

Supporting Information

Versatile Hybridization of Conjugated Polymers with Silica

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General

^1H 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 ($\lambda = 365$ 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**), $\text{Si}(\text{OEt})_4$, (*n*- C_6H_{13}) $\text{Si}(\text{OEt})_3$, $\text{Pd}(\text{PPh}_3)_4$, 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*-dioctylcarbonyl)-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(PPh₃)₄ (29 mg, 0.05 mmol), CuI (19 mg, 0.10 mmol), Et₃N (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, CHCl₃ was added to the mixture. It was washed with 28% aqueous NH₃ solution and water, and the organic layer was dried over MgSO₄. 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 (CDCl₃, 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; ¹³C NMR (CDCl₃, 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 (CDCl₃, 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; ¹³C NMR (CDCl₃, 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 (CDCl₃, 400 MHz) δ 0.84 (m), 1.19 (br), 1.23 (br), 3.19 (br), 3.77 (br), 7.4-7.6 (m) ppm; ¹³C NMR (CDCl₃, 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 (CDCl₃, 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; ¹³C NMR (CDCl₃, 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 (CDCl₃, 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; ¹³C NMR (CDCl₃, 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 (CDCl₃, 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; ¹³C NMR (CDCl₃, 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-didodecyloxybenzene⁸ and **2a** with the same procedure described above. Spectral data were matched with the literature's values.⁸

Synthesis of conjugated-polymer/SiO₂ hybrids

A typical procedure is as follows. Polymer (0.15 mg), Si(OEt)₄ (0.20mL), (*n*-C₆H₁₃)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.

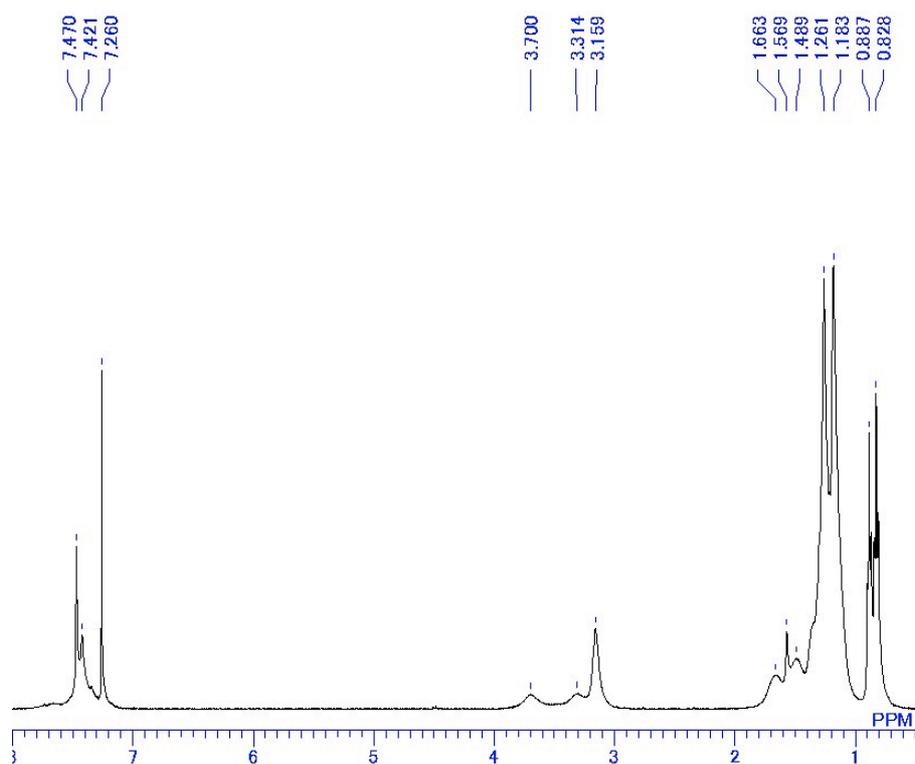


Figure S1. ^1H NMR spectrum of polymer **3a**, 400 MHz, CDCl_3 .

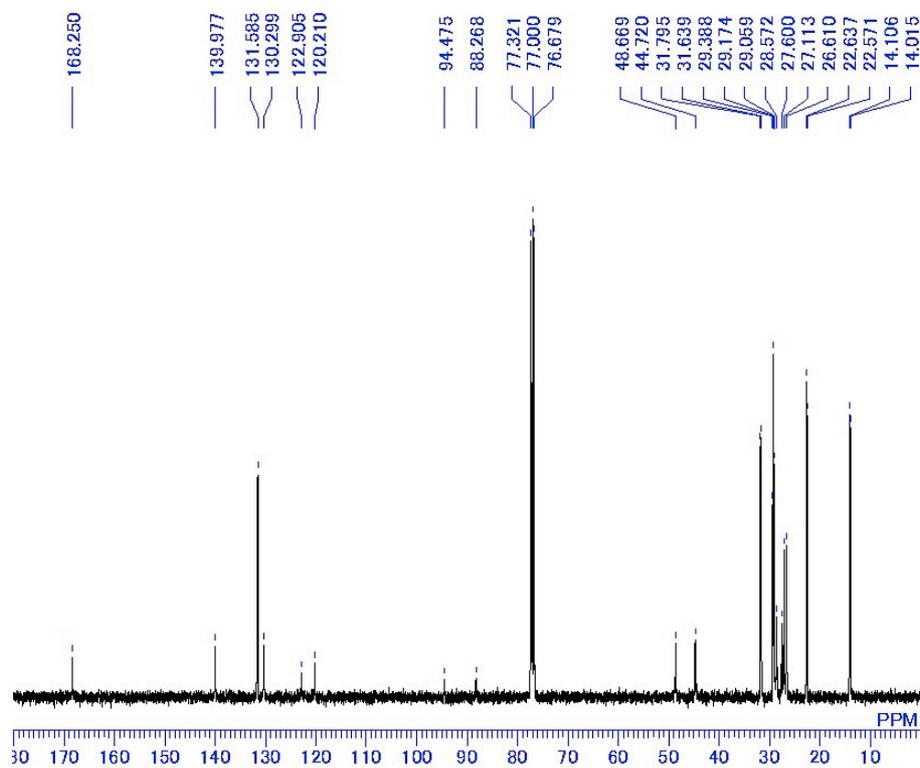


Figure S2. ^{13}C NMR spectrum of polymer **3a**, 100 MHz, CDCl_3 .

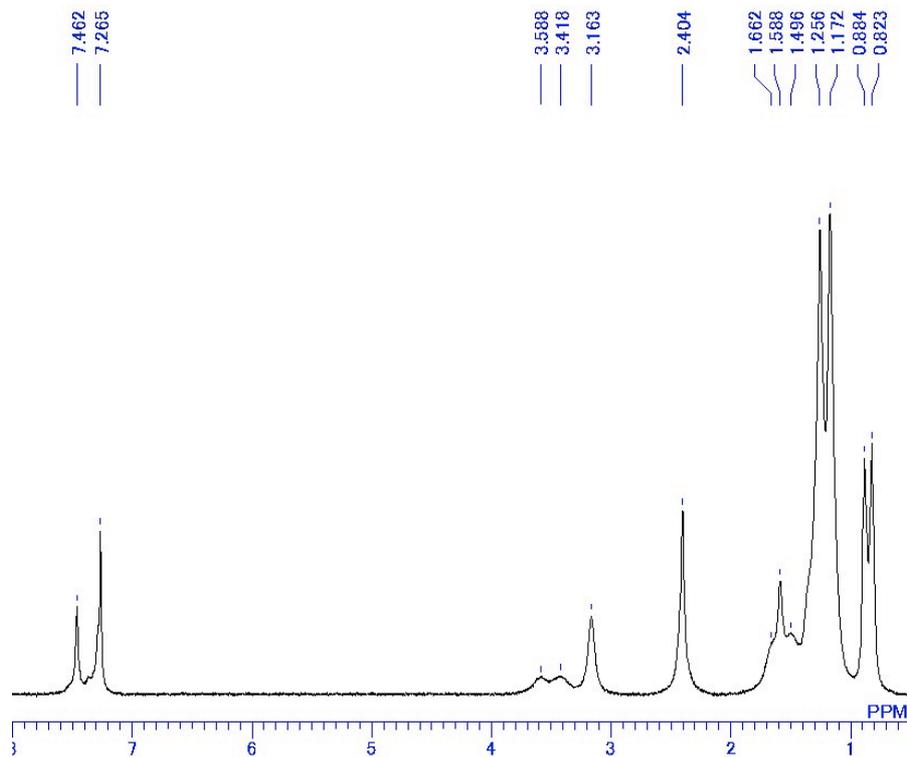


Figure S3. ^1H NMR spectrum of polymer **3b**, 400 MHz, CDCl_3 .

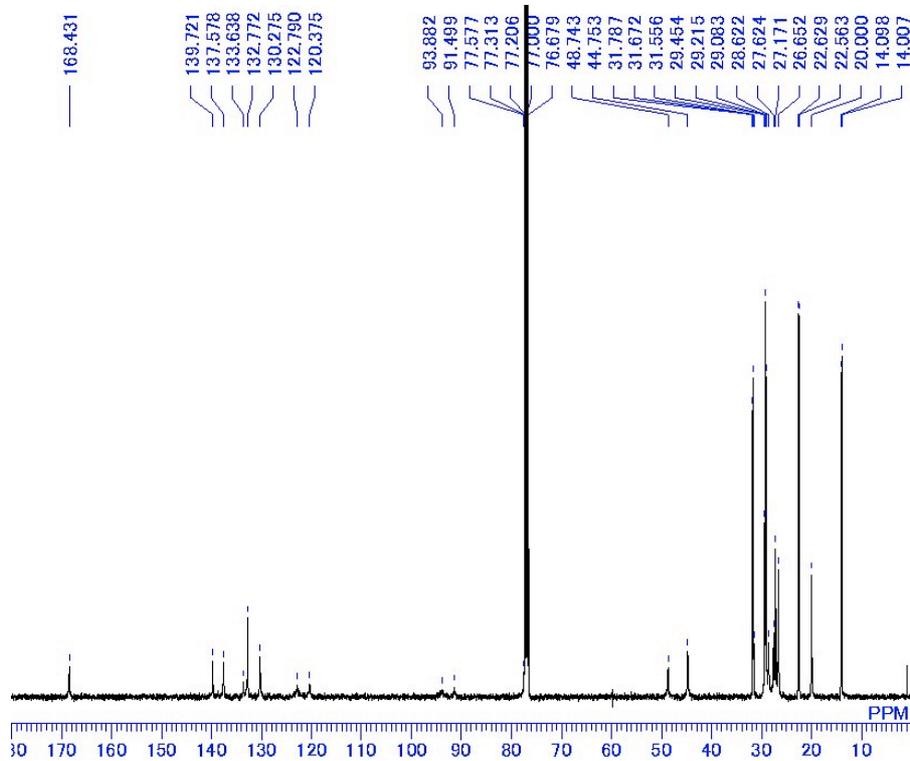


Figure S4. ^{13}C NMR spectrum of polymer **3b**, 100 MHz, CDCl_3 .

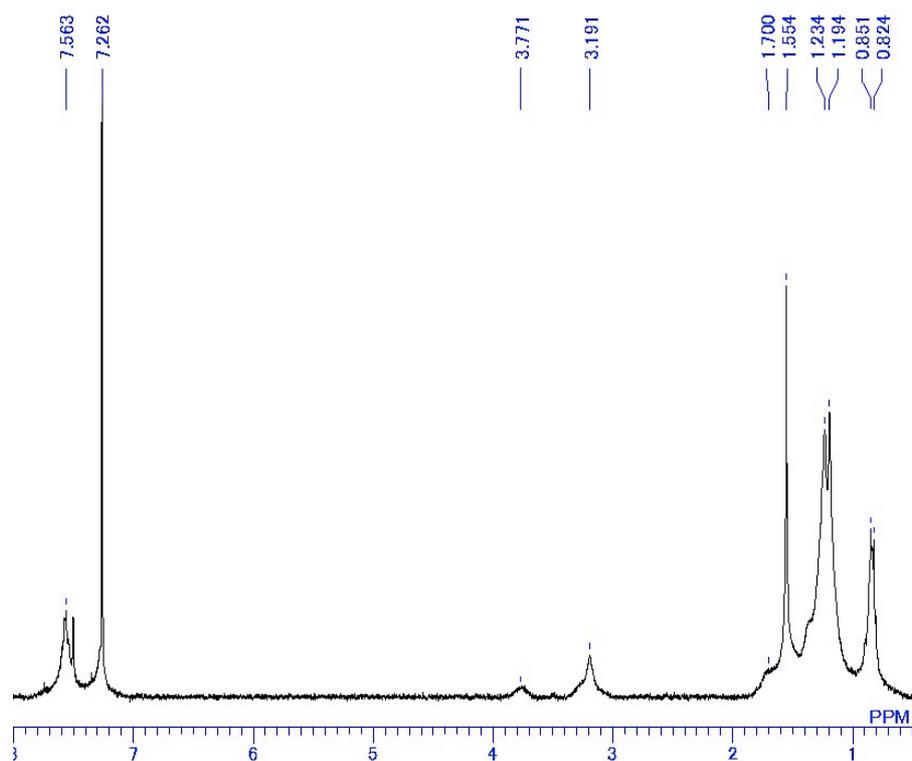


Figure S5. ^1H NMR spectrum of polymer **3c**, 400 MHz, CDCl_3 .

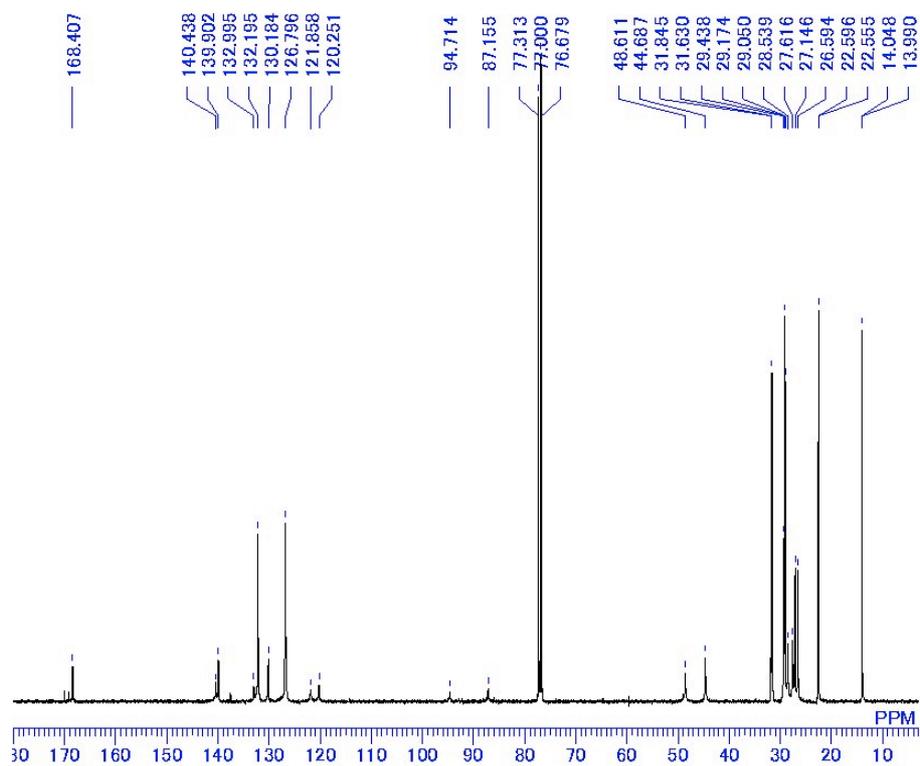


Figure S6. ^{13}C NMR spectrum of polymer **3c**, 100 MHz, CDCl_3 .

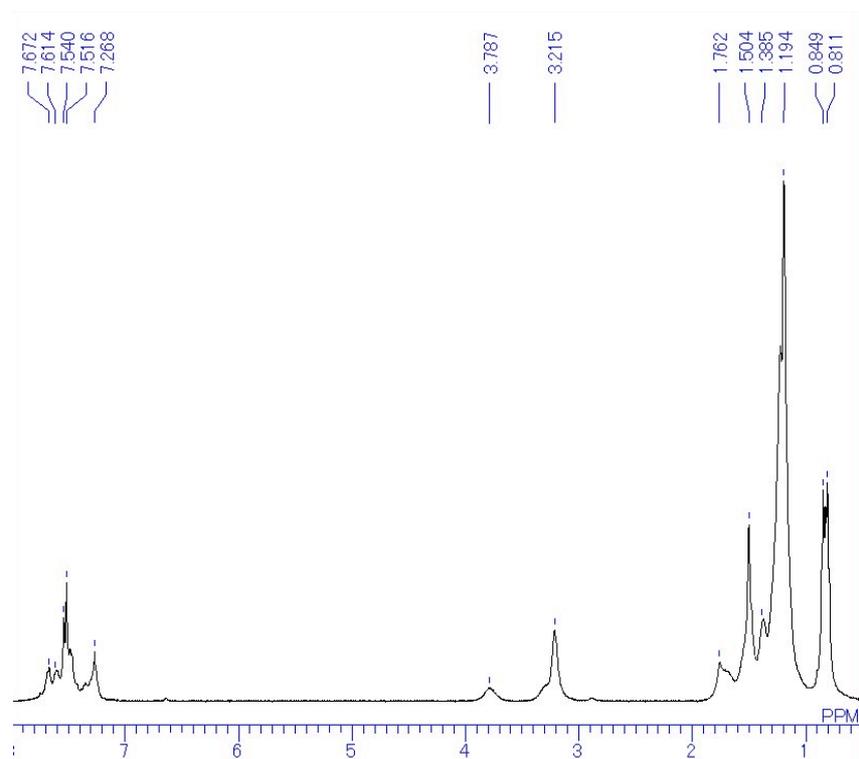


Figure S7. ^1H NMR spectrum of polymer **3d**, 400 MHz, CDCl_3 .

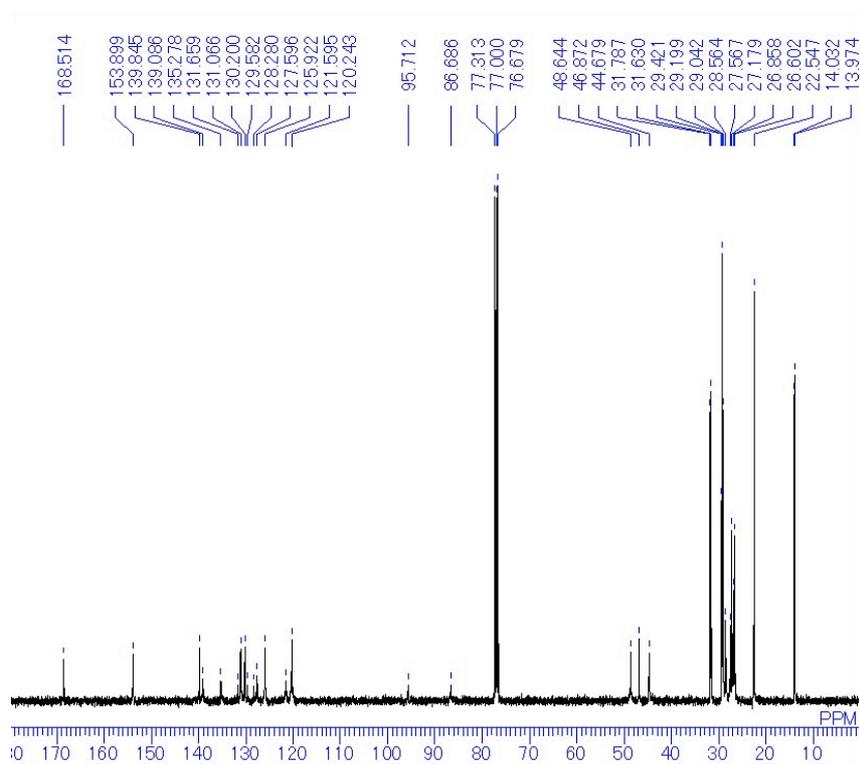


Figure S8. ^{13}C NMR spectrum of polymer **3d**, 100 MHz, CDCl_3 .

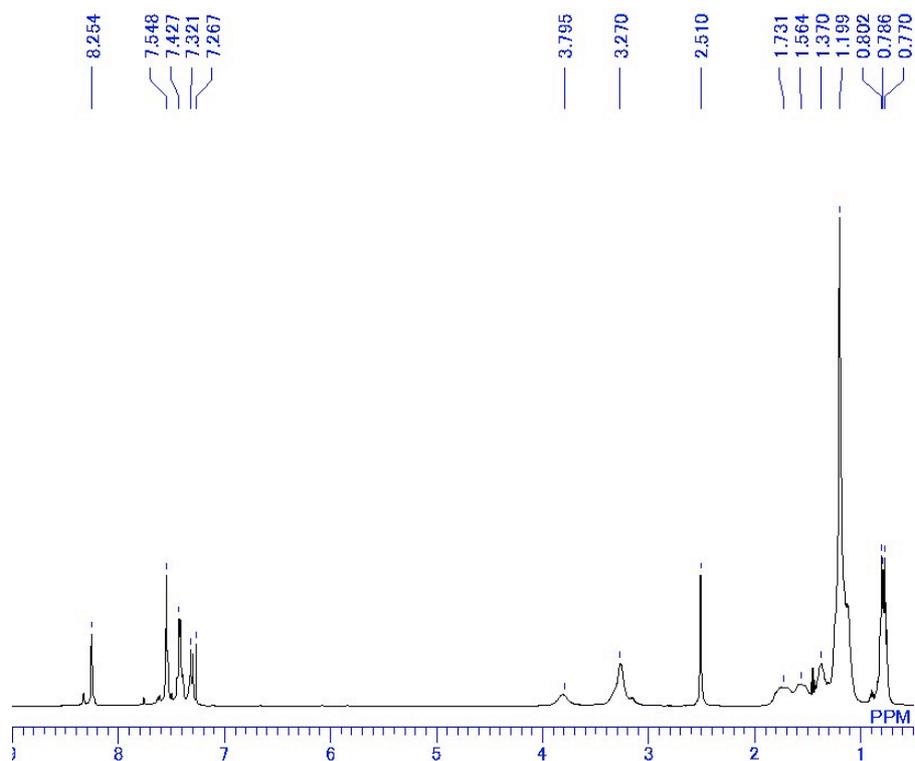


Figure S9. ^1H NMR spectrum of polymer **3e**, 400 MHz, CDCl_3 .

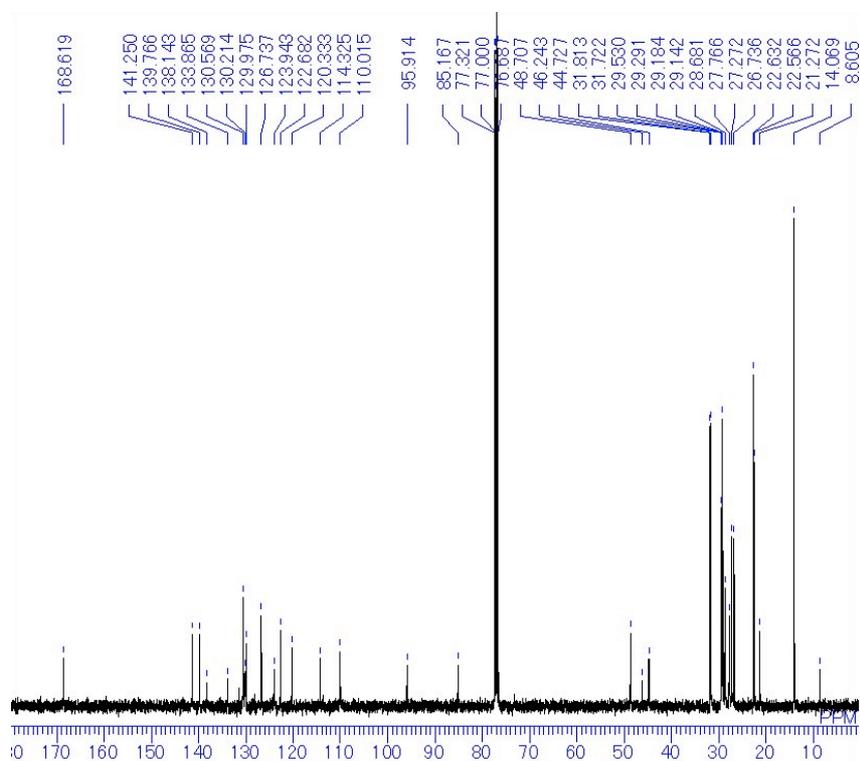


Figure S10. ^{13}C NMR spectrum of polymer **3e**, 100 MHz, CDCl_3 .

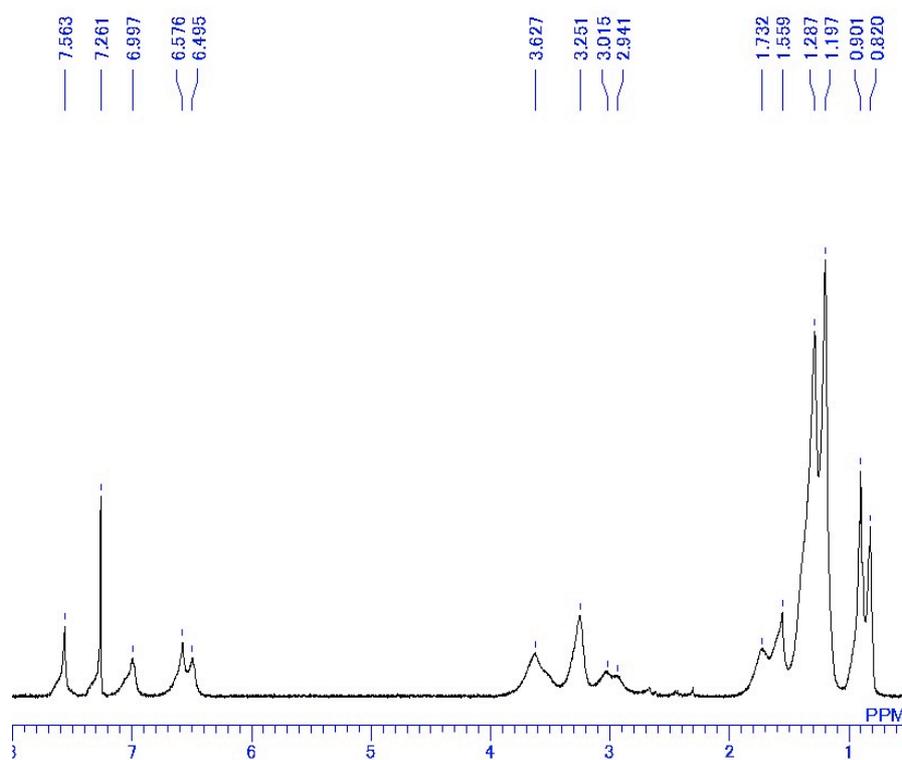


Figure S11. ^1H NMR spectrum of polymer **3f**, 400 MHz, CDCl_3 .

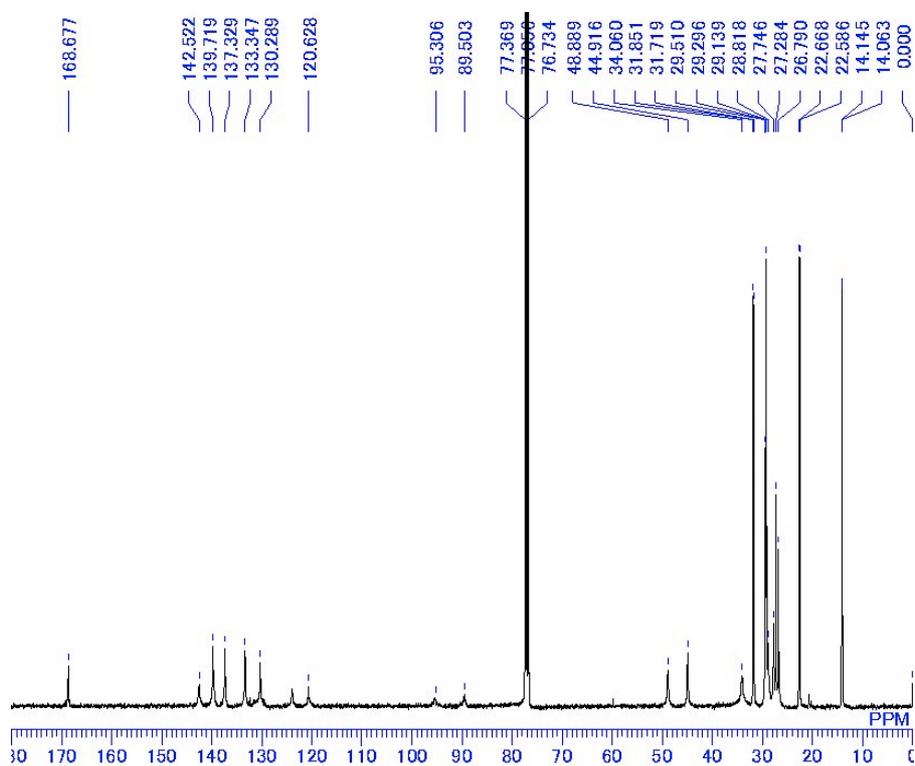
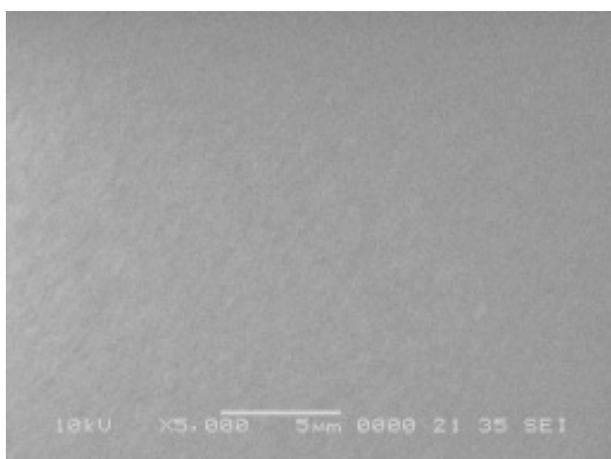


Figure S12. ^{13}C NMR spectrum of polymer **3f**, 100 MHz, CDCl_3 .

(A)

... of polymers possessing a liquid-crystal phase, which can be "melt processed" by heating above the liquid-crystal phase-transition temperature. The positive effect of this strategy has been demonstrated using a fluorene-bithiophene copolymer (F8T2) on porous TiO₂, although the effect is most pronounced only for thick films (Fig. 6).

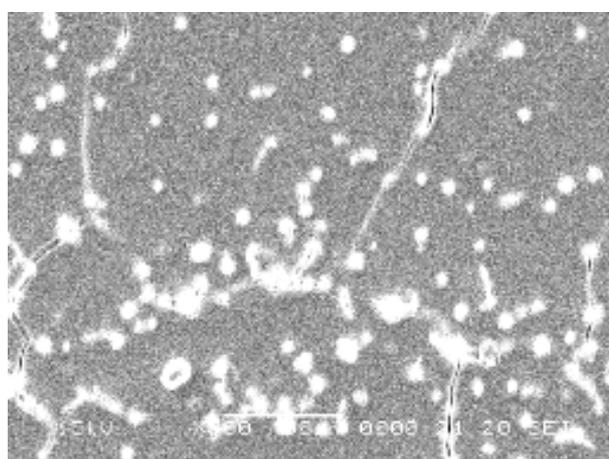
Another strategy is the use of polymers with polar side groups: in the case of solid dye-sensitized solar cells, inorganic polymers of high (~100 000) molecular weight successfully infiltrate into micron-thick nanocrystalline TiO₂ films, apparently aided by the affinity between the polar polymer units and the polar TiO₂ surface.³⁰ An alternative approach to the problem is to disguise the polar surface of TiO₂ by coating the oxide with an amphiphilic molecular monolayer, such that the outward facing part of the attached molecule is non-polar.



5 µm

(B)

... leading to decreased solubility.^{21b} To overcome this problem, Swager reported the introduction of a sterically hindered repeat unit into the CPE backbone to reduce aggregation in a slightly twisted polymer structure.¹ In the present investigation, we explore the properties of two classes of conjugated polyelectrolytes that feature sterically hindered polyionic side groups (Scheme 1). This series of experiments is intended to explore the ability of bulky, highly charged ionic side groups on the CPE side chains to reduce the hydrophobic chain interactions by increasing the electrostatic repulsion between polymer chains. The large number of ionic side groups is expected to enhance the solubility of the CPE in aqueous solutions. Furthermore, modulation of the aggregation



5 µm

Figure 13. Appearance and SEM images of hybrids **4a** (A) and **4g** (B) containing 0.04 wt% of polymers **3a** and **3g** in the SiO₂ matrix, respectively.

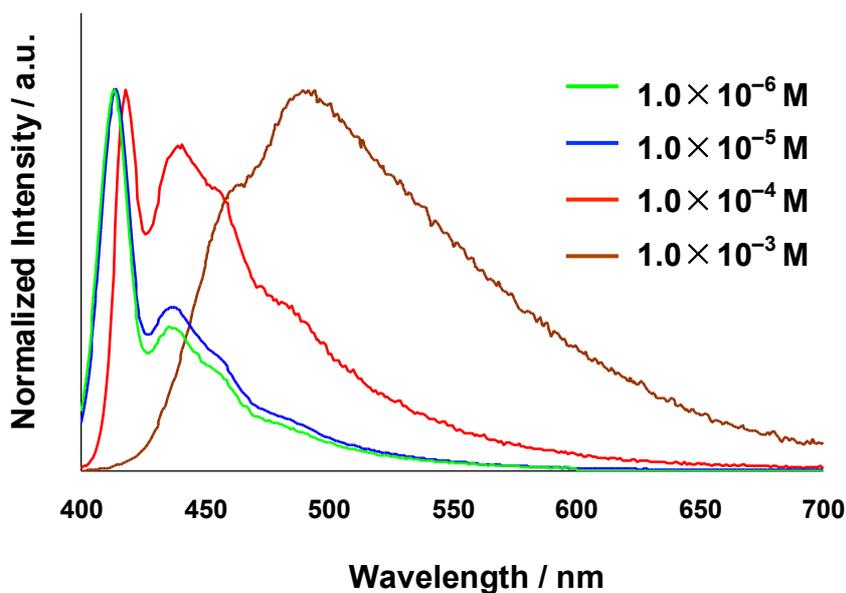


Figure S14. The concentration effect of the photoluminescence spectra of polymer **3a** in THF solution excited at 385 nm.

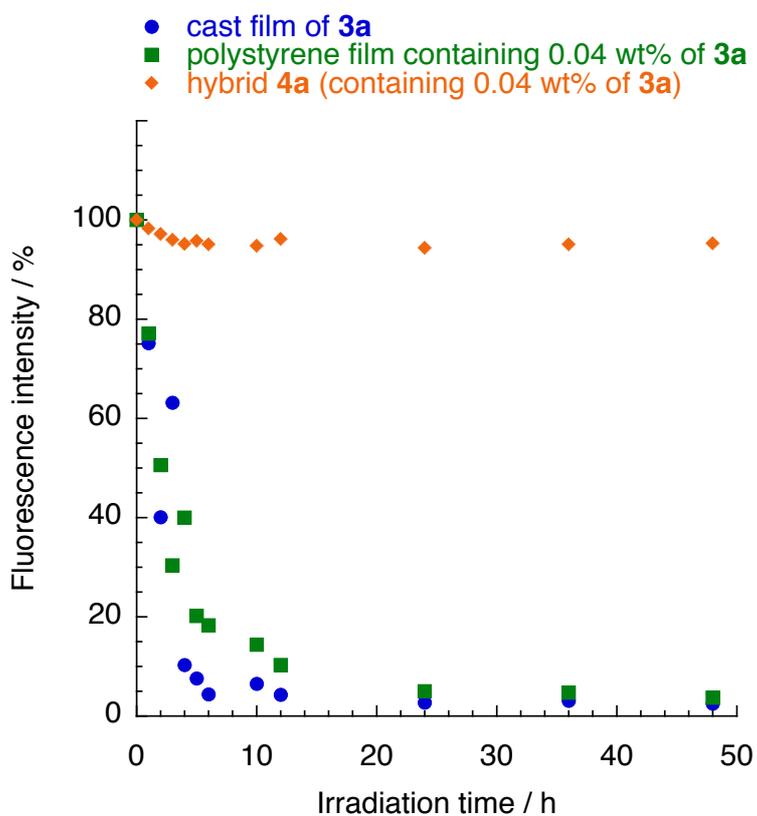


Figure S15. Photostability of the cast film of **3a**, polystyrene film containing 0.04 wt% of **3a**, and hybrid **4a** (containing 0.04 wt% of **3a**): UV (365 nm, 100V, 8W) irradiation under air.

References

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