

Solid state electrochemiluminescence from homogeneous and patterned monolayers of bifunctional spirobifluorene

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Electronic Supplementary Information (ESI)

General Information

Chemicals. All commercially available chemicals were purchased and used as received. Dichloromethane (DCM), tetrahydrofuran (THF), diethylether (Et₂O) and N,N-dimethylformamide (DMF) was dried by storage over molecular sieves (4 Å).

Mass spectrometry: Mass analysis were performed with electrospray ionization (ESI) technique by using Micro-TOF from Bruker Daltonics and Orbi-Trap LTQ-XL from Thermo Scientific instruments.

Nuclear Magnetic Resonance (NMR): NMR samples were measured with spectrometers ARX 300 and ARX 400 from Bruker. The samples were solely dissolved in deuterated solvents which were used as received. Referencing was done by using residual solvent protons. The chemical shifts (δ) are reported in parts per million (ppm) while the coupling constants (J) are reported in Hertz (Hz). The spectra were analyzed using the software MestReNova v 11.0 by Mestrelab Research S.L. Signals were reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, qu = quintet, m = multiplet, b = broad.

UV/Vis Spectroscopy: UV/Vis spectra were recorded with a V750 spectrophotometer from JASCO employing quartz cuvettes with optical length of 1 cm. Data analysis was performed using the Origin software.

Fluorescence Spectroscopy. Emission and excitation spectra were recorded with a Jobin-Horiba Fluorolog 3, equipped with Xe lamp as light source, double monochromators and R928p detector. Spectra from solid state were recorded by using slit of 2 nm in both monochromators and front-face configuration. Spectra measurements of unfunctionalized substrates were subtracted from sample signal to remove the background.

Electrochemistry. DMF (Sigma-Aldrich, 99.8 %) was treated with anhydrous Na₂CO₃ and then doubly distilled at reduced pressure under a nitrogen atmosphere. Tetra-*n*-butylammonium

perchlorate (TBAP, Fluka, 99%) was recrystallized from a 2:1 ethanol–water solution and dried at 60 °C under vacuum. The working electrode was a homemade glassy-carbon disk electrode (3 mm diameter, Tokai GC-20) connected to a copper wire with silver epoxy and sealed in a PEEK body. The electrode was polished as already described.¹ Before experiments, the electrode was further polished with a 0.25 μm diamond paste (Struer) and electrochemically activated in the background solution by means of several voltammetric cycles at 0.5 Vs⁻¹ between the anodic and the cathodic solvent/electrolyte discharges, until the expected quality features were attained.² A platinum wire served as the counter electrode and a silver wire, separated from the main electrolytic compartment by a Vycor® frit, was used as a quasi-reference electrode. At the end of each experiment, its potential was calibrated against the ferricenium/ferrocene couple, used as an internal redox standard. In DMF/0.1 M TBAP, ferricenium/ferrocene has a formal potential of 0.464 V against the KCl saturated calomel electrode (SCE);¹ all potentials will be given against SCE. The cyclic voltammetry (CV) experiments were carried out in DMF/0.1 M TBAP, using a 1 mM concentration for the electroactive compound. The CVs were conducted at 25 °C under an Ar atmosphere using a cell consisting of a purposely modified quartz cuvette. A CHI 760E Electrochemical Workstation (CH Instruments) was used. For the CV experiments, we employed the feedback correction to minimize the ohmic drop between the working and the reference electrodes.

ECL measurements: ECL measurements were carried out with PGSTAT302 AUTOLAB instrument in a three electrodes arrangement using SAM of compound **1** onto ITO substrate as working electrode, a Pt wire as counter electrode and Ag as quasi reference electrode. ECL measurements with 7 mM benzoyl peroxide (BPO) as coreactant were conducted in an airtight single-compartment cell using acetonitrile (ACN) as solvent with Tetrabutylammonium hexafluorophosphate (TBAH) 40 mM as supporting electrolyte. Oxygen was removed from the solution by Ar purging.

The ECL signal generated by performing the potential step program was measured with a photomultiplier tube (PMT, Hamamatsu R4220p) placed at a constant distance in front of the cell and inside a dark box. A voltage of 750 V was supplied to the PMT. The light/current/voltage curves were recorded by collecting the preamplified PMT output signal (by an ultralow-noise Acton research model 181) with the second input channel of the ADC module of the AUTOLAB instrument.

Atomic Force Microscopy (AFM): AFM imaging was performed employing a NanoWizard 3 from JPK Instruments operated in tapping mode with Veeco RTESP-Tapping Mode etched silicon Probes. The AFM was typically operated with a scan rate of 1 Hz and a set point of 0.9 V while images were recorded with a resolution of 512x512 pixels. Data evaluation was done using Gwyddion v2.38.

X-Ray Photoelectron Spectroscopy (XPS): XPS measurements were performed with an axis Ultra DLD from Kratos Analytical Ltd. A monochromatic Al K α source ($h\nu = 1486.6$ eV) at 10 mA filament current and 12 kV filament voltage source energies was used. The pass energy was set to 20 eV for high resolution and the charge neutralizer was used to compensate for sample charging. The data were evaluated with CasaXPS (version 2.3.15, Casa Software Ltd) and the spectra were calibrated to aliphatic carbon (C1s = 285 eV).

Optical and Fluorescence Microscopy: For optical and fluorescence microscopy imaging an Olympus BX 53 microscope was operated with an Olympus XC 10 camera and a X-Cite[®] series 120Q by Lumen Dynamics as the irradiation source. Also an Olympus CKX 41 microscope was operated with an Olympus XC 30 camera and a X-Cite[®] series 120Q by Lumen Dynamics as the irradiation source. Images were collected by using a blue filter (DAPI). Data processing was in both cases carried out with the software Olympus Stream Start 1.8 and GIMP v2.8.

Time of Flight Secondary Ion Mass Spectrometry (TOF-SIMS): TOF-SIMS measurements were carried out using TOF V compatible instrument equipped with a liquid metal ion gun (IONTOF GmbH, münster). As primary ions Bi₃⁺-clusters with an energy of 30 keV were used.

Deionized water: Ultrapure water was obtained using a PureLab UHQ water purification system by ELGA (High Wycombe, UK).

Contact angle: analyses were performed using a DSA 100 (KRÜSS) in combination with Drop Shape Analysis v1.90.0.14. Static contact angles were measured with 7 μ l drops of ultrapure water.

Column Chromatography: Preparative column chromatography was performed using Geduran[®] Si 60 silica gel with a grain size between 40 and 65 μ m (Merck KGaA, Darmstadt). The solvents used as mobile phase were used as received.

PDMS Stamp preparation: PDMS stamps were prepared using commercially available Sylgard[®] 184 Silicone Elastomer Kit supplied by Dow Corning. PDMS and the curing agent were mixed in a 10:1 ratio and blended with a stir rod for 10 minutes. This mixture was dispensed

onto a clean silicone master and degassed using desiccator. The PDMS mixture was cured at 80 °C overnight. The stamps were cut out with a knife.

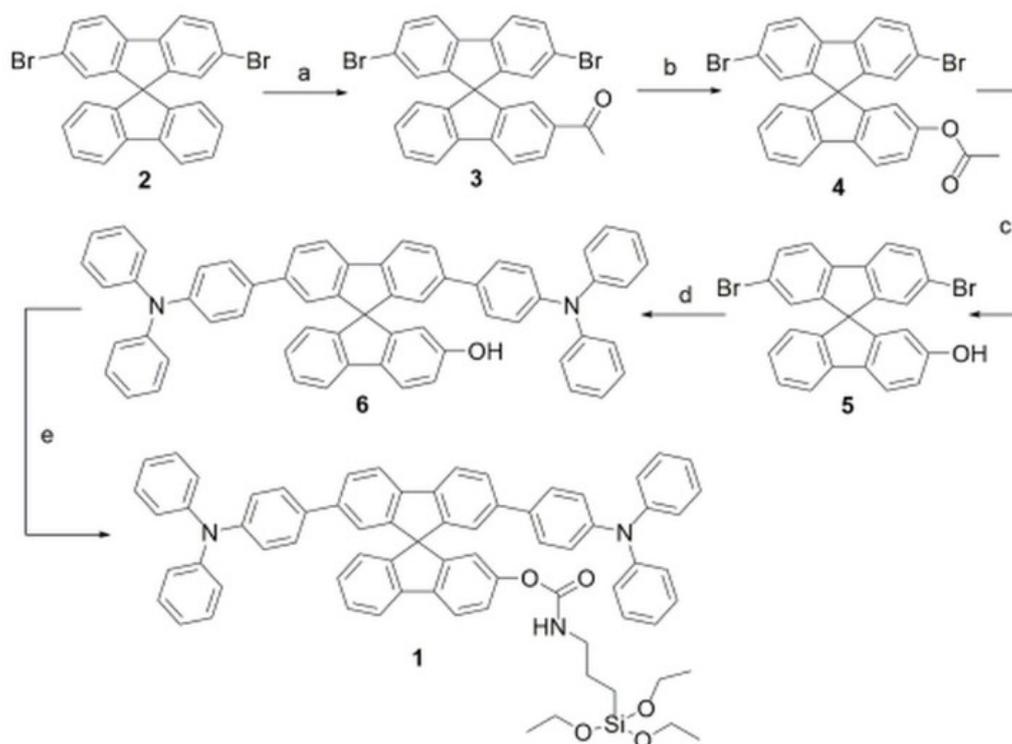
Silicon Wafers: Silicon Wafers ((1:0:0) orientation, 20-30 Ω) were supplied by Siltronic AG.

Glass substrates: Mediware® microscope slides (76 x 26 mm) from Servoprax were used.

Activation of glass and silica surfaces: At first glass/silica quadrangles were cut, washed and sonicated with acetone, ethanol and distilled water for ten minutes each. Substrates were put in piranha solution (3:1, H₂SO₄/H₂O₂) to activate the surface. Afterwards, the solid supports were rinsed plentifully with distilled water and dried carefully.

Activation of ITO surfaces: At first Indium Tin Oxide (ITO) coated glass slide (75 x 25 mm, 70-100 Ω/sq, Sigma-Aldrich) were cut, washed and sonicated with pentane, acetone and DCM for five minutes in each solvent. Then sonicated with MilliQ-water twice for two minutes and dried carefully with the argon stream. Surfaces were activated with the oxidizing mixture H₂O/NH₄OH/H₂O₂ (5:1:1) at 70 °C for 1 h. Afterwards the surface was rinsed by distilled water and dried carefully under argon.

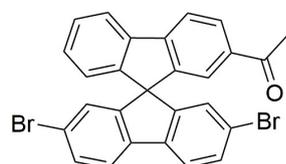
Micromolding in capillaries (MIMIC): Micromolding in capillaries (MIMIC) was used to pattern a surface of a substrate with micrometer structures. An elastomeric stamp made of PDMS with stripes (10 x 5 μm, 15 x 5 μm, 25 x 15 μm, 50 x 30 μm, 100 x 50 μm) was placed onto the substrate to form a network channels in the contact area. Thus, 2 μL of solution of dye **1** (100 mM in DMF) was dropped around the stamp edge observing the diffusion of the solution by capillarity. The substrate was heated for 20 min at 40 °C. Thereafter, the elastomeric stamp was removed and the substrate washed with DCM in ultrasonic bath for 5 min, then rinsed extensively with DCM and EtOH and dried carefully under an argon stream. The microstructures formed on the surface had a pattern complementary to that present on the stamp.



Scheme S1. Synthetic route for the preparation of dye **1**. a) AlCl_3 , AcCl , CH_2Cl_2 ; b) mCPBA , CH_2Cl_2 ; c) NaOH , MeOH ; d) 4-(diphenylamino)phenylboronic acid pinacol ester, $\text{Pd}(\text{PPh}_3)_4$, Na_2CO_3 , THF ; e) (3-isocyanatopropyl)triethoxysilane, NEt_3 , THF .

Synthesis

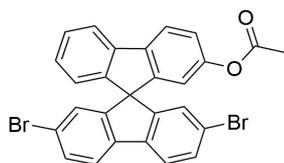
The 2,7-dibromo-9,9'-spirobifluorene (**2**) was prepared following the literature procedure.³



1-(2',7'-dibromo-9,9'-spirobifluoren-2-yl)ethan-1-one (3)

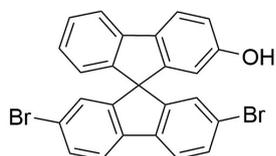
In a dried round flask **2** (311 mg, 0.657 mmol, 1 eq) was solubilized in CS_2 (12 ml) under inert atmosphere and AlCl_3 (299 mg, 2.24 mmol, 3.3 eq) was added under stirring. Acetylchloride (45 μl , 0.657 mmol, 1 eq) solubilized in CS_2 (1 ml) was slowly added dropwise under stirring, thus the mixture was refluxed for 30 min by monitoring by TLC (Hex/EtOAc (6:1), $R_f = 0.37$). After cooling at RT, the solvent was removed under vacuum and ice and HCl 10% (12 ml) were added and stirred for 10 min. The mixture was extracted with DCM (3 x 15 ml), and the collected organic phases were washed with water (1 x 20 ml) and dried over MgSO_4 . The crude was purified by column chromatography with Pentane/DCM (2:1) as eluent. Eventually mixed portions were further purified by precipitation from hot EtOH (284 mg, 0.550 mmol, 84%). $^1\text{H-NMR}$ (300 MHz, CDCl_3) $\delta = 8.04$ (dd, $J_1 = 8.0$, $J_2 = 1.6$ Hz, 1H, ArH), 7.97 – 7.87 (m, 2H, ArH), 7.70 (d, $J = 8.0$ Hz, 2H, ArH), 7.51 (dd, $J_1 = 8.0$, $J_2 = 1.6$ Hz, 2H, ArH), 7.44 (td, $J_1 = 7.5$, $J_2 = 1.1$

Hz, 1H, ArH), 7.38 – 7.28 (m, 1H, ArH), 7.22 (td, $J_1 = 7.5$, $J_2 = 1.1$ Hz, 1H, ArH), 6.84 – 6.72 (m, 3H, ArH), 2.51 (s, 3H, CH₃) ppm.



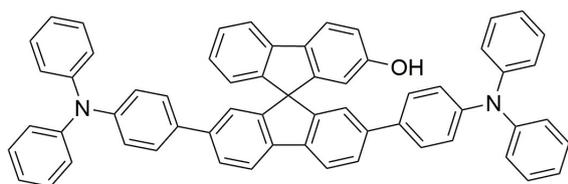
2',7'-dibromo-9,9'-spirobifluoren-2-yl acetate (4)

In a round flask mCPBA (1.2 g, 6.95 mmol, 2.7 eq) was solubilized in DCM (25 ml). Under stirring, **3** (1.3 g, 2.52 mmol, 1 eq) dissolved in CH₂Cl₂ (10 ml) was added dropwise and the solution was refluxed for 48 h. The solvent was then removed under vacuum and the crude dissolved in diethyl ether, washed with saturated NaHCO₃ (2 x 20 ml) and water. The collected organic phases were dried over MgSO₄. The crude was purified over chromatography by eluting with CH₂Cl₂/Pentane (1:1) to give the product as white solid (920 mg, 1.73 mmol, 69 %). ¹H NMR (300 MHz, CDCl₃) δ = 7.88 – 7.77 (m, 2H, ArH), 7.66 (d, $J = 8.1$ Hz, 2H, ArH), 7.49 (dd, $J_1 = 8.1$, $J_2 = 1.8$ Hz, 2H, ArH), 7.40 (td, $J_1 = 7.5$, $J_2 = 1.1$ Hz, 1H, ArH), 7.21 – 7.09 (m, 2H, ArH), 6.86 (d, $J = 1.8$ Hz, 2H, ArH), 6.71 (d, $J = 7.5$ Hz, 1H, ArH), 6.46 (m, 1H, ArH), 2.19 (s, 3H, CH₃) ppm. ¹³C NMR (75 MHz, CDCl₃) δ = 169.31, 150.67, 150.08, 148.60, 147.30, 140.99, 139.70, 139.44, 131.46, 128.56, 128.15, 127.53, 124.18, 122.14, 122.03, 121.54, 120.33, 117.43, 65.65, 27.05, 21.19 ppm.



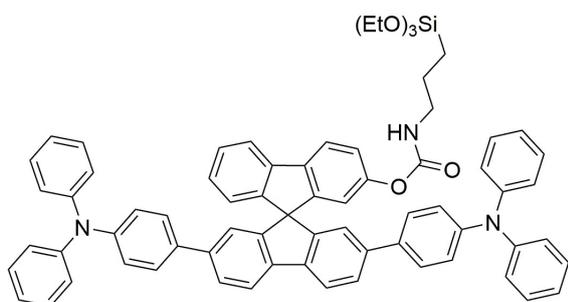
2',7'-dibromo-9,9'-spirobifluoren-2-ol (5)

To a suspension of **4** (625 mg, 1.17 mmol, 1 eq) in MeOH (20 ml), NaOH (52 mg, 1.30 mmol, 1.1 eq) dissolved in H₂O (2 ml) was added dropwise under stirring. The final suspension was heated at 60 °C for 1.5 h and the reaction was monitored by TLC (CH/EtOAc, (8:1)). After cooling at RT, HCl 10% (20 ml) was added inducing precipitation of the pure product collected by filtration. To collect also the product remains in solution, the aqueous mixture was extracted with Et₂O (2 x 50 ml), dried over MgSO₄ and the solvent was removed under vacuum. The product was obtained as white powder in quantitative yield (570 mg, 1.16 mmol, 99 %). ¹H NMR (400 MHz, CDCl₃) δ = 7.80 – 7.62 (m, 4H), 7.49 (d, $J = 8.2$ Hz, 2H), 7.37 (t, $J = 7.6$ Hz, 1H), 7.08 (t, $J = 7.6$ Hz, 1H), 6.87 (s, 3H), 6.69 (d, $J = 7.6$ Hz, 1H), 6.18 (s, 1H), 4.69 (s, 1H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 155.89, 150.63, 149.26, 146.62, 141.75, 139.73, 134.86, 131.25, 128.49, 127.64, 127.07, 124.17, 121.97, 121.63, 121.47, 119.52, 115.80, 111.30, 65.57 ppm. MALDI-TOF (m/z) = 488.9369 [M], calculated for C₂₅H₁₄Br₂O: 488.9320.



2',7'-bis(4-(diphenylamino)phenyl)-9,9'-spirobifluoren-2-ol (**6**)

In a Schlenk-tube, a stirred mixture of **5** (358 mg, 0.730 mmol, 1 eq), 4-(diphenylamino)phenylboronic acid pinacol ester (543 mg, 1.46 mmol, 2 eq.), aqueous Na₂CO₃ 1M (4.4 ml, 6 eq) and Pd(PPh₃)₄ (50 mg, 0.044 mmol, 0.06 eq) in dry THF (10 ml) was refluxed overnight. After cooling at RT, the solvent was removed under vacuum and the solid solubilized in CH₂Cl₂, washed with H₂O (2 x 25 ml) and the aqueous phase extracted with CH₂Cl₂ (1 x 20 ml). The collected organic phases were dried over MgSO₄ and the crude purified by chromatography over silica gel by eluting with Cyclohexane/EtOAc (9:1). The desired product was obtained as a yellowish powder (414 mg, 0.506 mmol, 69 %). ¹H-NMR (300 MHz, CDCl₃) δ = 7.78 (d, *J* = 7.9 Hz, 3H, ArH), 7.69 – 7.45 (m, 9H, ArH), 7.29 – 7.05 (m, 7H, ArH), 7.02 – 6.82 (m, 27H, ArH), 6.79 – 6.64 (m, 3H, ArH), 6.15 (d, *J* = 2.4 Hz, 3H, ArH) ppm. ¹³C-NMR (75 MHz, CDCl₃) δ = 155.91, 151.01, 149.97, 148.33, 147.71, 147.19, 141.88, 140.42, 140.32, 135.04, 134.86, 129.34, 127.83, 126.87, 126.53, 124.40, 124.26, 123.99, 122.98, 122.37, 121.16, 120.33, 119.30, 115.25, 111.41, 66.06 ppm. MS (ESI⁺) *m/z* = 841.3161 [M+Na]⁺, calculated for C₆₁H₄₂N₂ONa⁺: 841.3200.



2',7'-bis(4-(diphenylamino)phenyl)-9,9'-spirobifluoren-2-yl-(3-(triethoxysilyl)propyl) carbamate (**1**)

(3-Isocyanatopropyl)-triethoxysilane (38 μl, 0.147 mmol, 1 eq), **6** (120 mg, 0.147 mmol, 1 eq) and triethylamine (6 μl, 0.041 mmol, 0.3 eq) were dissolved in dry THF (7 ml) in a Schlenk-tube and refluxed for 48 h. After removing the solvent under vacuum, the crude was purified by column chromatography by using CH₂Cl₂ as eluent (*R*_f = 0.25) to give the product as a yellowish powder (47 mg, 0.044 mmol, 30 %). ¹H-NMR (300 MHz, CDCl₃) δ = 7.92 – 7.76 (m, 4H, ArH), 7.60 (dd, *J*₁ = 8.0, *J*₂ = 1.7 Hz, 2H, ArH), 7.43 – 6.83 (m, 33H, ArH), 6.79 (d, *J* = 7.5 Hz, 1H, ArH),

6.60 (d, $J = 2.2$ Hz, 1H, ArH), 5.18 (t, $J = 6.0$ Hz, 1H, NH), 3.89 – 3.69 (m, 6H, OCH_2CH_3), 3.18 (q, $J = 6.6$ Hz, 2H, CH_2NH), 1.76 – 1.53 (m, 2H, CH_2Si), 1.35 – 1.09 (m, 9H, OCH_2CH_3), 0.70 – 0.49 (m, 2H, $CH_2CH_2CH_2$) ppm. ^{13}C -NMR (75 MHz, $CDCl_3$) $\delta = 159.80, 154.44, 151.05, 150.04, 149.47, 149.08, 147.70, 147.12, 141.23, 140.46, 140.35, 138.97, 135.06, 129.31, 127.87, 126.60, 124.32, 124.05, 122.89, 122.42, 120.55, 120.33, 119.96, 117.63, 92.53, 66.12, 58.59, 43.55, 23.18, 18.40, 7.71$ ppm. MS (ESI⁺) $m/z = 1088.4380$ [$M+Na$]⁺, calculated for $C_{71}H_{63}N_3O_5SiNa^+$: 1088.4400

Photophysical Data

Table S1. Photophysical data of **1** in solution and solid state. Data of Spiro-TPA are reported for comparison.⁴

Compound	λ_{abs} (nm)	λ_{em} (nm) ^a	τ (ns)	QY (%)
1 in DCM	370	437	1.4	78
1 in DMF	374	456	-	-
1 onto ITO	368	420 ^b	-	1.2
Spiro-TPA ^c	374	456	1.3	87

^a excited at maximum absorption, ^b excited at 370 nm, ^c from Reference 4.

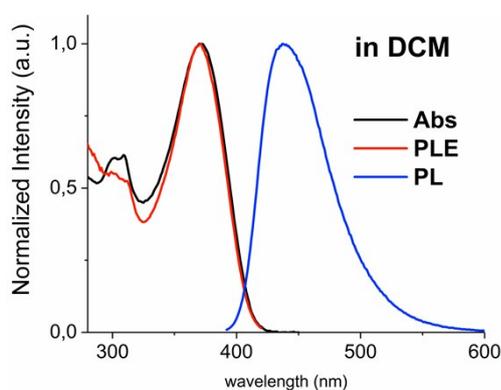


Figure S1. Absorption (black), excitation (red) and emission (blue) spectra of **1** (2 μ M) in DCM (left) and in DMF (right).
 in DCM: $\lambda_{Abs} = 372$ nm, $\lambda_{PLE} = 372$ nm and $\lambda_{PL} = 437$ nm (with $\lambda_{exc} = 372$ nm)).
 in DMF: $\lambda_{Abs} = 374$ nm, $\lambda_{PLE} = 374$ nm and $\lambda_{PL} = 456$ nm (with $\lambda_{exc} = 374$ nm)).

Surface characterization

XPS measurements

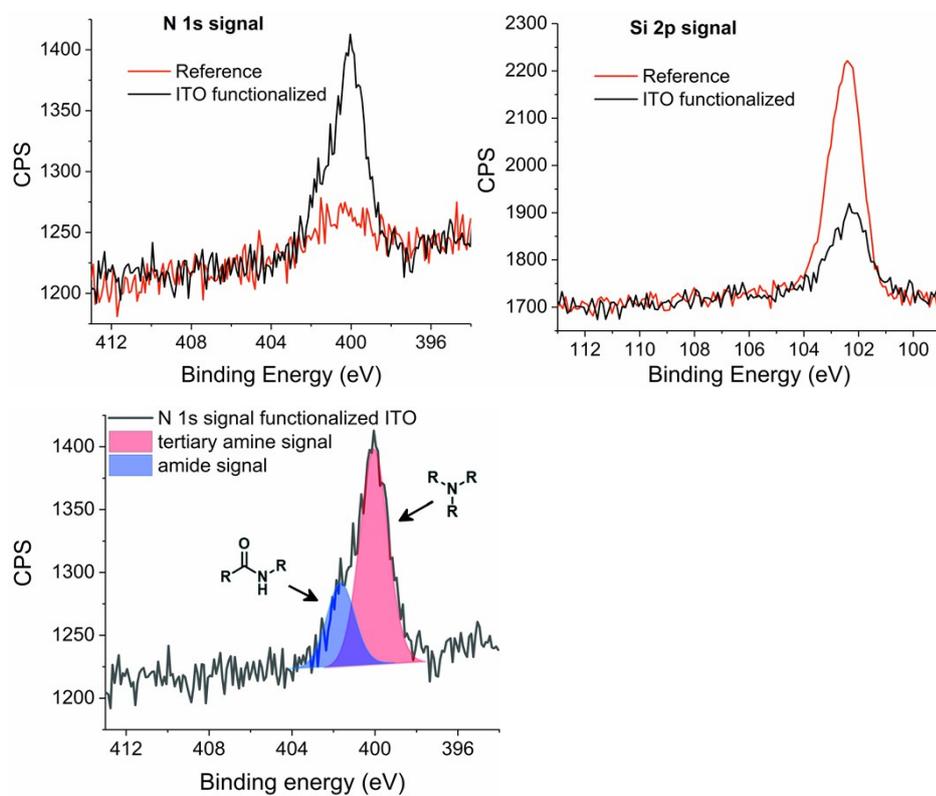


Figure S2. Top: XPS analysis of **1** functionalized ITO substrate vs. activated ITO (reference). Below: deconvolution of the nitrogen signal indicating the presence of two different groups containing nitrogen atoms: tertiary amine at 400 eV and amide at 402 eV.

Static water contact angle measurements

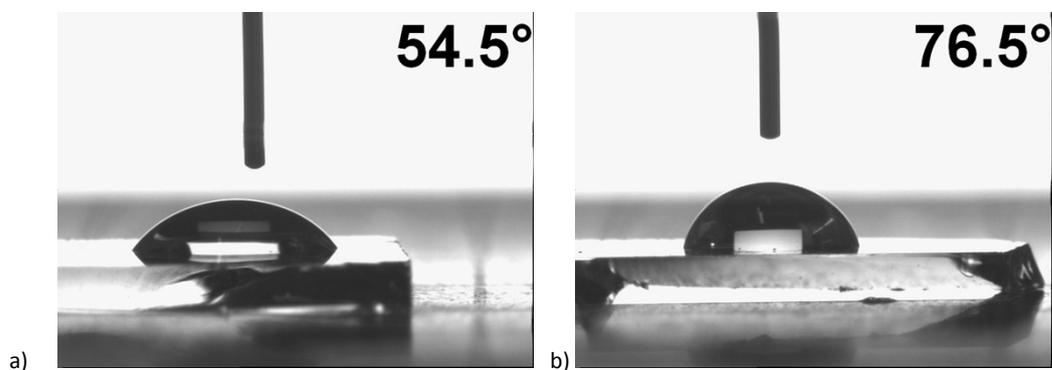


Figure S3. Contact angle measurements performed on (a) activated ITO and (b) functionalized ITO with SAM.

TOF-SIMS measurements

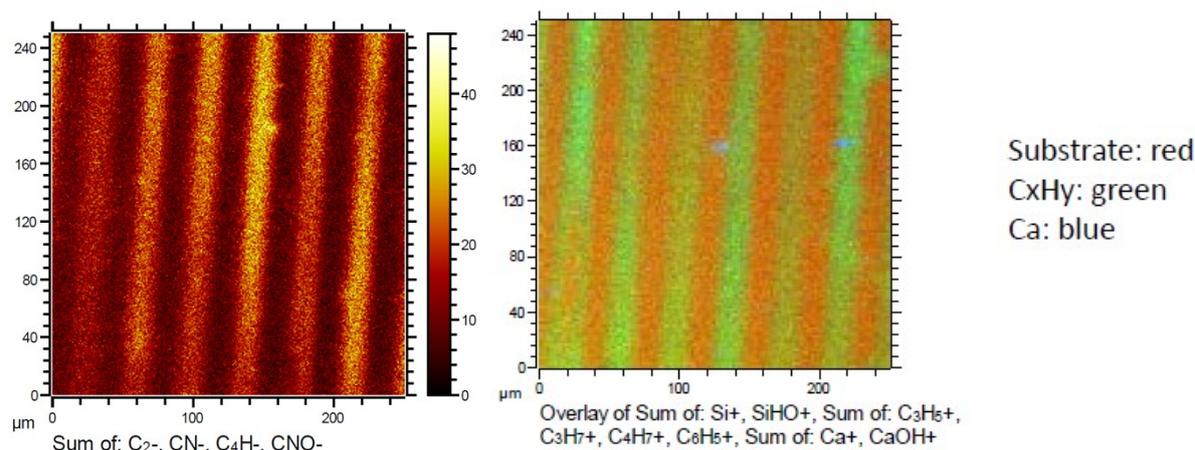


Figure S4. TOF-SIMS analysis of lines of **1** (25 x 15 μm) printed via MIMIC on silicon wafer. Overlay of signals in negative ion mode (left) and positive ion mode (right).

AFM measurements

The AFM analysis of the silicon wafer surface functionalized with **1** using a pattern of lines (15 x 5 μm) is reported below in Figure S5. The difference in phase allowed showing the pattern even with a low height difference between functionalized and naked substrate, indicating the formation of the monolayer.

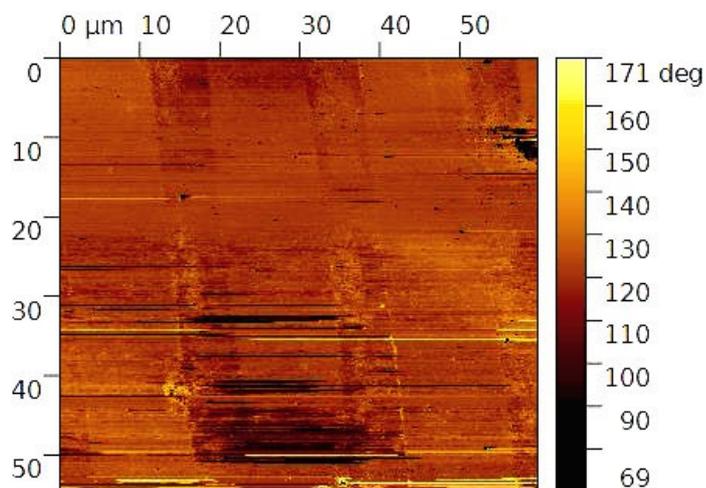


Figure S5. AFM picture of 15 x 5 μm stripes of **1** printed via MIMIC on silicon wafer.

Condensation experiment

In Figure S6 is reported the condensation experiment performed on silicon wafer functionalized with **1** in lines (25 x 15 μm). The water drops accumulate on the more hydrophilic part, i.e. on the naked substrate where are present free hydroxy groups (small lines). The hydrophobic part of the substrate functionalized with **1** is not covered by water.

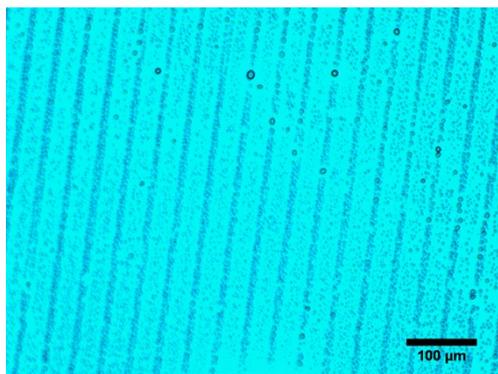


Figure S6. Silica substrate (25 x 15 μm) with lines pattern of **1** via MIMIC, condensation experiment. 20x magnification.

Photophysical characterization

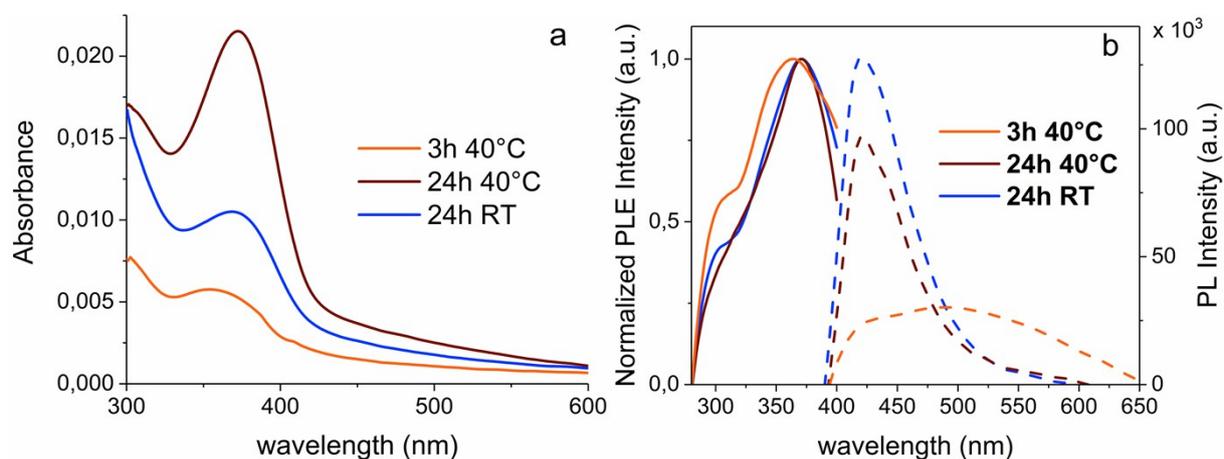


Figure S7. Comparison of SAM of **1** on ITO prepared in different conditions. a) Absorption spectra and b) excited (solid line) and emission (dashed line) spectra.

Electrochemical characterization

Table S2. Electrochemical data of **1** in DMF/0.1 M TBAP.

	E°_O ^a (V)	$\Delta E_{p,O}$ (mV)	E°_{R1} (V)	$\Delta E_{p,R1}$ (mV)	$i_{p,O}/i_{p,R1}$ ^b	E°_{R2} (V)
1	0.979	70	-2.205	72	1.84	-2.423

^a This is an apparent E°_O because the peak is caused by oxidation on both triphenylamine units: see reference 12a in the manuscript. ^b Absolute ratio at 0.2 V s⁻¹, where $i_{p,R1}$ corresponds to a one-electron process.

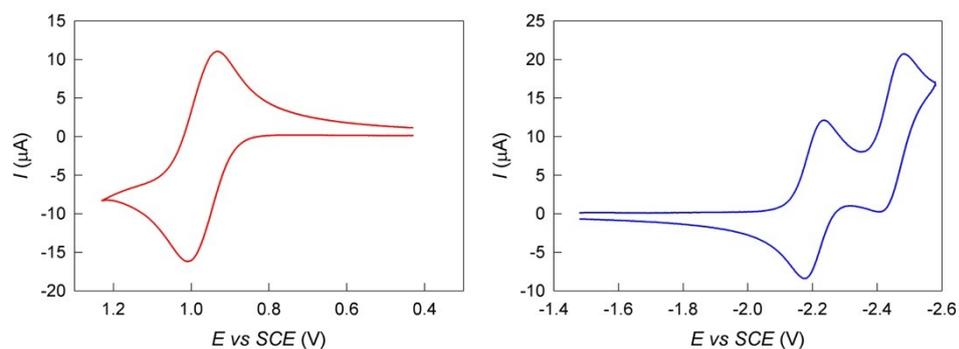


Figure S8. CVs in DMF/0.1 M TBAP for the oxidation (a) and reduction (b) of 1 mM compound **1**. Scan rate 0.2 V s⁻¹.

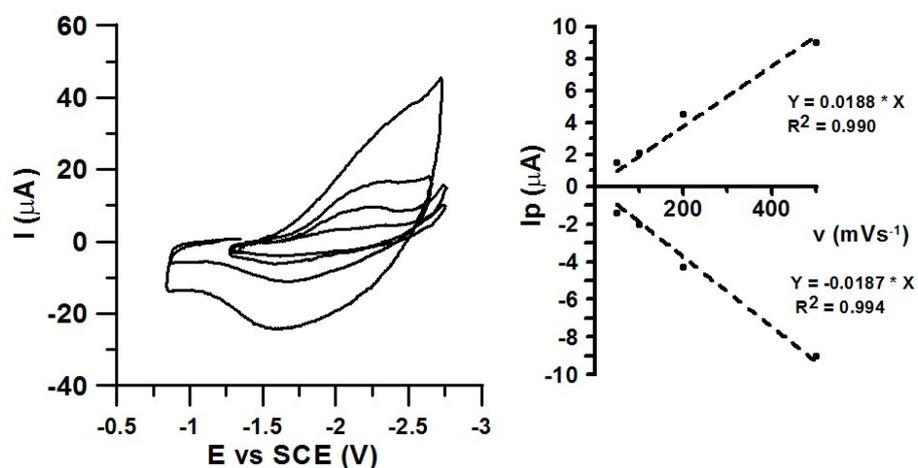


Figure S9. CVs in DMF/0.1 M TBAP for the compound **1**. Scan rate (bottom to top) 50, 100, 200, 500 mV s⁻¹. Peaks current as function of the scan rate. Furthermore, through the analysis of the scan rate dependence of the peak currents, a surface coverage of **1** of $\Gamma_1 = 2.4 \times 10^{-11}$ mol cm⁻² was determined.

Electrochemiluminescence characterization

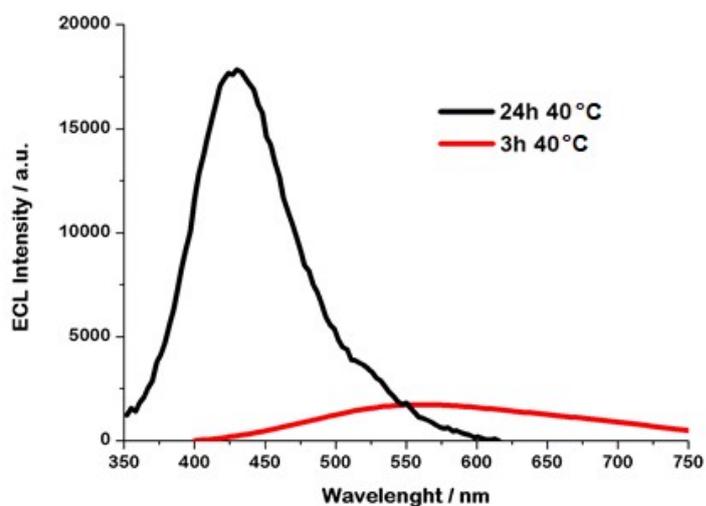


Figure S10. ECL emission spectra with BPO of SAM of **1** onto ITO substrate. Measurements performed in deaerated ACN with BPO 7 mM and TBAH 40 mM. PMT bias 750 V. Potentials reported vs Ag/AgCl 3 M. ECL emission spectra: voltage applied -2.5 V vs Ag. Integration time: 1 s. Increment: 3 nm. PMT bias 750 V.

In order to quantify the ECL efficiency of the SAM of **1** onto ITO substrate we prepare for the comparison a SAM of standard $\text{Ru}(\text{bpy})_3^{2+}$ onto ITO. ITO functionalization with standard ECL dye, such as $\text{Ru}(\text{bpy})_3^{2+}$, was prepared following the literature procedure.⁵ Bis(2,2'-bipyridine)-[4-(4'-methyl-2,2'-bipyridin-4-yl)butanoic acid] ruthenium bis(hexafluorophosphate) was purchase from Cyanagen srl (<http://www.cyanagen.com/>). Briefly a clean, dried indium tin oxide (ITO) electrode with dimensions of 3 x 1.5 cm was immersed in a 5% of $(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{NH}_2$ (APTES) toluene solution and kept in a desiccator for 24 h. During this process, the APTES is immobilized by formation of ITO/O-Si(CH₂)₃-NH₂ bonds. The electrode was then washed with EtOH and transferred into a 0.10 M 1-methylimidazole/HCl buffer solution (pH = 7) containing 10 mM $\text{Ru}(\text{bpy})_2[\text{bpy}(\text{COOH})]^{2+}$ and 10 mM EDAC.

After a 45 min incubation at 70 °C, the ITO electrode was washed thoroughly with EtOH and then water. By this treatment, a layer of $\text{Ru}(\text{bpy})_2[\text{bpy}(\text{COOH})]^{2+}$ was covalently attached to the aminosilane monolayer formed previously on the ITO, to produce ITO/O-Si(CH₂)₃NH-[CO(bpy)](bpy)₂Ru(II). The substrate was subsequently immersed in a 0.10 M Tris/HCl buffer (pH = 8) and maintained in the dark until further use. Furthermore, through the analysis of the scan rate dependence of the peak currents, the surface coverage of ITO/O-Si(CH₂)₃NH-[CO(bpy)](bpy)₂Ru(II) of 8.66×10^{-11} molecules of Ru for cm⁻² was determined. This surface coverage was used to estimate the ECL efficiency of the **1**.

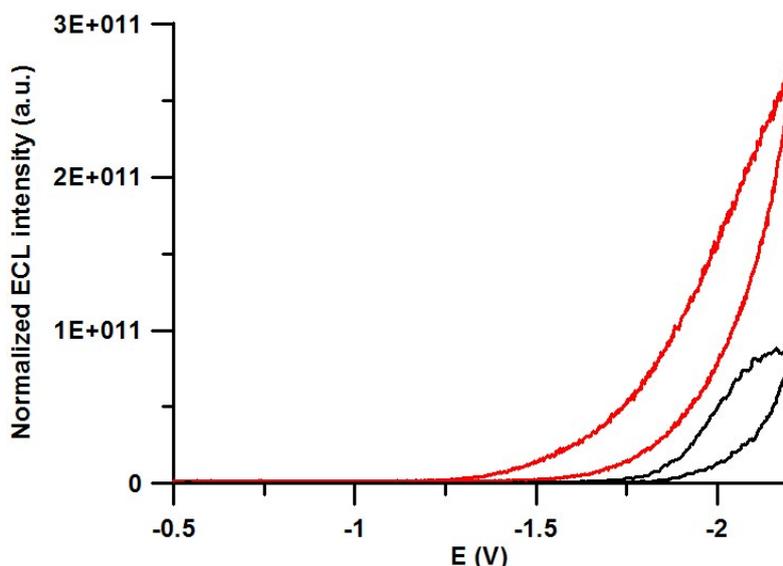


Figure S11 Normalized ECL emission (ECL intensity / Γ) with BPO of SAM of **1** (red signal) and $\text{Ru}(\text{bpy})_3^{2+}$ (black signal) onto ITO substrate. Measurements performed in deaerated ACN with BPO 7 mM and TBAH 40 mM. PMT bias 750 V. Potentials reported vs Ag/AgCl 3 M. The ECL intensities were normalized for the surface coverage obtained by CV measurements, i.e. **1** ($\Gamma_1 = 2.4 \times 10^{-11}$ mol cm⁻²) and $\text{Ru}(\text{bpy})_3^{2+}$ ($\Gamma_{\text{Ru}} = 8.66 \times 10^{-11}$ mol cm⁻²), respectively.

Reference

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- [4] F. Polo, F. Rizzo, M. Veiga-Gutierrez, L. De Cola and S. Quici, *J. Am. Chem. Soc.*, 2012, **134**, 15402.
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NMR-Spectra

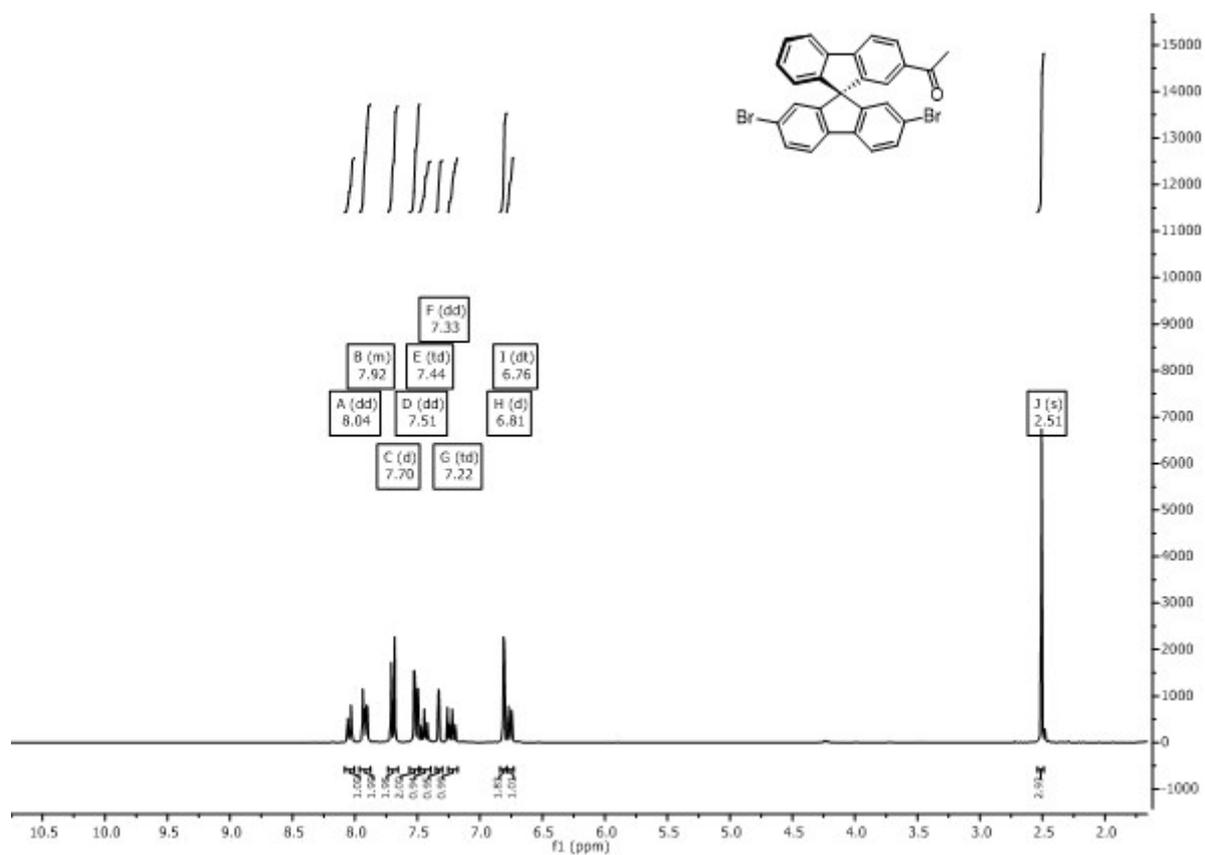


Figure S12. ¹H NMR spectrum of 3.

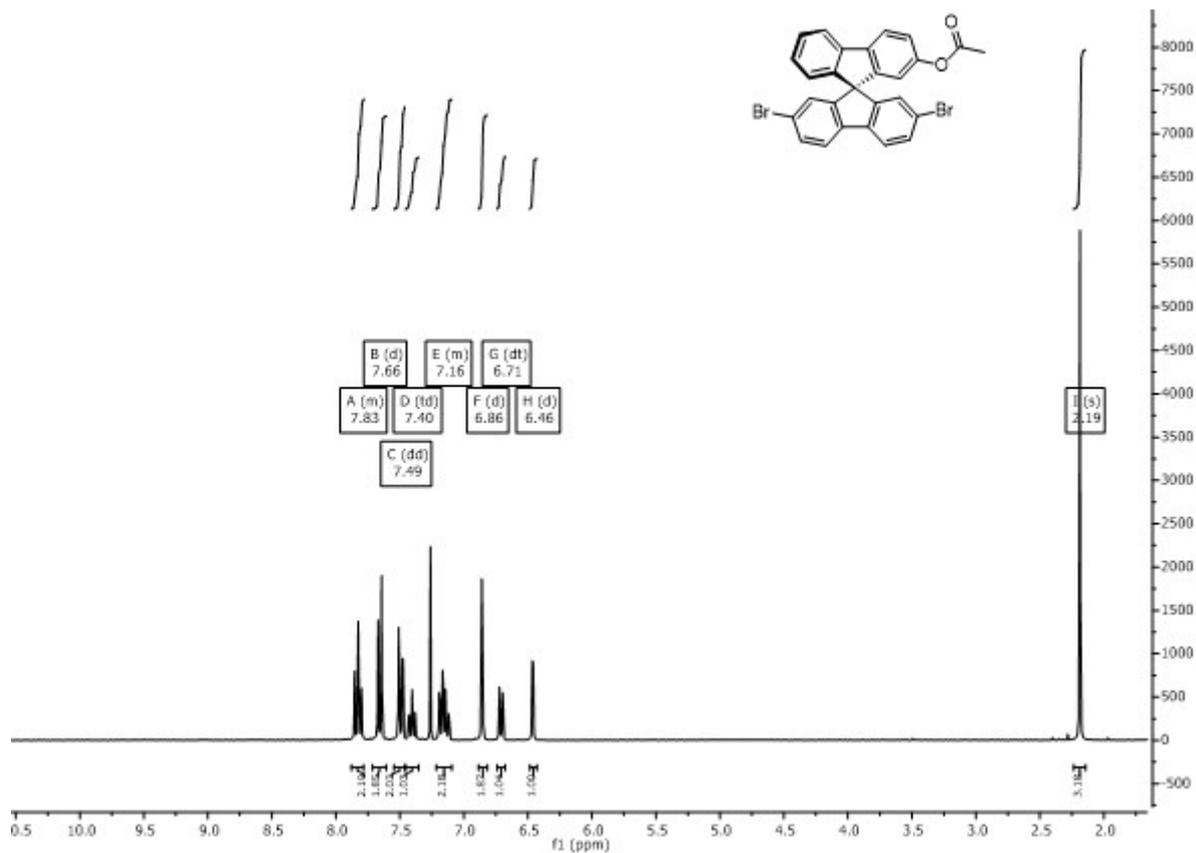


Figure S13. $^1\text{H-NMR}$ spectrum of 3.

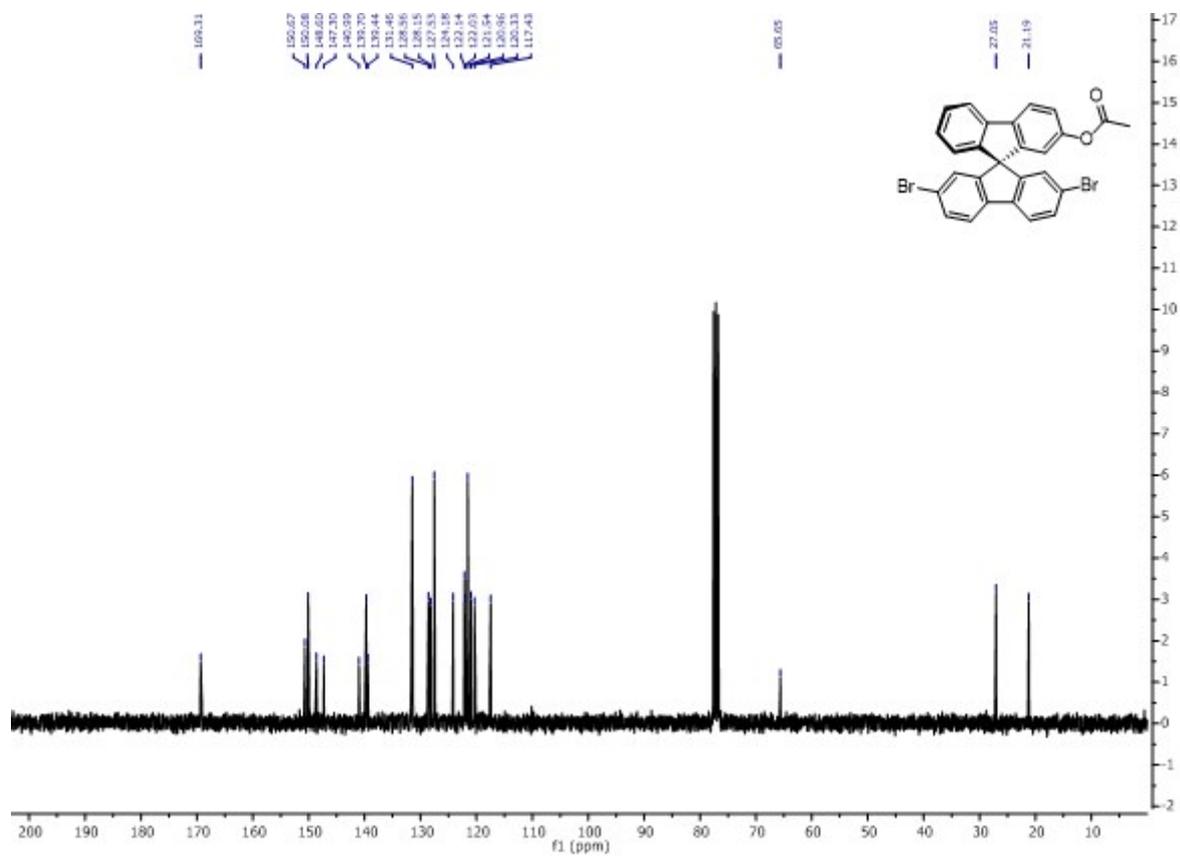


Figure S14. $^{13}\text{C-NMR}$ spectrum of 3.

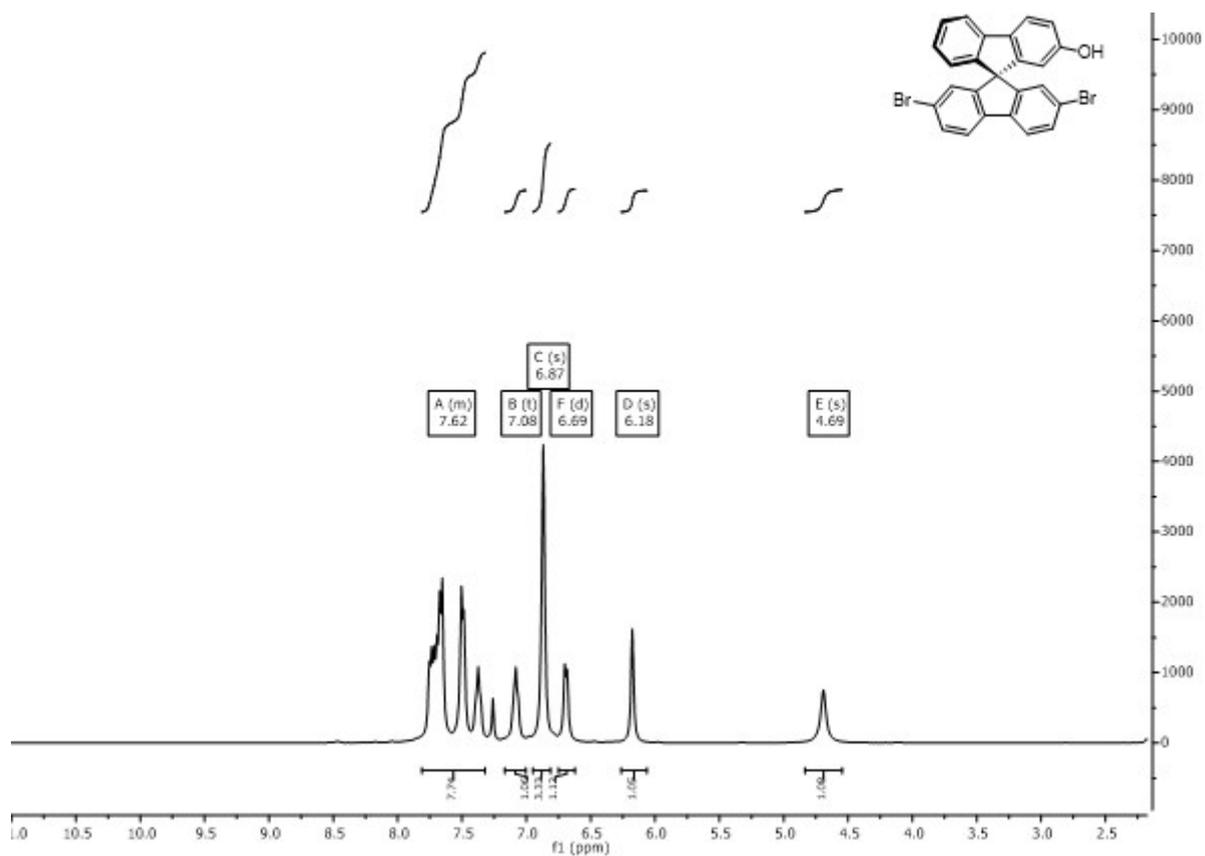


Figure S15. $^1\text{H-NMR}$ spectrum of **4**.

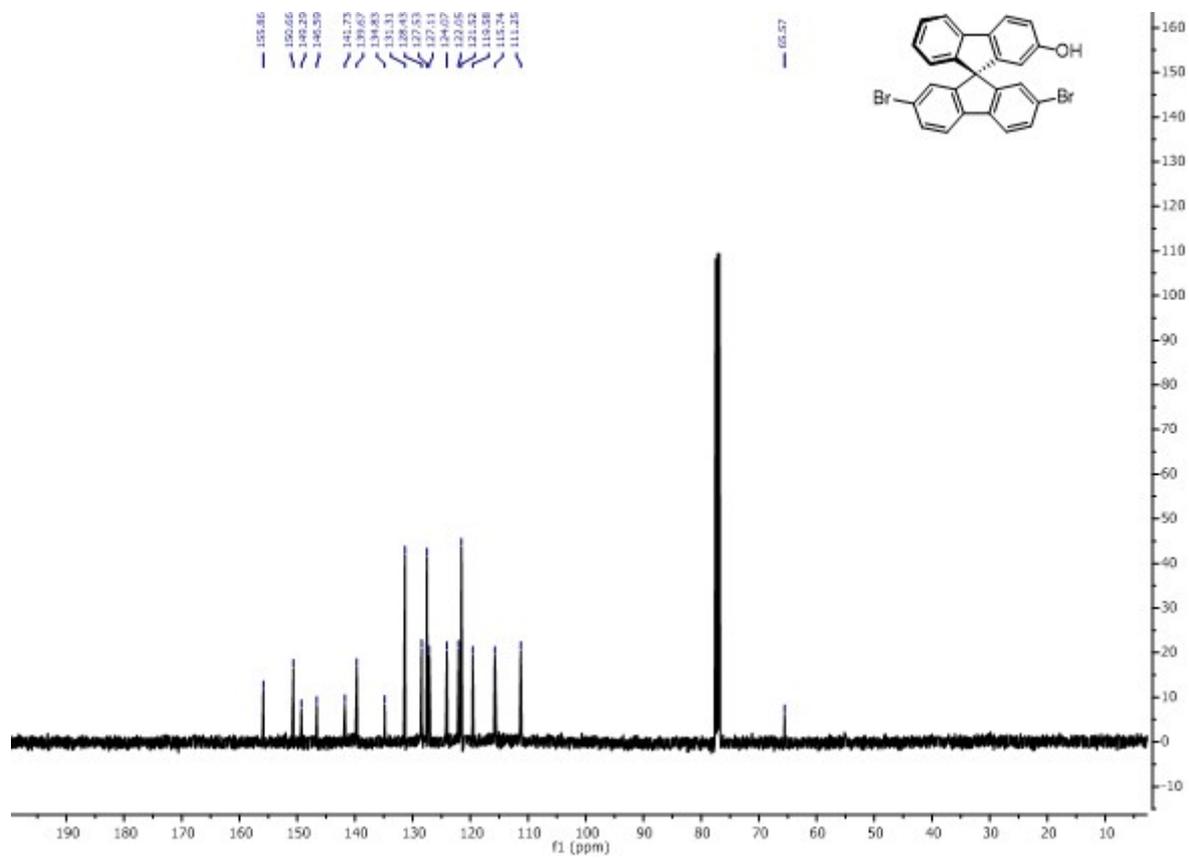


Figure S16. $^{13}\text{C-NMR}$ spectrum of **4**.

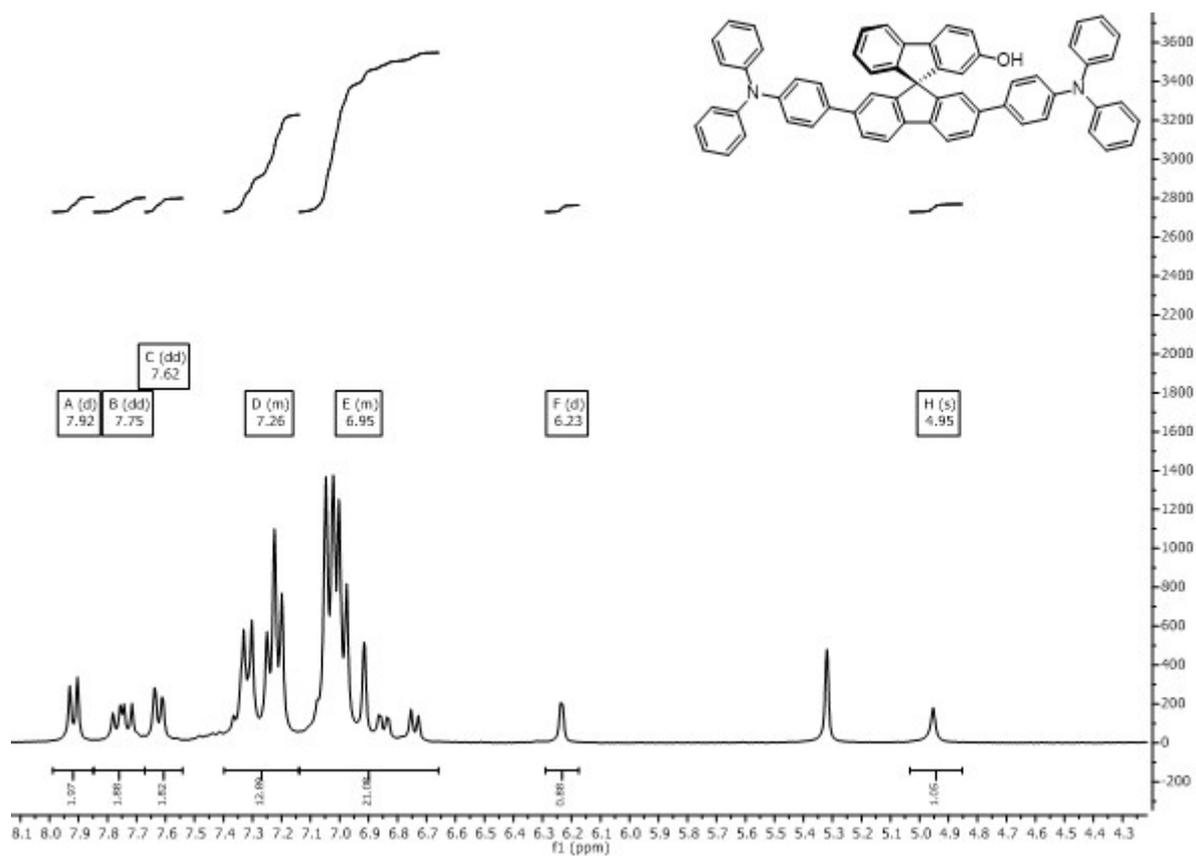


Figure S17. $^1\text{H-NMR}$ spectrum of 5.

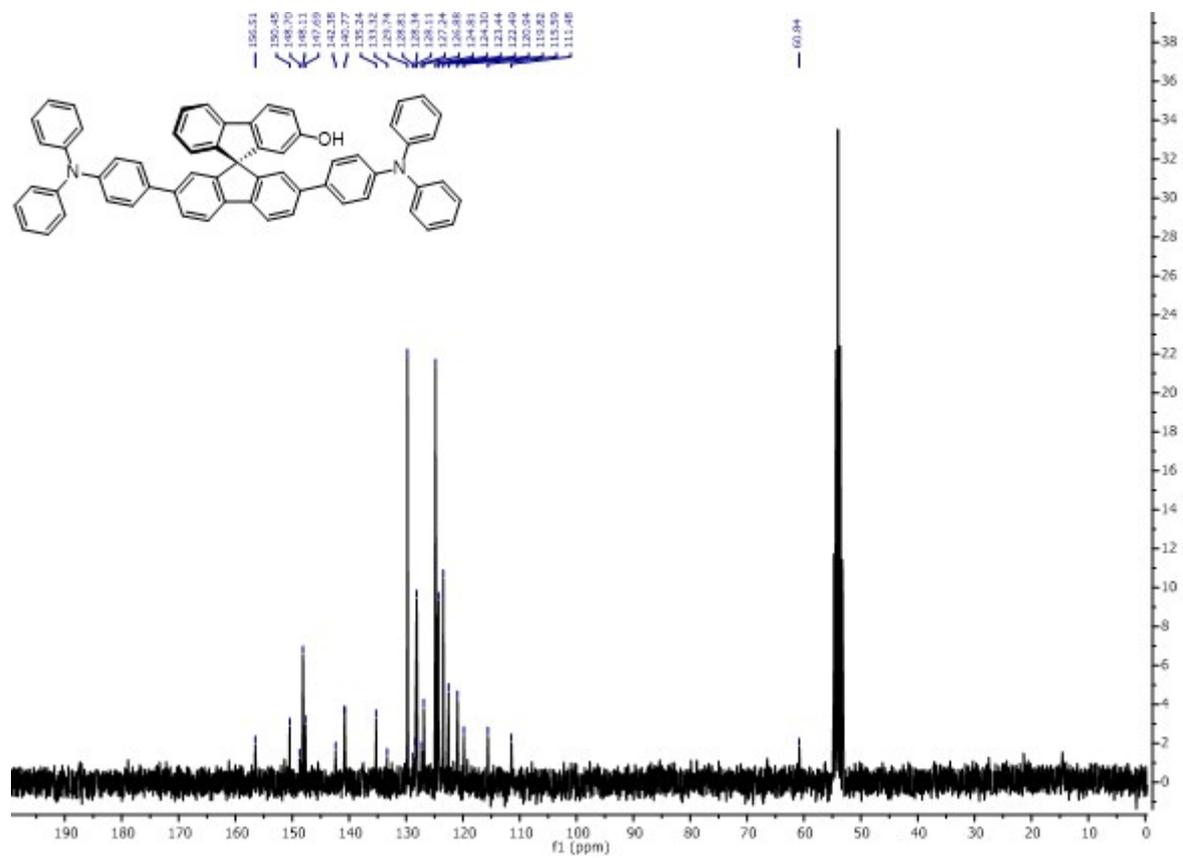


Figure S18. $^{13}\text{C-NMR}$ spectrum of 5.

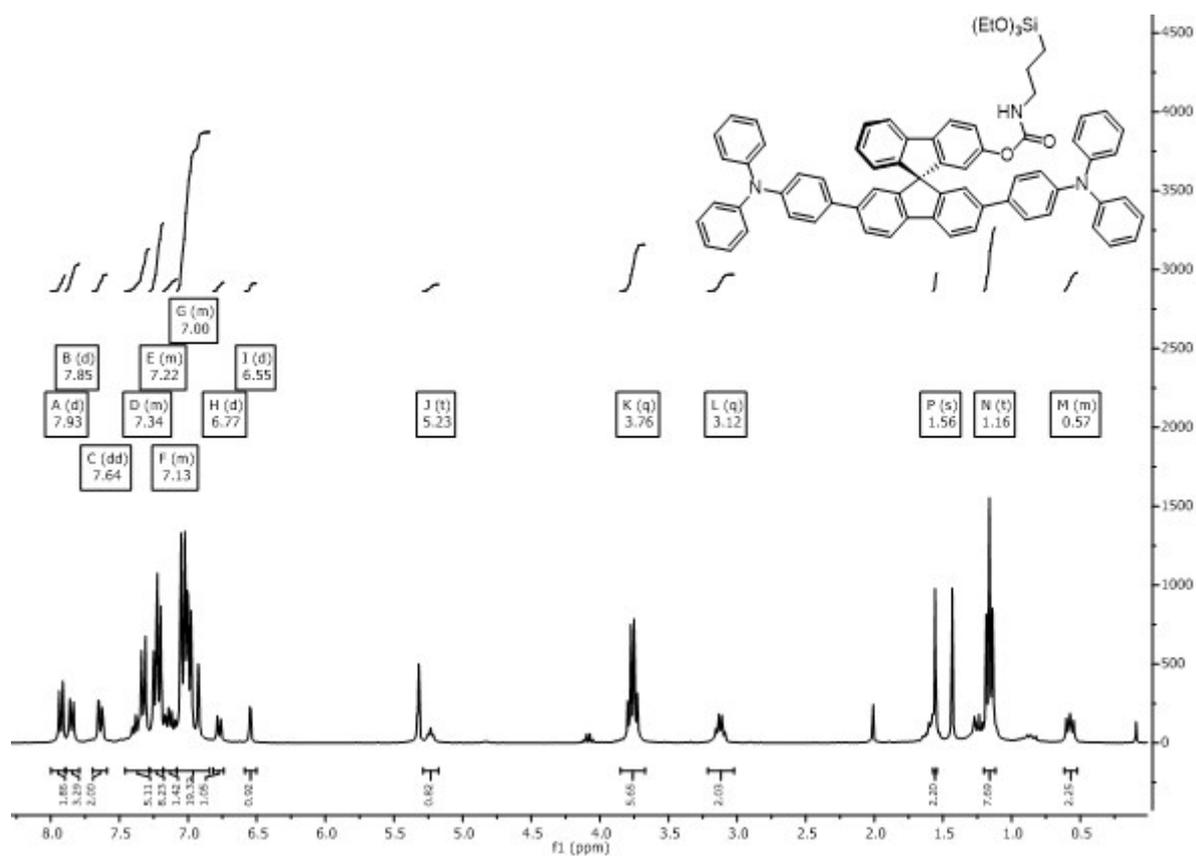


Figure S19. $^1\text{H-NMR}$ spectrum of 6.

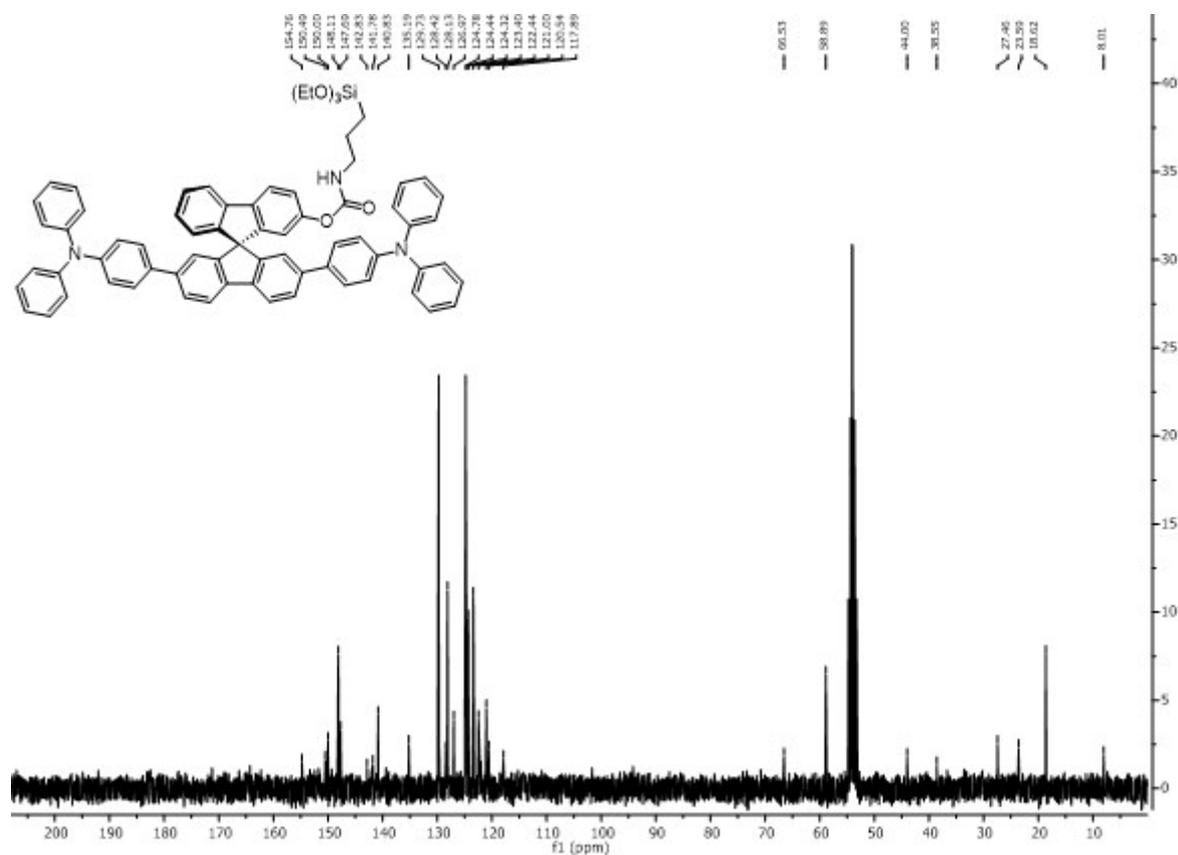


Figure S20. $^{13}\text{C-NMR}$ spectrum of 6.

Mass spectra

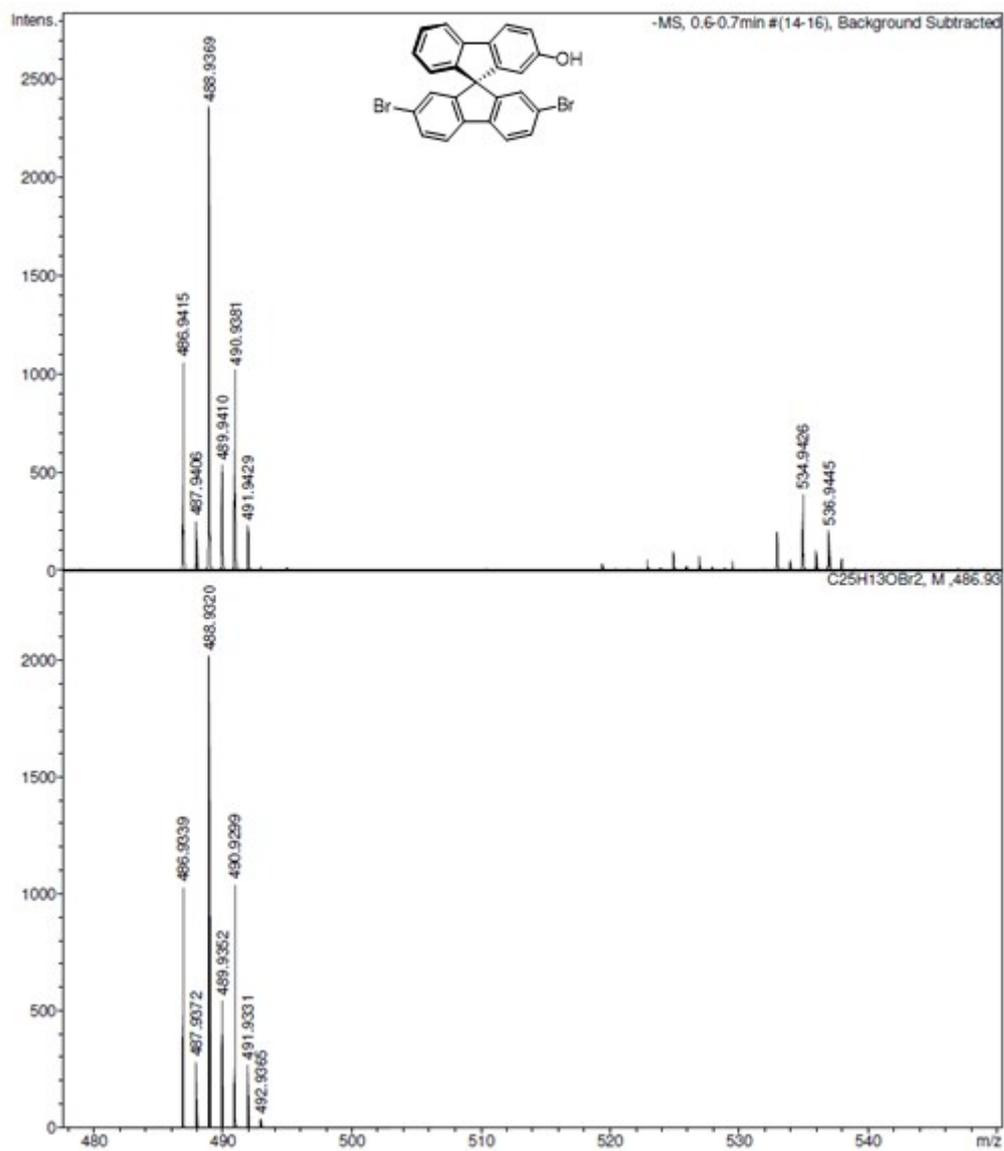


Figure S21. Mass spectrum of 4.

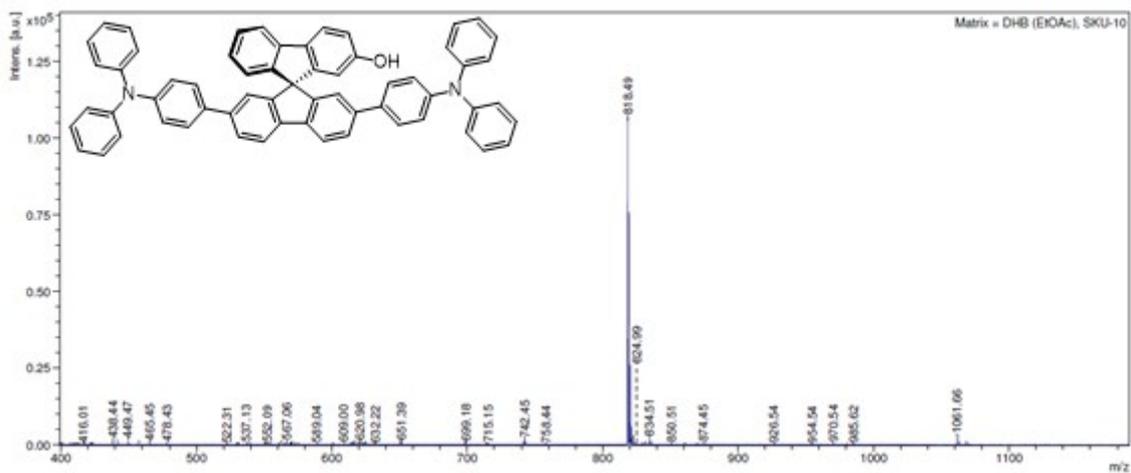


Figure S22. Mass spectrum of 5.

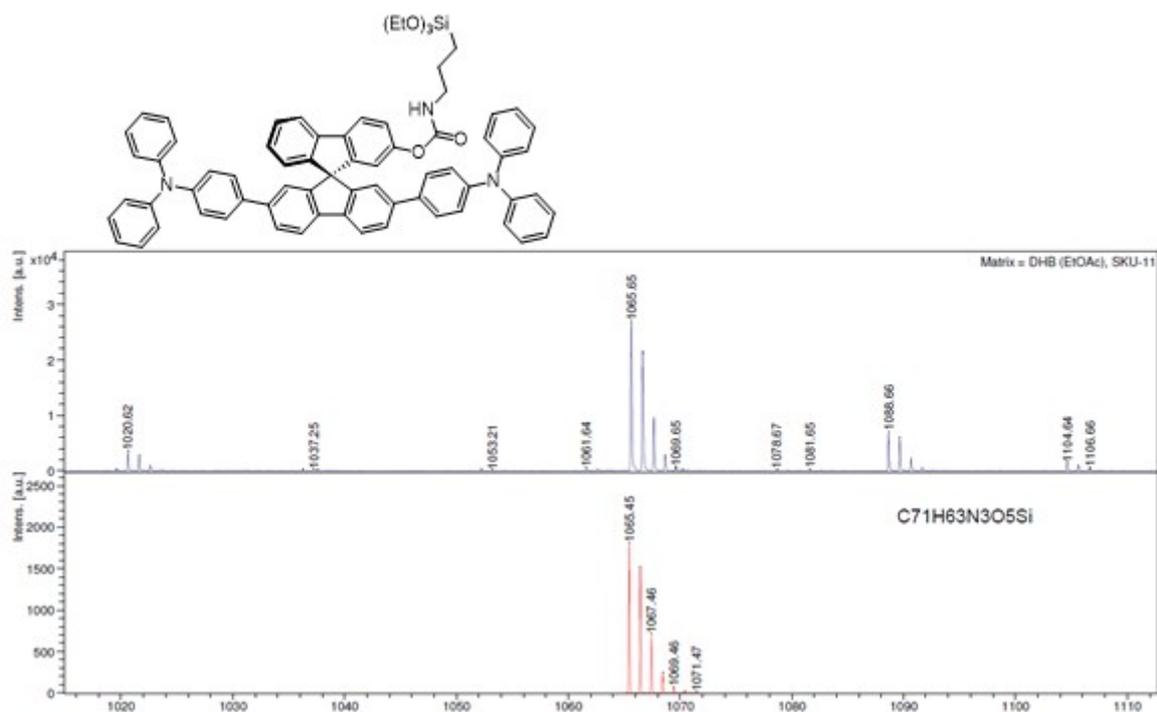


Figure S23. Mass spectrum of 6.