Ultra-photostable n-type PPVs

Youngmi Kim and Timothy M. Swager*

Poly(*p*-phenylenevinylene)s containing trifluoromethyl substituted aromatic rings (CF3-PPVs) exhibit high photooxidative stability to give robust materials suitable for demanding applications.

Luminescent conjugated polymers (CPs), especially poly(*p*-phenylenevinylene) (PPV) based polymers, have been widely investigated in a variety of applications including light-emitting diodes,[1] solar cells,[2] and optically pumped lasers.[3] In spite of their desirable attributes of high emission efficiency, fine-tunability of their band gap, and good processibility, dramatic improvements in the durability and stability of CPs are necessary for many applications. The design of organic electronic polymers having enhanced photooxidative stability and charge transport properties is of particular importance for application in solar cells.[4] Efforts to increase the stability of CPs include encapsulation to protect them from oxygen and moisture[5] and the incorporation of electron-withdrawing groups such as cyano or trifluoromethyl on the vinylene units of PPV to decrease photooxidation.[6]

Although PPV derivatives containing electron-withdrawing substituents at vinylene units have shown improved photooxidative stability, undesirable conformational changes arise from this substitution as a result of increased steric hindrance.[7] The resulting nonplanarity can disturb the transport properties and result in a strong reduction of fluorescence yields due to torsional induced nonradiative deactivation.[8]

Herein, we report the synthesis of PPVs containing perfluoroalkyl groups attached to the phenyl rings and the dramatic improvement in their stability against photooxidation. The chemical structures of the perfluorinated CPs and their syntheses are depicted in Schemes 1 and 2. As shown in Scheme 1, the synthesis of monomer **5**,† 1,4-bis(trifluoromethyl)-2,5-dibromomethylbenzene, involves bromination of 1,4-bis(trifluoromethyl)-benzene (**1**) to obtain **2** with 91% yield in the presence of NBS/CF3COOH and H_2SO_4. Lithiation of **2** with n-butyllithium in THF followed by addition of CO_2 gives 2,5-bis(trifluoromethyl)-terephthalic acid (**3**), and reduction leads to the corresponding diol (**4**). Monomer **5** is prepared from bromination of **4** and is polymerized by treatment with excess of KO^{t}Bu in THF at room temperature for 1 day. The reaction mixture was poured into methanol, and the resulting precipitate was filtered and washed with methanol, hexane, and acetone. The solid was dried to give poly-[2,5-bis(trifluoromethyl)-*p*-phenylenevinylene] (CF3-PPV) as a green fluorescent solid with a yield of *ca.* 65%. In order to compare its stability with that of other CPs, poly-2-methoxy-5-(2′-ethylhexyloxy)-phenylenevinylene (MEH-PPV), a widely used molecular electronic material, was prepared by the literature

*tswager@mit.edu
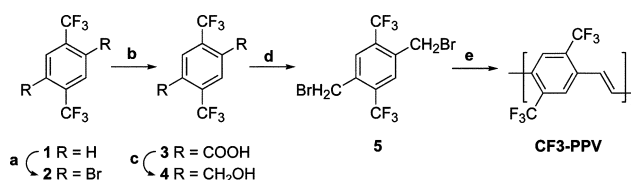
Scheme 1 (a) NBS, CF_3CO_2H, H_2SO_4, 60 °C; (b) (i) n-BuLi, THF, −78 °C, (ii) CO_2; (c) BH_3–THF, RT; (d) PBr_3, THF; (e) KO^{t}Bu, THF, RT.

procedure and poly(9,9-dioctylfluorene-2,7-diyl) (PF, M_n 64,000, PDI = 2.9) was purchased from H.W. SANDS Corp.[9]

We also synthesized an alternating copolymer containing CF3-PV and MEH-PV units, poly-[2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene-*alt*-2,5-bis(trifluoromethyl)-1,4-phenylenevinylene] (*alt-co*-PPV) by Wittig condensation of 2,5-bis(trifluoromethyl)-1,4-benzenedicarboxaldehyde (**7**) with 2-methoxy-5-(2′-ethylhexyloxy)-1,4-xylenebis(triphenylphosphonium bromide) (**9**) as shown in Scheme 2. The mixture was quenched with 2% HCl solution and then poured into methanol. The polymer was isolated by filtration, dried, and reprecipitated in MeOH to give an orange solid with a yield of *ca.* 55%. The *alt-co*-PPV (M_n 5500, PDI = 1.35, THF) was highly soluble in common organic solvents whereas CF3-PPV (M_n 25,000, PDI = 1.25, THF) showed poor solubility in CH_2Cl_2, or $CHCl_3$ and partial solubility in THF and DMF.‡ The latter solvents allowed solution photoluminescence studies and the spin coating of thin films.

As shown in Fig. 1, the UV-visible absorption spectrum of the CF3-PPV in THF has a maximum at 361 nm and the emission spectrum displays a large Stokes-shift with a peak maximum at 489 nm and a shoulder at 514 nm. The magnitude of the Stokes shift suggests large differences in the conformation of the polymer's ground and excited states and energy migration to minority segments having greater conjugation lengths.[10] As expected with CF3 substitution the absorption and emission spectra of *alt-co*-PPV are blue shifted relative to MEH-PPV. CF3-PPV showed relatively high fluorescence quantum yields in both THF solution (0.63, standard: quinine sulfate in 0.1 N H_2SO_4) and in thin films (0.25, standard: 0.01 mol% 9,10-diphenylanthracene in PMMA). In contrast we find MEH-PPV to have lower fluorescence quantum yields in solution (0.08, standard: fluorescein in 0.1 N NaOH) and in thin films (0.03, standard: 0.01 mol% 9,10-diphenylanthracene in PMMA).§

We have investigated photostabilities of CF3-PPV, *alt-co*-PPV, MEH-PPV, and PF thin films. The photooxidation studies were performed by continuous UV irradiation of polymer thin films using a 450 W steady-state Xe lamp as the irradiation source (slit width = 10 nm) under aerobic conditions. Polymer films having
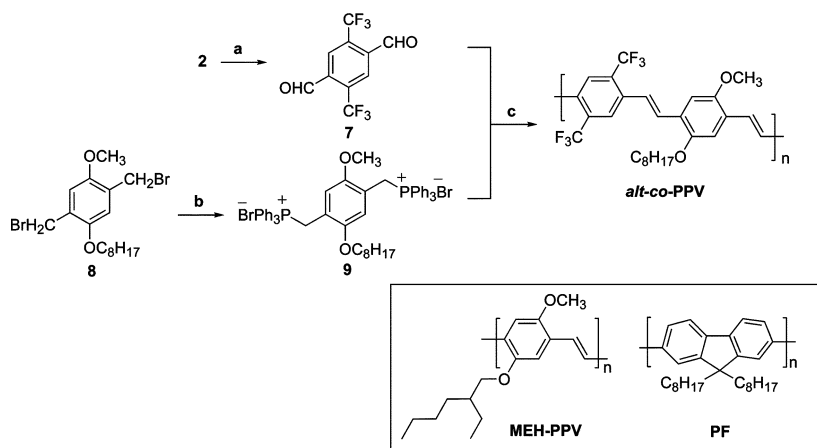
Scheme 2 (a) (i) n-BuLi, THF, −78 °C, (ii) DMF; (b) PPh₃, DMF, reflux; (c) NaOEt, CHCl₃/ethanol, RT.

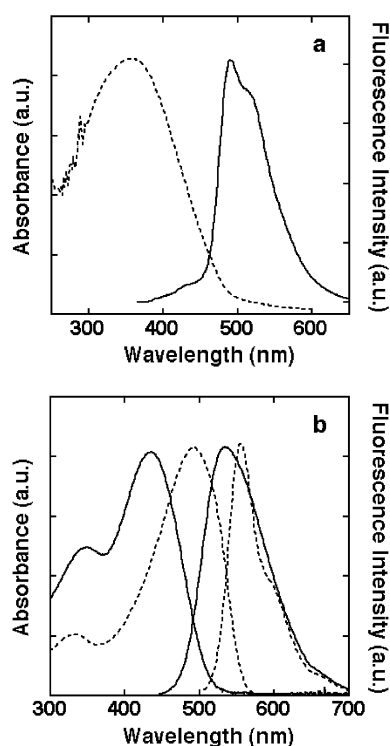**Fig. 1** The absorption and emission spectra of (a) CF3-PPV in THF and (b) *alt-co*-PPV (solid line) and MEH-PPV (dotted line) in chloroform.

Fig. 2 The time dependence of fluorescence intensity of CF3-PPV, *alt-co*-PPV, MEH-PPV and PF thin films under UV irradiation.

similar optical density (0.05 ± 0.01) at their maximum absorption wavelength were irradiated at an excitation wavelength of 370 nm for CF3-PPV, 380 nm for both *alt-co*-PPV and PF, 505 nm for MEH-PPV. The photoinduced degradation was quantified by monitoring the decrease of fluorescence intensity of CF3-PPV, *alt-co*-PPV, MEH-PPV, and PF thin films as a function of elapsed photolysis time (Fig. 2). The fluorescence intensity of CF3-PPV did not show any decrease after 2 hours of irradiation even with the strongest light, whereas fluorescence intensity of MEH-PPV and PF decreased rapidly as indicated by the fact that only 10% fluorescence intensity remained after irradiation of 2 hours. As indicated by photolysis experiments with *alt-co*-PPV, the incorporation of the electron-withdrawing substituents
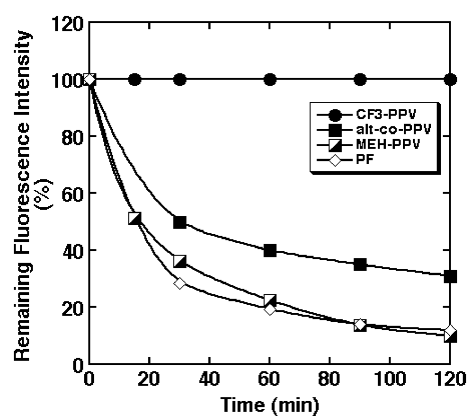
contributes to the decrease of the rate of photobleaching. However, only the homopolymer CF3-PPV demonstrated extraordinary photostability: its emission spectra remained unchanged after hours of UV irradiation. This level of stability is unprecedented for a semiconductive conjugated organic polymer and indicates that this material may be a promising photovoltaic material.

In summary, we have synthesized PPVs containing trifluoromethyl groups directly attached onto the phenyl ring to provide materials with high electron affinity that prevents photooxidative degradation. Their superior photostability revealed by photobleaching studies endows these materials with the critical stability needed for optoelectronic devices and sensory applications.

Youngmi Kim and Timothy M. Swager*
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139, USA. E-mail: tswager@mit.edu

Notes and references

† Compound **5**: mp 80–81 °C; ¹H NMR (300 MHz, CDCl₃): 7.89 (2H, s), 4.65 (4H, s); ¹³C NMR (75 MHz, CDCl₃): 137.1, 130.8, 124.9, 121.3, 27.1;

^{19}F NMR (282 MHz, CDCl$_3$): −61.2; HR-MS (EI) calcd. for C$_{10}$H$_6$F$_6$Br$_2$ (M$^+$): 397.8735, found: 397.8744. Compound **7**: mp 56–57 °C; ^{1}H NMR (300 MHz, CDCl$_3$): 10.47 (2H, s), 8.55 (2H, s); ^{13}C NMR (75 MHz, CDCl$_3$): 186.7, 164.6, 136.9, 127.6, 119.0; ^{19}F NMR (282 MHz, CDCl$_3$): −56.8; HR-MS (EI) calcd. for C$_{10}$H$_4$F$_6$O$_2$ (M$^+$): 270.0110, found: 270.0111.

‡ The low PDIs for polymers reflect the fractionation during the isolation and purification.

§ The quantum yield measurements were performed in a self-consistent fashion for all of the samples. Fluorescein was used as a standard for the quantum yield of MEH-PPV because their emission spectra have the best overlap to minimize variations in the detector response.

1 (*a*) A. J. Heeger and M. A. Díaz-García, *Curr. Opin. Solid Phys. Mater. Sci.*, 1998, **3**, 16; (*b*) J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burns and A. B. Holmes, *Nature*, 1990, **347**, 539.

2 J. J. Halls, C. A. Walsh, N. C. Greenham, E. A. Marseglia, R. H. Friend, S. C. Moratti and A. B. Holmes, *Nature*, 1995, **376**, 498.

3 M. A. Díaz-García, F. Hide, B. J. Schwartz, M. R. Andersson, Q. Pei and A. J. Heeger, *Synth. Met.*, 1997, **84**, 455.

4 J. Nelson, *Curr. Opin. Solid Phys. Mater. Sci.*, 2002, **6**, 87.

5 D. J. Cardin, *Adv. Mater.*, 2002, **14**, 553.

6 R. D. Scurlock, B. Wang, P. R. Ogilby, J. R. Sheats and R. L. Clough, *J. Am. Chem. Soc.*, 1995, **117**, 10194.

7 (*a*) A. Lux, A. B. Holmes, R. Cervini, J. E. Davies, S. C. Moratti, J. Grüner, F. Cacialli and R. H. Friend, *Synth. Met.*, 1997, **84**, 293; (*b*) B. H. Cumpston and K. F. Jensen, *J. Appl. Polym. Sci.*, 2002, **69**, 2451.

8 (*a*) D. Oelkrug, A. Tompert, J. Gierschner, H.-J. Egelhaaf, M. Hanack, M. Hohloch and E. Steinhuber, *J. Phys. Chem. B*, 1998, **102**, 1902; (*b*) M. Fahlman and J. L. Brédas, *Synth. Met.*, 1996, **78**, 39.

9 U. Scherf and E. J. W. List, *Adv. Mater.*, 2002, **14**, 477.

10 (*a*) L. Li, K. E. Counts, S. Kurosawa, A. S. Teja and D. M. Collard, *Adv. Mater.*, 2004, **16**, 180; (*b*) T.-Q. Nguyen, V. Doan and B. J. Schwartz, *Chem. Phys.*, 1999, **110**, 4068.