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 ($\lambda$ = 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-Diethylnylbenzene (2a), Si(OEt)$_4$, (n-C$_6$H$_{13}$)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-diethylnylxylene (2b),$^3$ 4,4'-diethynyl-1,1'-biphenyl (2e),$^4$ 2,7-diethynyl-9,9-dimethylfluorene (2d),$^5$ 3,6-diethynyl-9-(4-methylphenyl)-carbazole (2e),$^6$ and pseudo-para-diethynyl[2.2]paracyclopahne (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, S–3
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-didodecyloxygenzene\textsuperscript{8} and 2a with the same procedure described above. Spectral data were matched with the literature’s values.\textsuperscript{8}

**Synthesis of conjugated-polymer/SiO\textsubscript{2} hybrids**

A typical procedure is as follows. Polymer (0.15 mg), Si(OEt)$_4$ (0.20 mL), (n-C$_6$H$_{13}$)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$_3$. 

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can be “melt processed” by heating above the liquid-crystalline phase-transition temperature. The positive effect of this strategy has been demonstrated using a fluorine-bithiophene copolymer (F8T2) on porous TiO₂, although the effect is more pronounced only for thick films (Fig. 6).

Another strategy is the use of polymers with polar side groups: in the case of solid dye-sensitised solar cells, it has been shown that 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. An alternative approach to this 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.

To overcome the issue of decreased solubility, Swager reported the introduction of a hindered repeat unit into the CPE backbone to reduce aggregation in a slightly twisted polymer structure. In our recent investigation, we explore the properties of two different polymeric materials for use in solid-state polymer electrolytes (Scheme 1). This series of polymeric materials consists of polymeric electrolytes with sterically crowded polyionic side groups.

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


