Supporting Information

Versatile Hybridization of Conjugated Polymers with Silica

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General

^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-EX400 instrument at 400 and 100 MHz, respectively. Gel permeation chromatography (GPC) was carried out on a TOSOH 8020 (TSKgel G3000HXL column) instrument using $CHCl_3$ as an eluent after calibration with standard polystyrene samples. FTIR spectra were obtained on a SHIMADZU IRPrestige-21 spectrophotometer. UV-vis absorption spectra were obtained on a SHIMADZU UV3600 spectrophotometer. Photoluminescence spectra were obtained on a HORIBA FluoroMax-4 spectrofluorometer. Fluorescence lifetime analysis was carried out on a HORIBA FluoreCube spectrofluorometer system; excitation at 375 nm was carried out using a UV diode laser (NanoLED-375L). Scanning electron microscopy (SEM) measurement was carried out on a JEOL JSM-5600B system. UV irradiation (λ = 365 nm, 100V, 8W) was carried out with a Funakoshi LMS-20 (3UV) UV transilluminator.

Materials

THF and NEt_3 were purchased and purified by passage through purification column under Ar pressure.[1] 1,4-Diethynylbenzene (**2a**), $Si(OEt)_4$, (n-C_6H_{13})$Si(OEt)_3$, $Pd(PPh_3)_4$, and CuI were obtained commercially, and used without further purification. Polystyrene (degree of polymerization n = approximately 3000) for the study of photostability was purchased and purified by recrystallization from toluene and MeOH. 1,4-Bis(*N,N*-dioctylcarbamoyl)-2,5-diiodobenzene (**1**),[2] 1,4-diethynylxylene (**2b**),[3] 4,4'-diethynyl-1,1'-biphenyl (**2c**),[4] 2,7-diethynyl-9,9-dimethylfluorene (**2d**),[5] 3,6-diethynyl-9-(4-methylphenyl)-carbazole (**2e**),[6] and pseudo-*para*-diethynyl[2.2]paracyclophane (**2f**)[7] were synthesized according to the procedure we previously reported. All reactions were performed under Ar atmosphere.

Polymerization

A typical procedure is as follows. A mixture of **1** (432 mg, 0.50 mmol), **2** (0.50 mmol), $Pd(PPh_3)_4$ (29 mg, 0.05 mmol), CuI (19 mg, 0.10 mmol), Et_3N (2.0 mL), and THF (5.0 mL) was placed in a round-bottom flask equipped with a magnetic stirring bar and a reflux condenser. After degassing the reaction mixture several times, the reaction was carried out at reflux temperature for 6 h with stirring. After the reaction mixture was cooled to room temperature, $CHCl_3$ was added to the mixture. It was washed with 28% aqueous NH_3 solution and water, and the organic layer was dried over $MgSO_4$. The solvent was concentrated in vacuo, and it was reprecipitated with MeOH (two times) and hexane (two times) to obtain the polymer.

3a, 88%. ^1H NMR ($CDCl_3$, 400 MHz) δ 0.83 (m), 0.89(m), 1.18 (br), 1.26 (br), 1.49 (br), 1.66 (br), 3.16 (br), 3.31 (br), 3.70 (br), 7.3-7.5 (m) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.1, 22.6, 26.6, 27.1, 27.6, 29 (m), 31.8 (m), 44.7, 48.7, 88.3, 94.5, 120.2, 122.9, 130.2, 131.6, 140.0, 168.2 ppm.

3b, 74%. ^1H NMR ($CDCl_3$, 400 MHz) δ 0.82 (br), 0.88 (br), 1.17 (br), 1.26 (br), 1.50 (br), 1.66 (br), 2.40 (br s), 3.16 (br), 3.42 (br), 3.59 (br), 7.5 (br) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.0, 20.0, 22.6, 26.6, 27.2, 27.6, 29 (m), 31.7 (m), 44.8, 48.8, 91.5, 93.9, 120.4, 122.8, 130.3, 132.8, 133.6, 137.6, 139.7, 168.4 ppm.

3c, 92%. ^1H NMR ($CDCl_3$, 400 MHz) δ 0.84 (m), 1.19 (br), 1.23 (br), 3.19 (br), 3.77 (br), 7.4-7.6 (m) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.0, 22.6, 26.6, 27.1, 27.6, 29 (m), 31.7 (m), 44.7, 48.6, 87.2, 94.7, 120.3, 121.9, 130.2, 132.2, 133.0, 139.9, 140.4, 168.4 ppm.

3d, 73%. ^1H NMR ($CDCl_3$, 400 MHz) δ 0.83 (m), 1.19 (br), 1.34 (br), 1.77 (br), 3.21 (br), 3.79 (br), 7.2-7.7 (m) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.0, 22.5, 27 (m), 29 (m), 31.7 (m), 44.7, 46.9, 48.6, 86.7, 95.7, 120.2, 121.6, 125.9, 127.6, 128.3, 129.6, 130.2, 131.1, 131.7, 135.3, 139.1, 139.8, 153.9, 168.5 ppm.

3e, 69%. ^1H NMR ($CDCl_3$, 400 MHz) δ 0.79 (m), 1.20 (br), 1.37 (br), 1.5-1.8 (br), 3.27 (br), 3.80 (br), 7.32 (m), 7.43 (m), 7.55 (m), 8.25 (s) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.1, 22.6, 26.7, 27.3, 27.8, 29 (m), 31.8, 44.7, 46.2, 48.7, 85.2, 95.9, 110.0, 114.3, 120.3, 122.7, 123.9, 126.7, 130 (m), 133.9, 138.1, 139.8, 141.3, 168.6 ppm.

3f, 81%. ^1H NMR ($CDCl_3$, 400 MHz) δ 0.82 (br), 0.90 (br), 1.20 (br), 1.28 (br), 1.5-1.9 (br m), 2.94 (br), 3.0 (br), 3.25 (br), 3.63 (br), 6.50 (br), 6.58 (br), 7.00 (br), 7.56 (br) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.1, 22.6, 26.8, 27.3, 27.7, 29 (m), 31.8, 34.1, 44.9, 48.8, 89.5, 95.3, 120.6, 123.7, 130.3, 133.3, 137,3, 139.7, 142.6, 168.7 ppm.

Polymer **3g** was obtained from 1,4-diiodo-2,5-didodecyloxybenzene[8] and **2a** with the same procedure described above. Spectral data were matched with the literature's values.[8]

Synthesis of conjugated-polymer/SiO_2 hybrids

A typical procedure is as follows. Polymer (0.15 mg), $Si(OEt)_4$ (0.20mL), (n-C_6H_{13})$Si(OMe)_3$ (0.25 mL), and 1N HCl aq (0.10 mL) were dissolved in THF (2.0 mL), and the mixture was stirred for 2~3 h at room temperature. The reaction mixture was placed in a polypropylene vessel covered with an aluminum foil having a few pinholes and left under air in an oven at 60 °C for 24h to obtain the target hybrid.

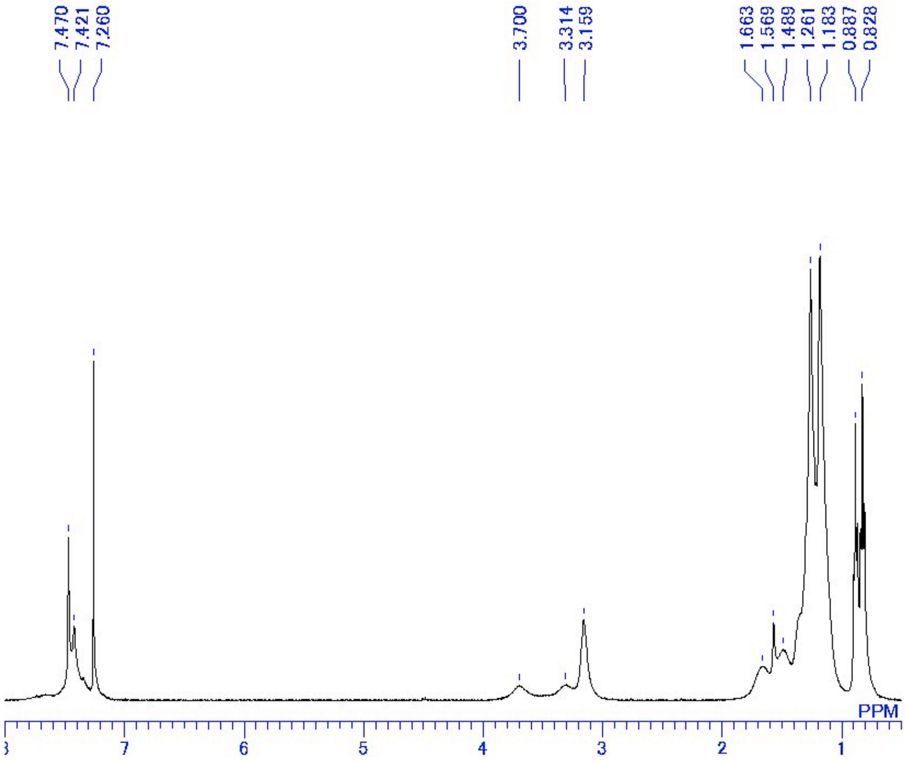

Figure S1. ^{1}H NMR spectrum of polymer **3a**, 400 MHz, $CDCl_3$.

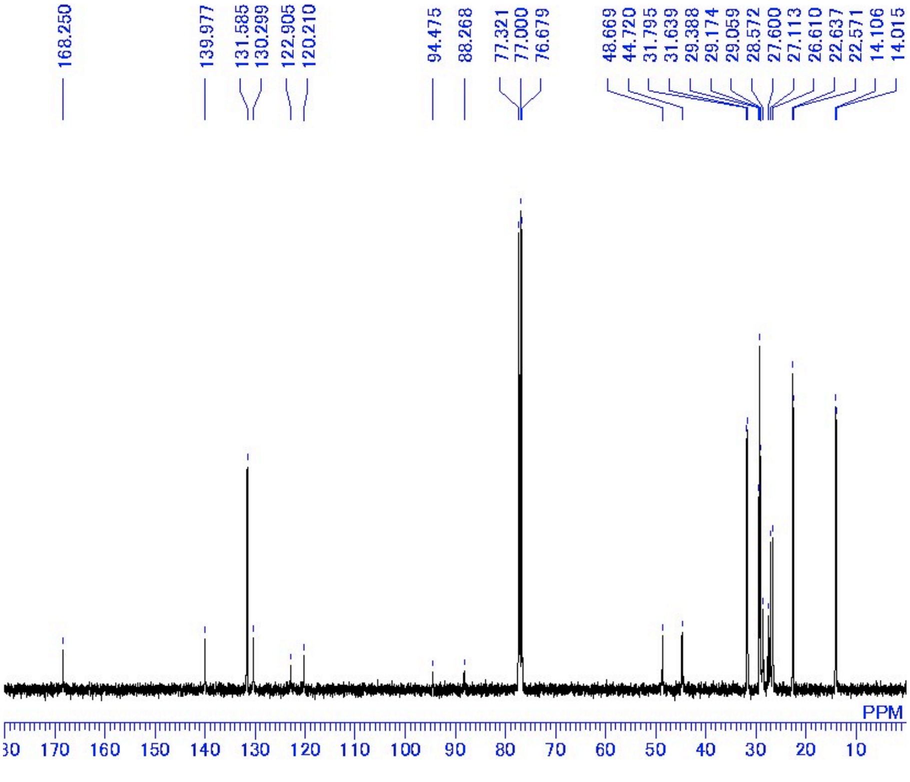

Figure S2. ^{13}C NMR spectrum of polymer **3a**, 100 MHz, $CDCl_3$.

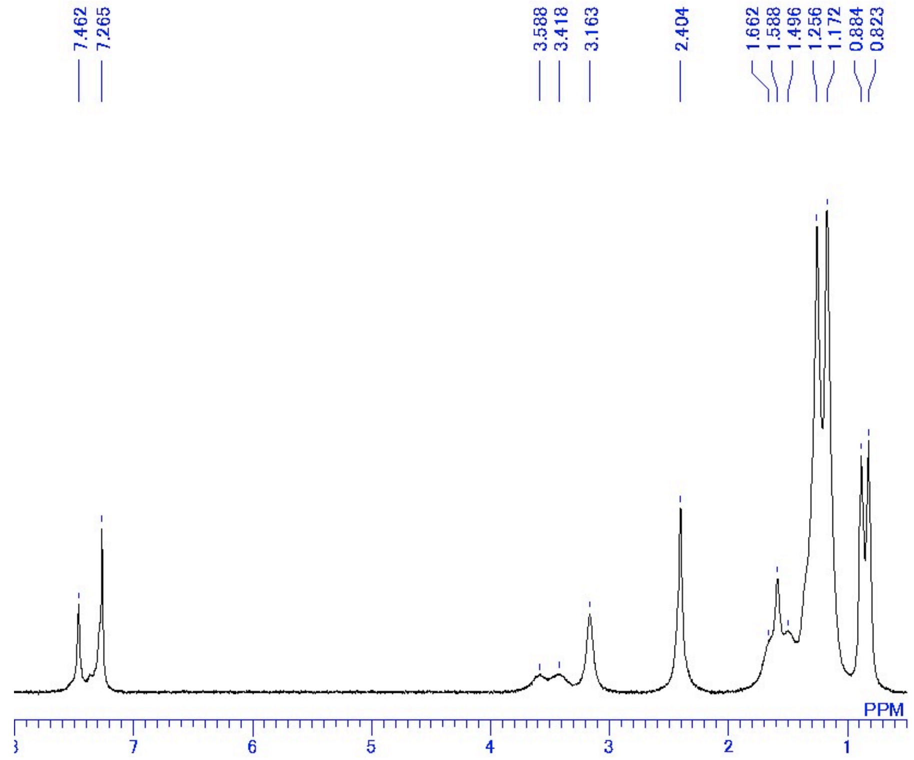

Figure S3. ^{1}H NMR spectrum of polymer **3b**, 400 MHz, $CDCl_3$.

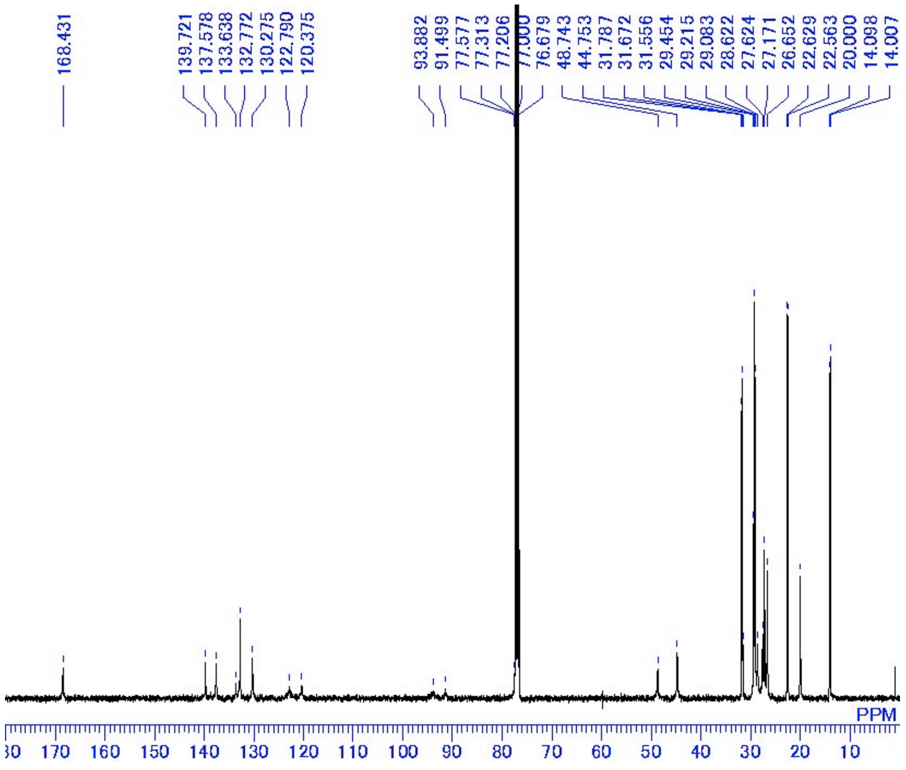

Figure S4. ^{13}C NMR spectrum of polymer **3b**, 100 MHz, $CDCl_3$.

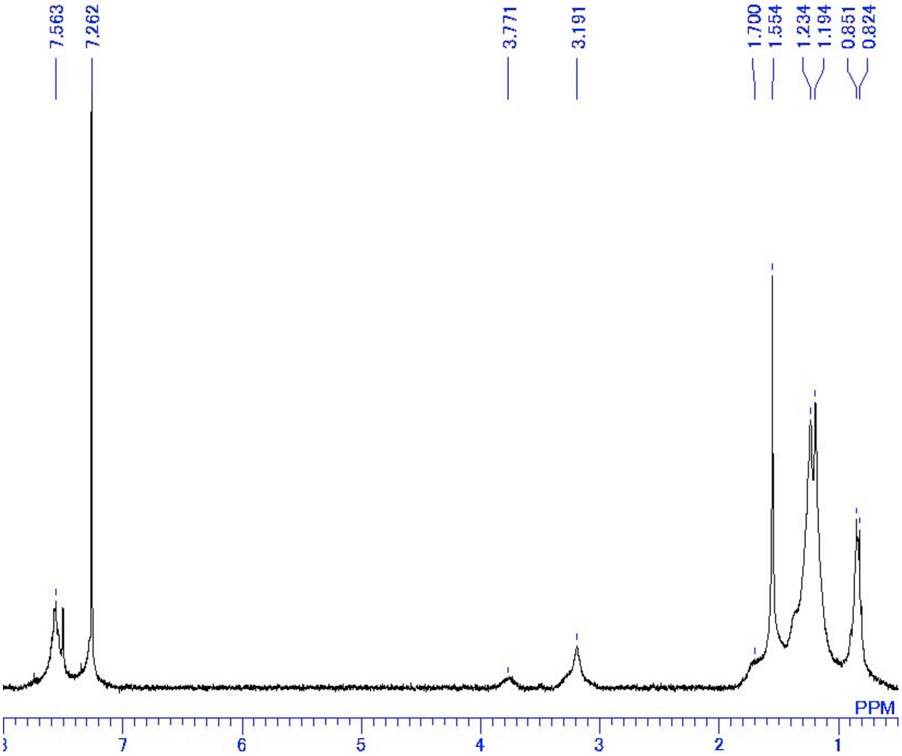

Figure S5. ^{1}H NMR spectrum of polymer **3c**, 400 MHz, CDCl$_3$.

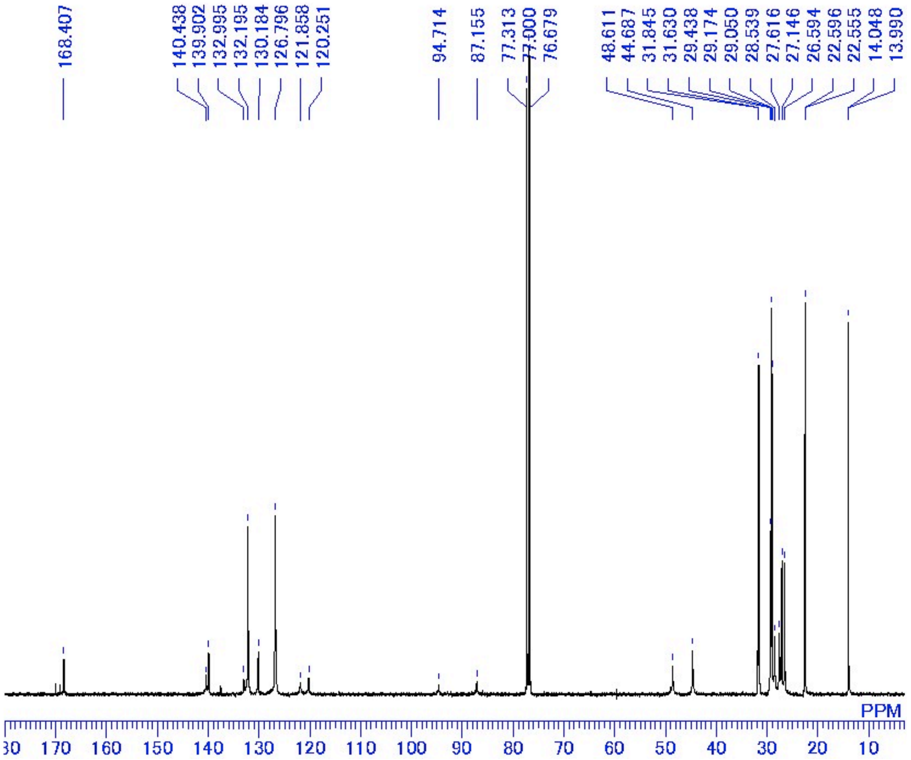

Figure S6. ^{13}C NMR spectrum of polymer **3c**, 100 MHz, CDCl$_3$.

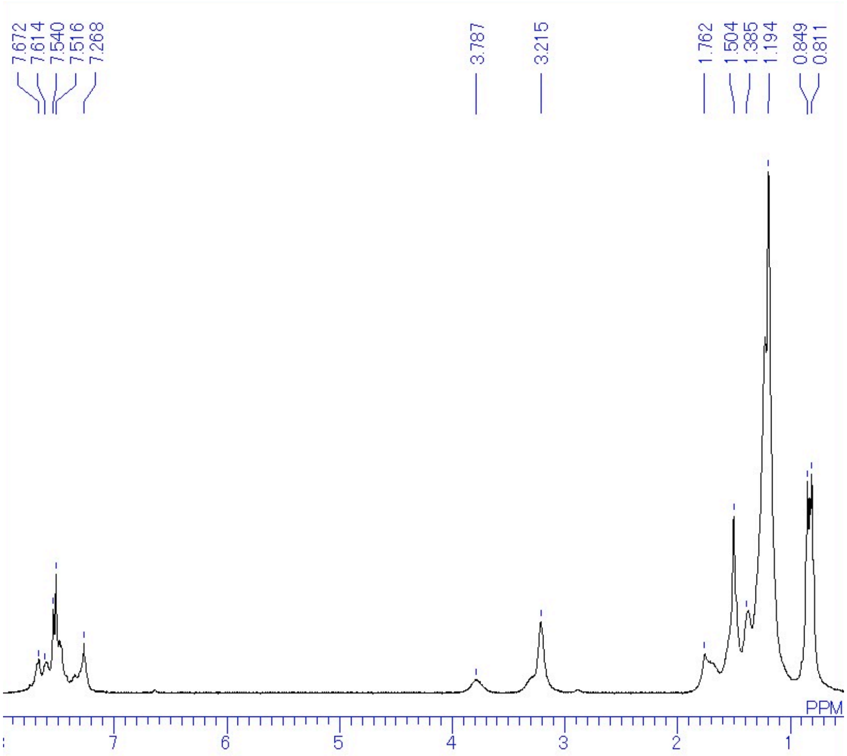

Figure S7. ^{1}H NMR spectrum of polymer **3d**, 400 MHz, $CDCl_3$.

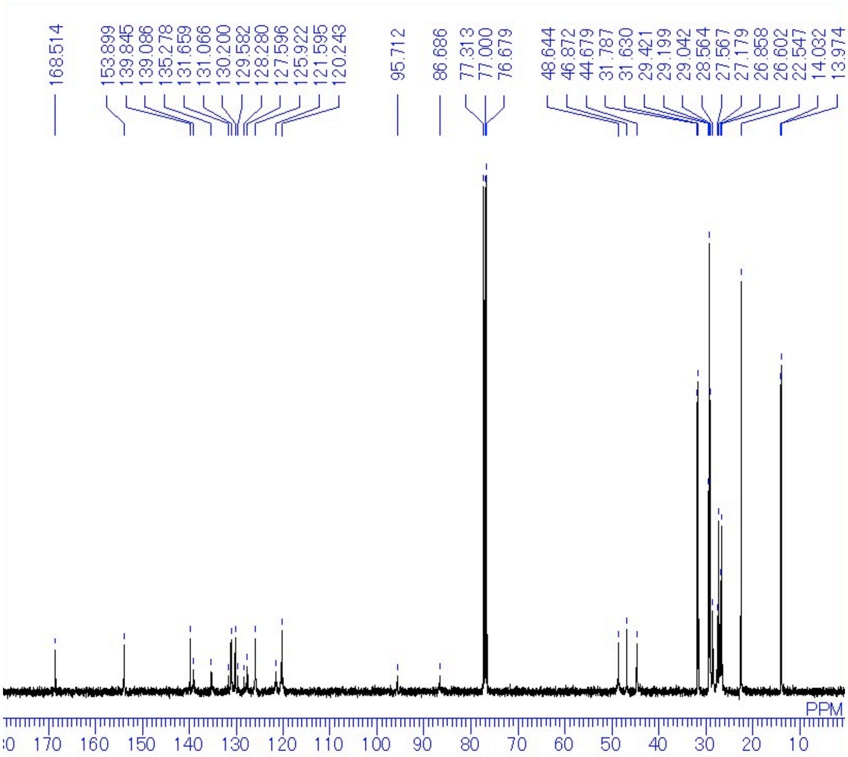

Figure S8. ^{13}C NMR spectrum of polymer **3d**, 100 MHz, $CDCl_3$.

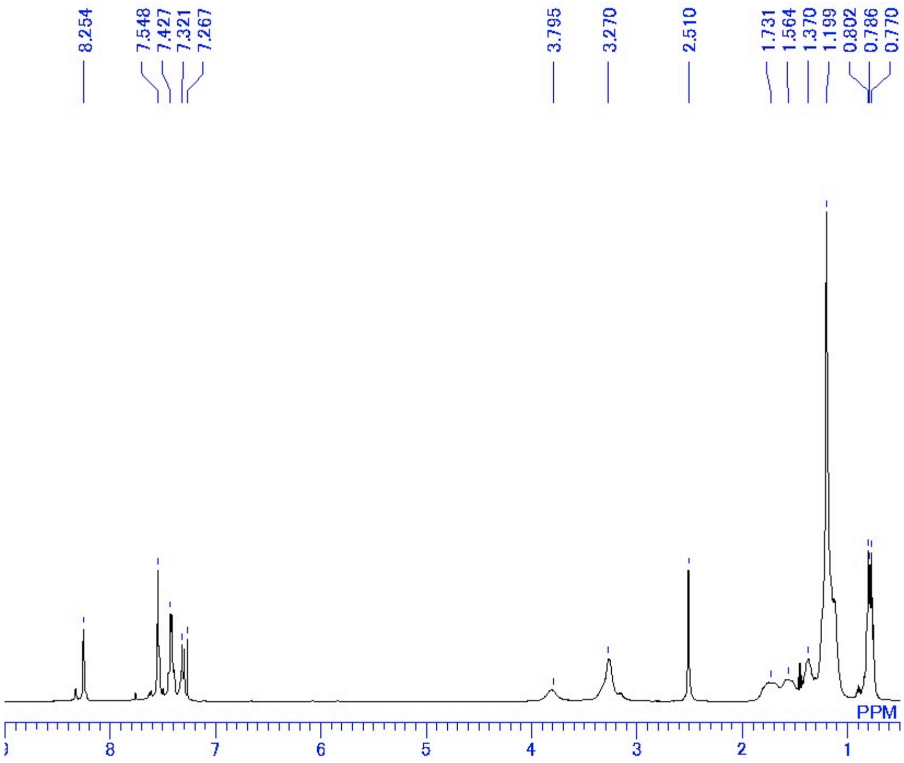

Figure S9. ^{1}H NMR spectrum of polymer **3e**, 400 MHz, $CDCl_3$.

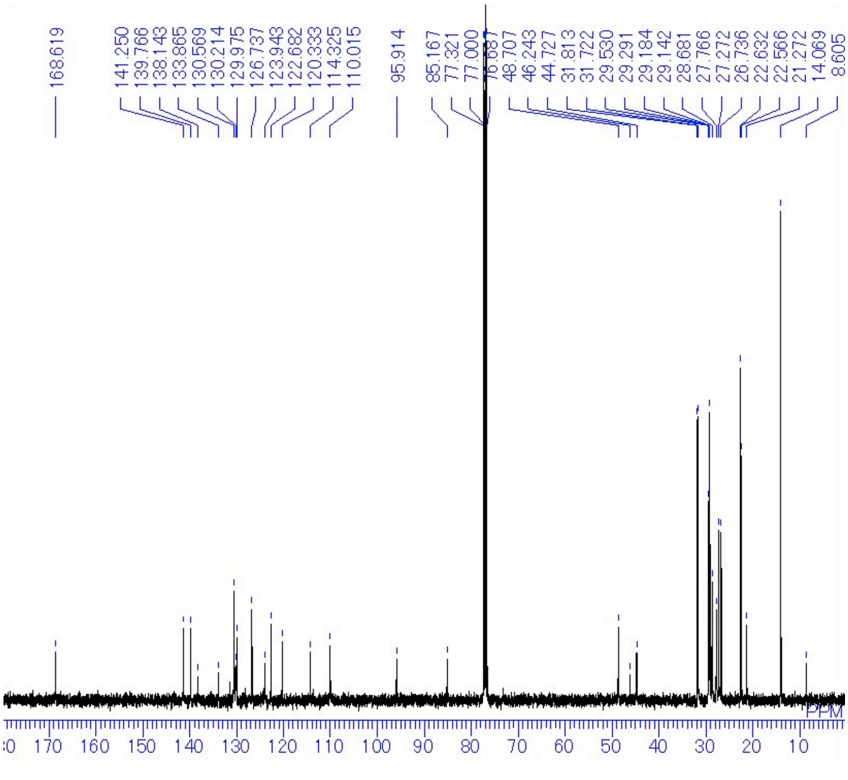

Figure S10. ^{13}C NMR spectrum of polymer **3e**, 100 MHz, $CDCl_3$.

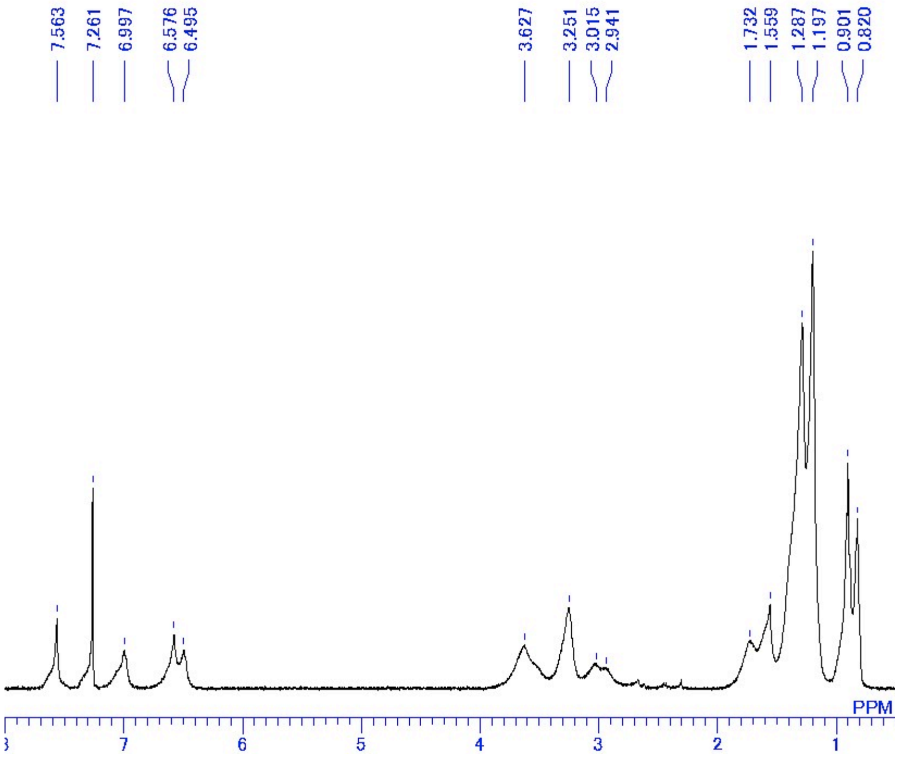

Figure S11. ^{1}H NMR spectrum of polymer **3f**, 400 MHz, $CDCl_3$.

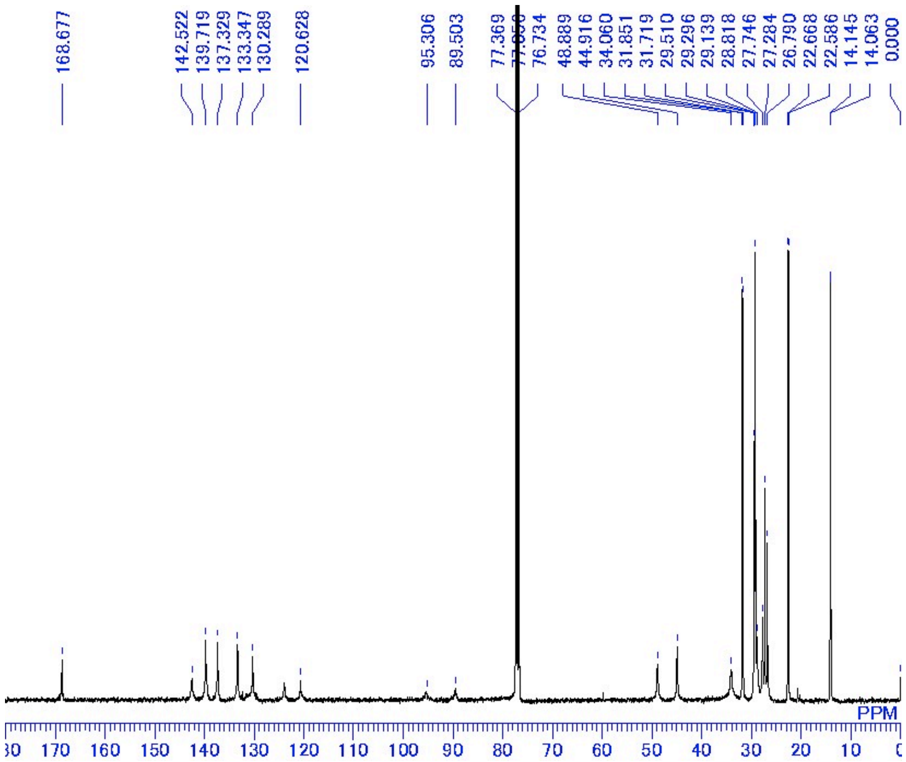

Figure S12. ^{13}C NMR spectrum of polymer **3f**, 100 MHz, $CDCl_3$.

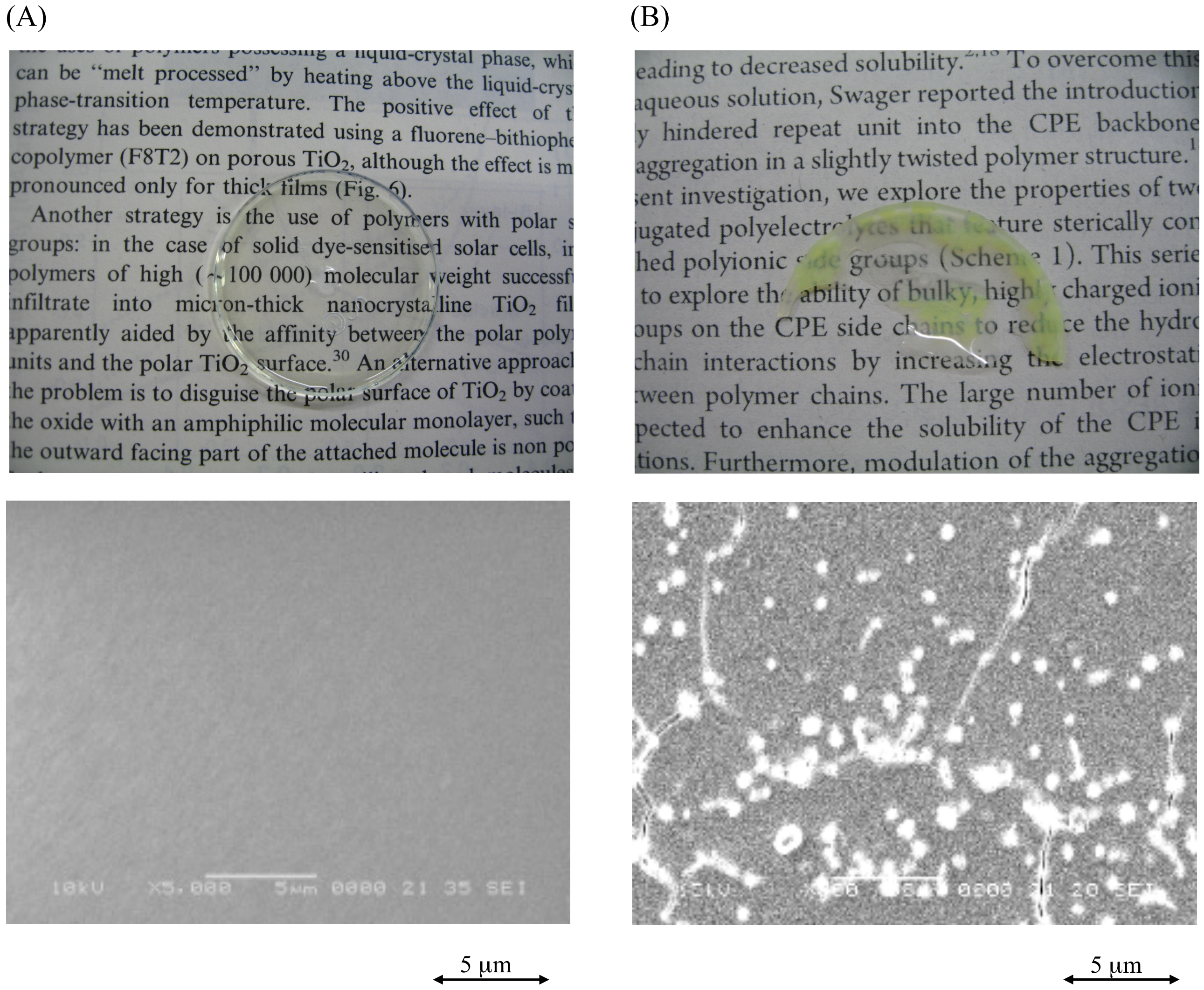

Figure 13. Appearance and SEM images of hybrids **4a** (A) and **4g** (B) containing 0.04 wt% of polymers **3a** and **3g** in the SiO_2 matrix, respectively.

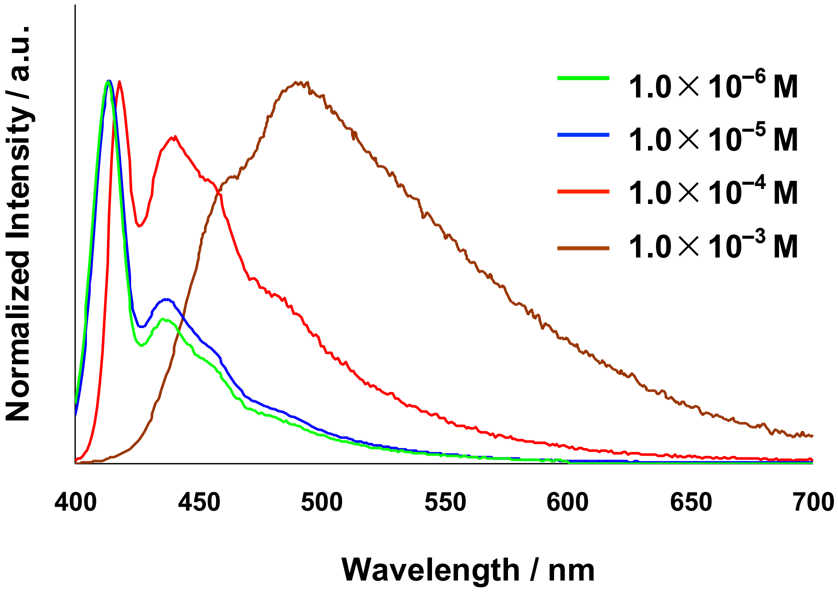

Figure S14. The concentration effect of the photoluminescence spectra of polymer **3a** in THF solution excited at 385 nm.

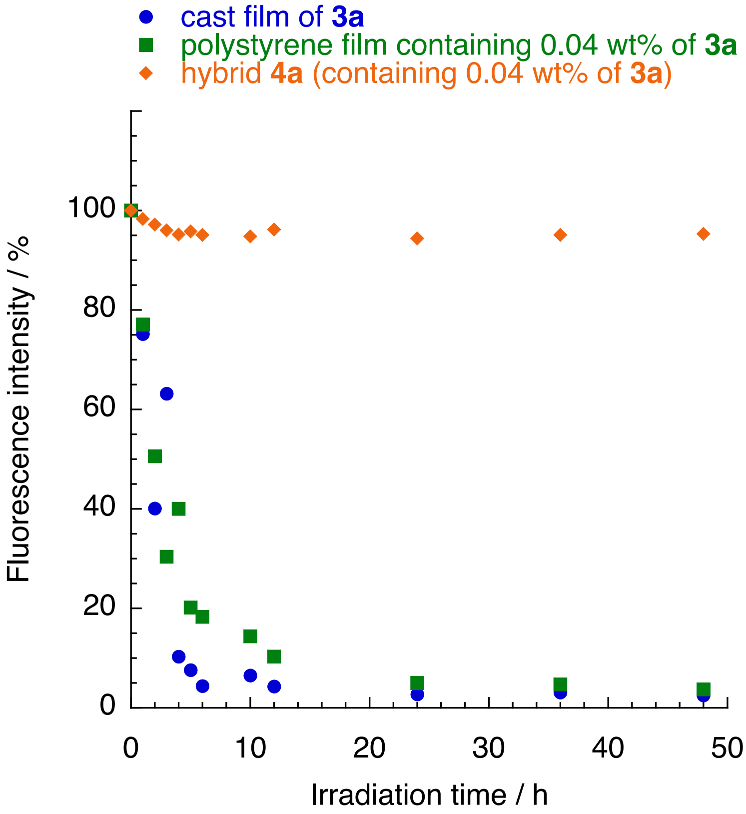

Figure S15. Photostability of the cast film of **3a**, polystyrene film containing 0.04 wt% of **3a**, and hybrid **4a** (containing 0.04 wt% of **3a**): UV (365 nm, 100V, 8W) irradiation under air.

References

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