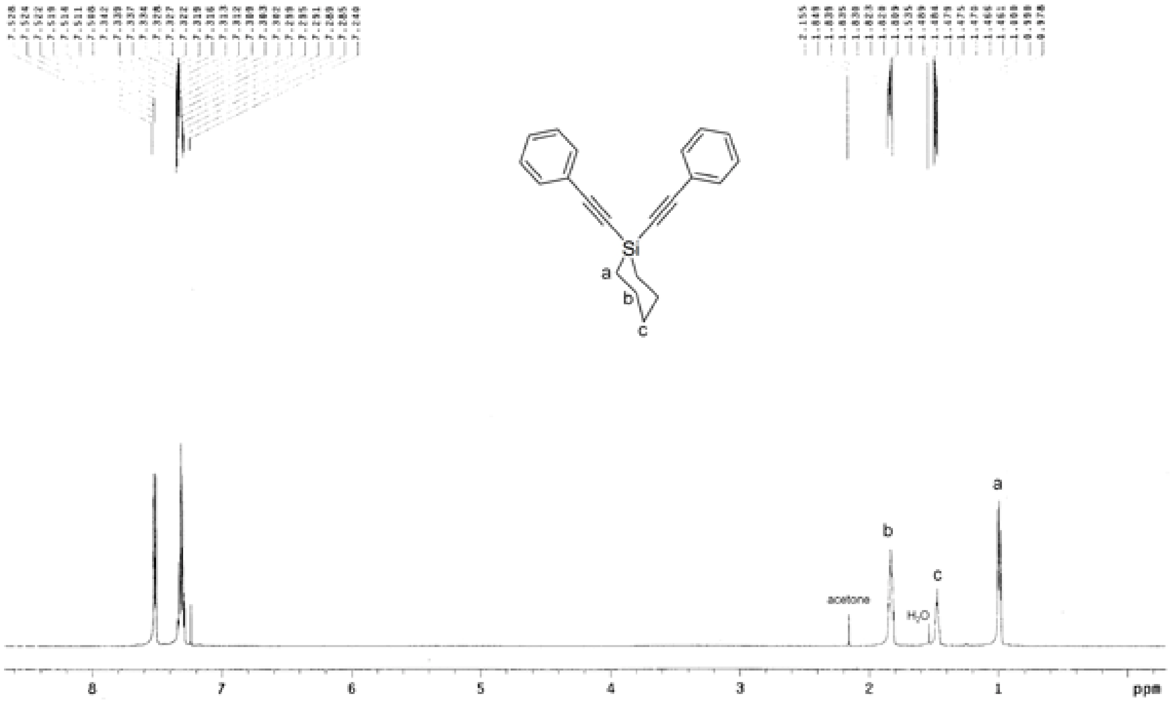

Figure S1 (b). ^{1}H-NMR spectroscopic view of **2-Cy6** in $CDCl_3$.

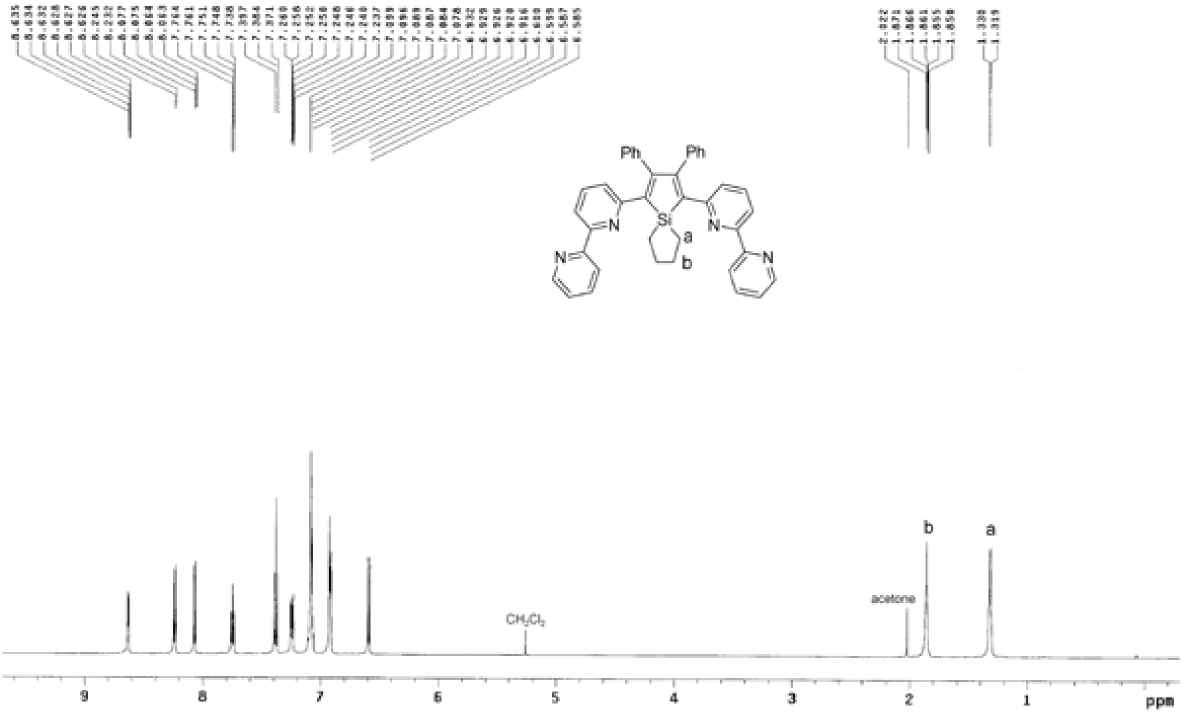

Figure S1 (c). ^{1}H-NMR spectroscopic view of **3-Cy5** in $CDCl_3$.

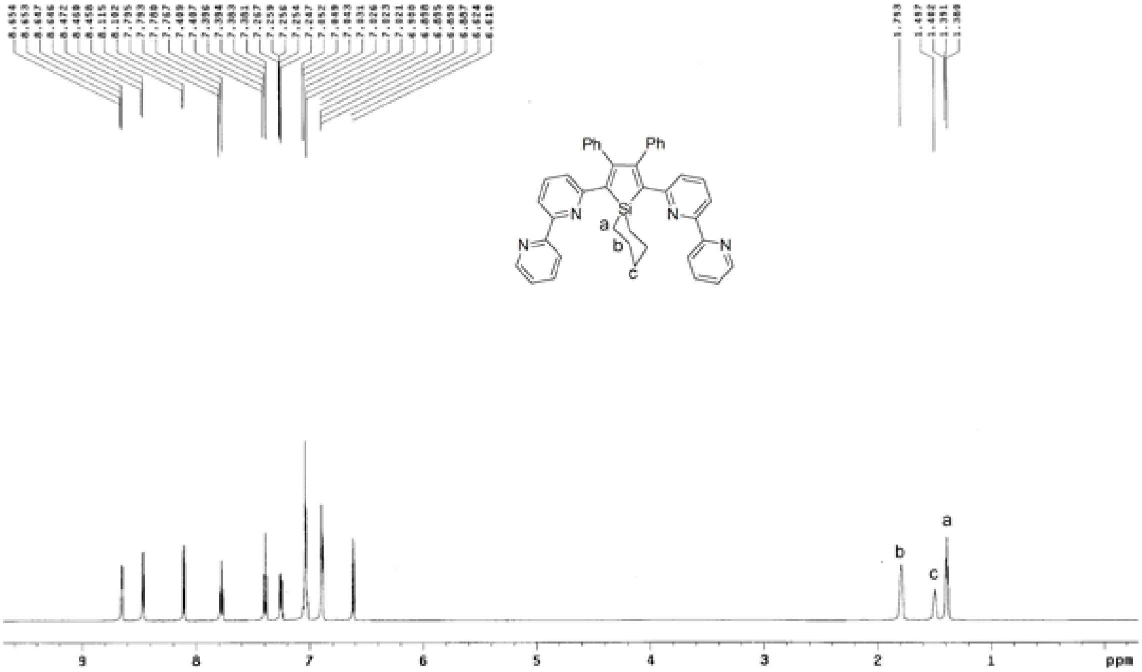

Figure S1 (d). ^{1}H-NMR spectroscopic view of **3-Cy6** in $CDCl_3$.

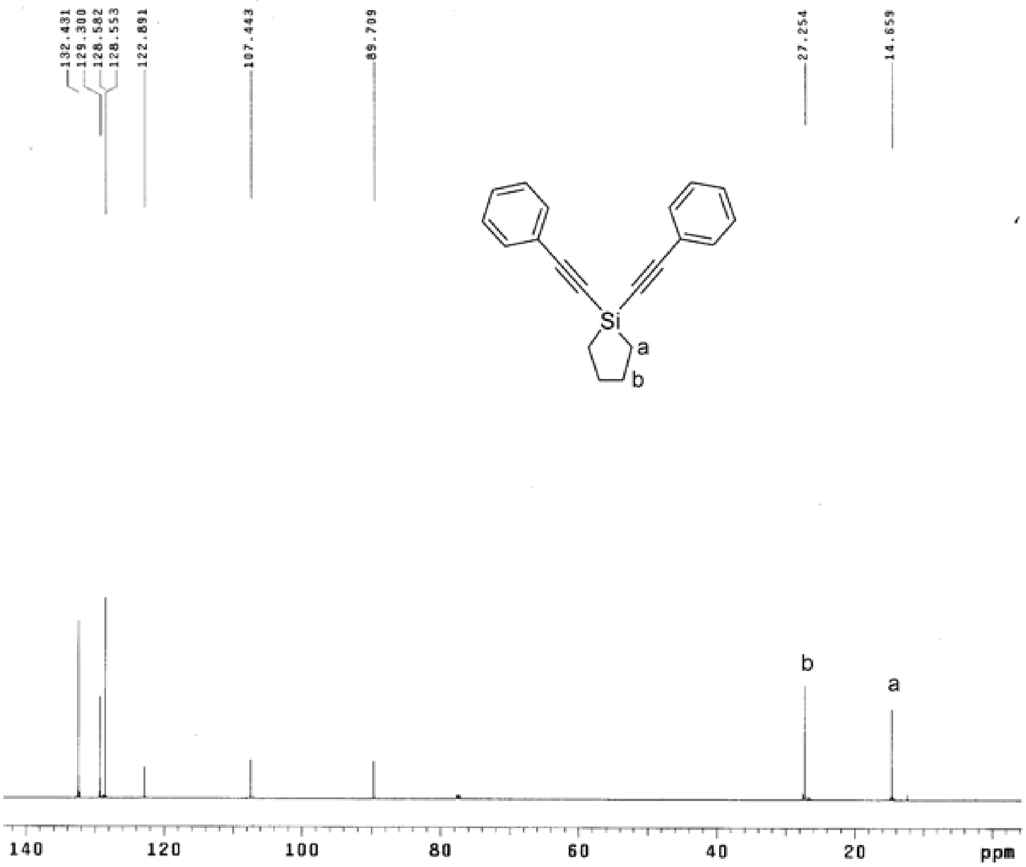

Figure S2 (a). ^{13}C-NMR spectroscopic view of **2-Cy5** in CDCl$_3$.

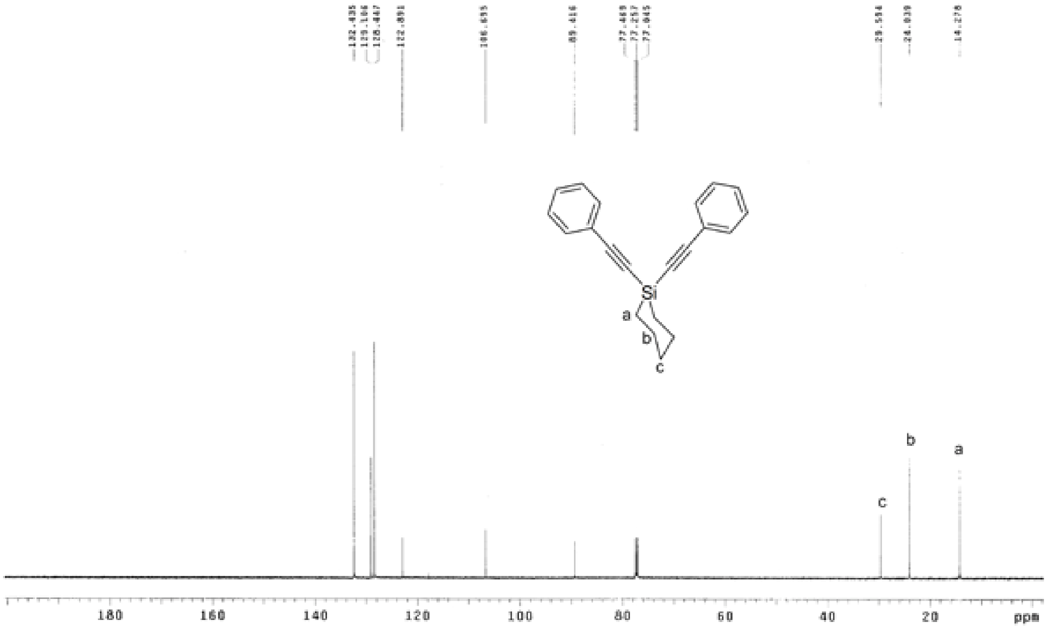

Figure S2 (b). ^{13}C-NMR spectroscopic view of **2-Cy6** in CDCl$_3$.

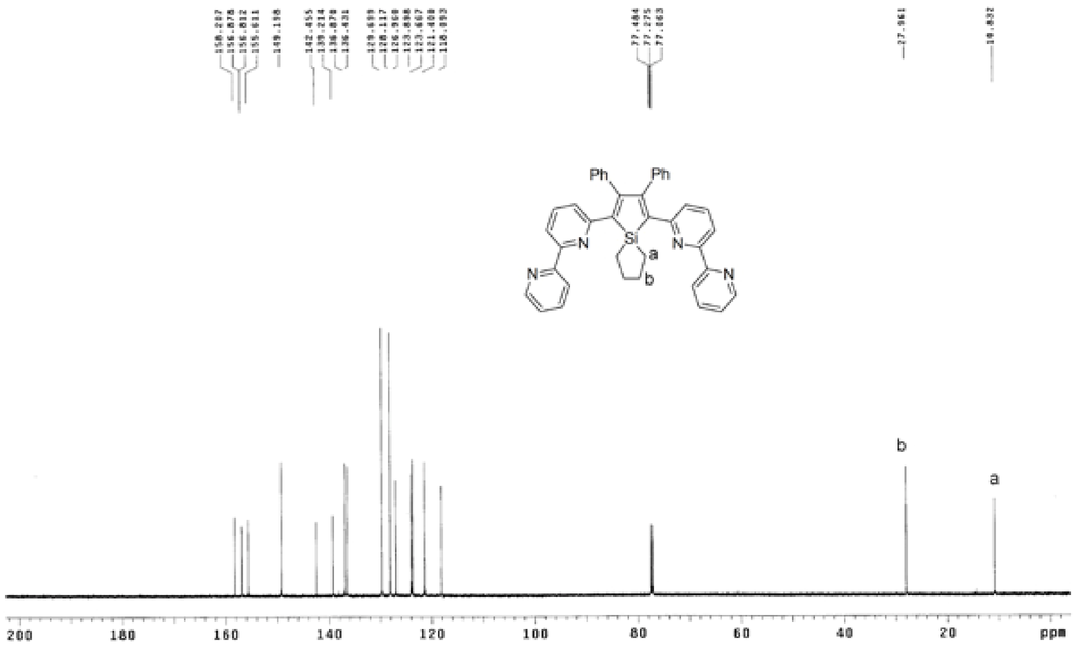

Figure S2 (c). ^{13}C-NMR spectroscopic view of **3-Cy5** in CDCl$_3$.

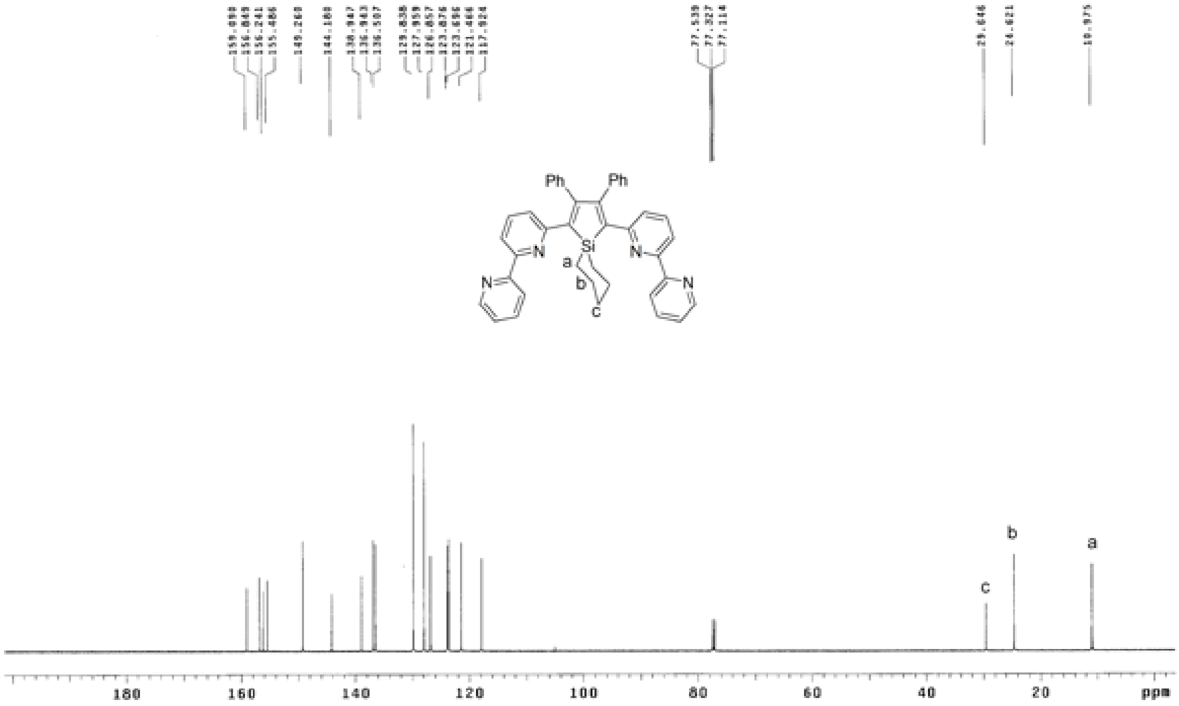

Figure S2 (d). ^{13}C-NMR spectroscopic view of **3-Cy6** in CDCl$_3$.

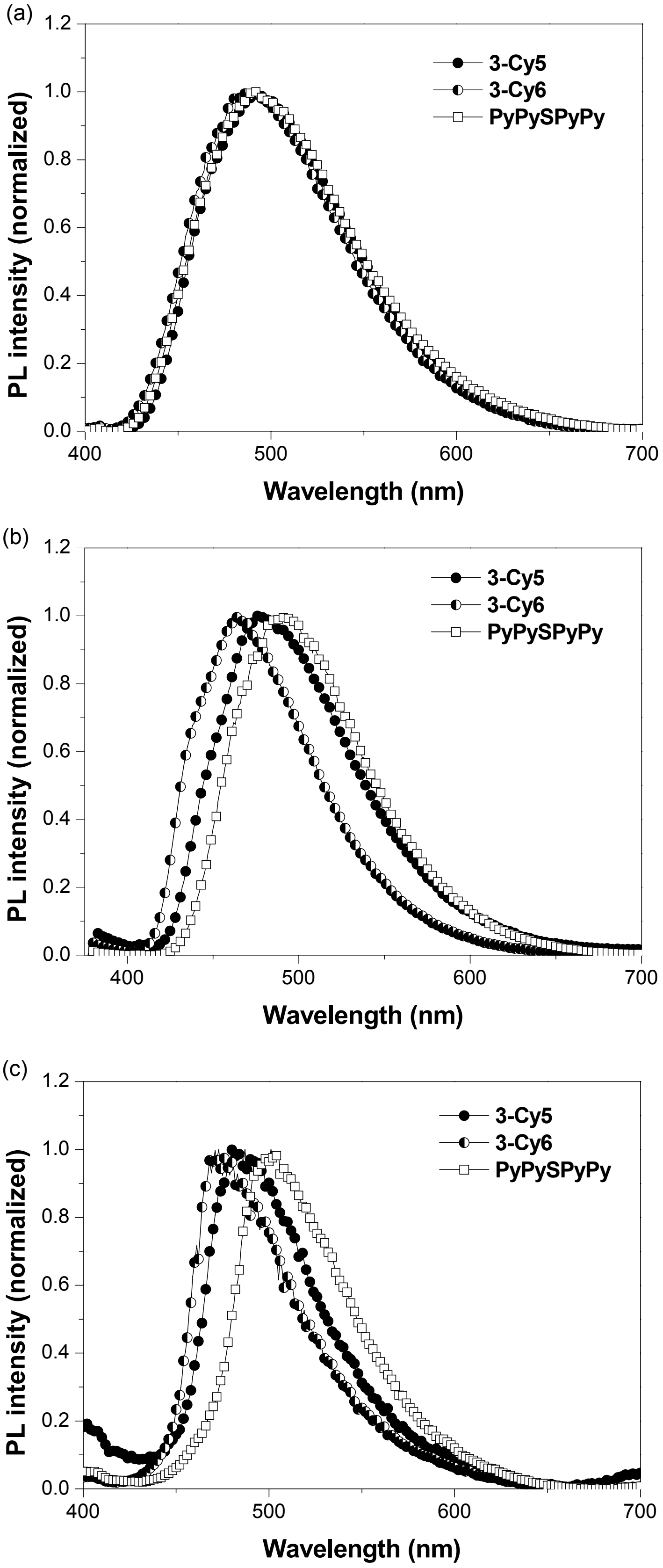

Figure S3. PL spectra changes of 2,5-bipyridylsiloles depending on aggregation order: (a) amorphous film, (b) aggregated film induced by alcohol vapor, and (c) crystal powders.

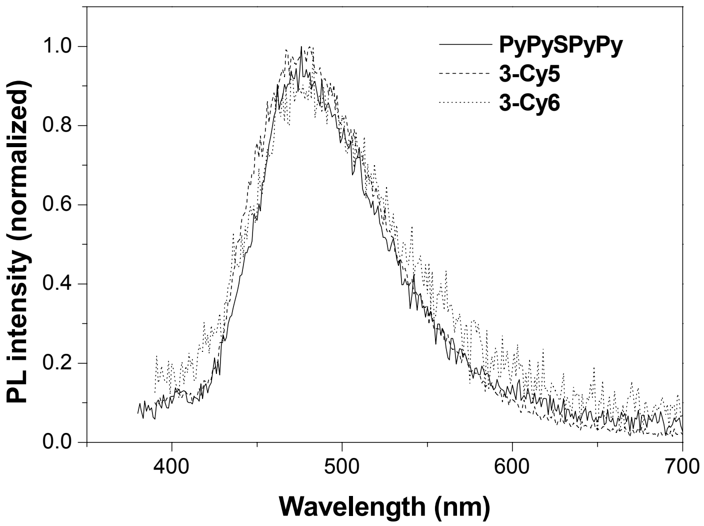

Figure S4. PL spectra of 2,5-bipyridylsiloles in chloroform.

Theoretical Calculation

The HOMO and LUMO levels of 2,5-bipyridylsiloles (**3-Cy5**, **3-Cy6**, and **PyPySPyPy**) were calculated using the double numerical plus d-functions (DND), and the geometric parameters from their X-ray analyses were used for the calculation.

```
Task parameters
Calculate            energy
Symmetry               on

# Electronic parameters
Spin_polarization:  restricted
Charge: 0
Basis: dnd
Pseudopotential: none
Functional: pwc
Harris: off
Aux_density: octupole
Integration_grid: medium
Occupation: fermi
Cutoff_Global: 3.3000 angstrom
Scf_density_convergence: 1.0000e-005
Scf_charge_mixing: 0.2000
Scf_iterations: 50
Scf_diis: 6 pulay
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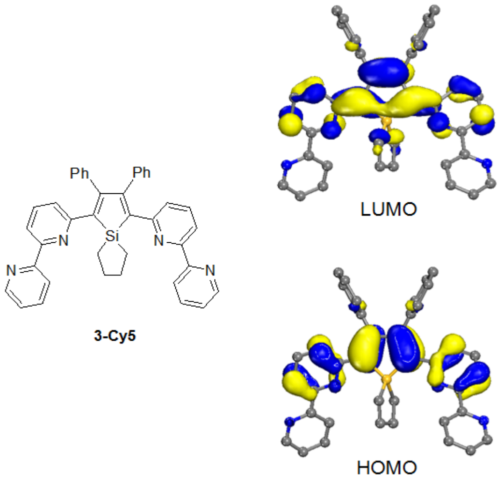

Figure S5 (a). HOMO and LUMO diagrams of **3-Cy5**.

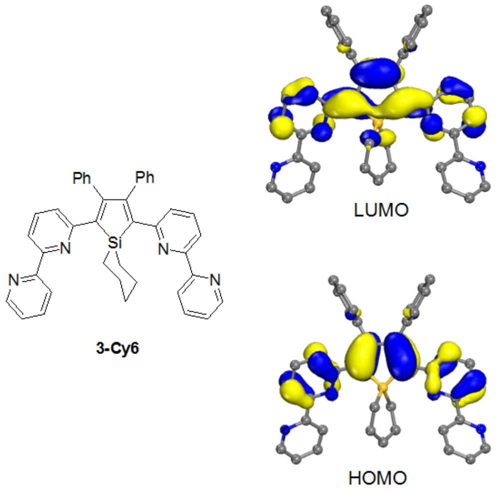

Figure S5 (b). HOMO and LUMO diagrams of **3-Cy6**.

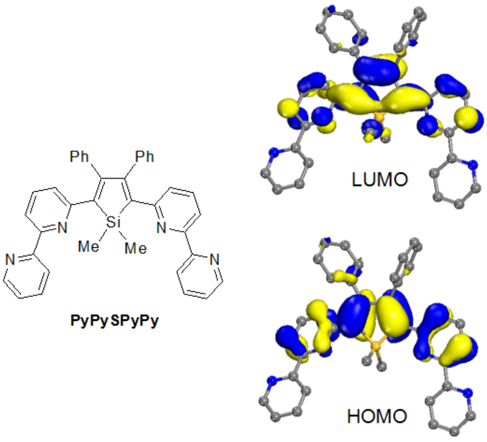

Figure S5 (c). HOMO and LUMO diagrams of **PyPySPyPy**.