

TPA-PPEs – New Alternating Donor Copolymers for Potential Application in Photovoltaic Devices

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ABSTRACT: A series of phenyleneethynylene copolymers with triphenylamine units as hole-transporting moieties (TPA-PPEs) were synthesized by the palladium-catalyzed cross-coupling polycondensation of diethynyltriphenylamines and selected dihalogen comonomers, for instance substituted benzene, thiophene, benzothiadiazole, or anthracene. Incorporation of the electron-rich amino group into the PPE backbone does not interrupt the main chain conjugation. Furthermore, it has a decreasing effect on the oxidation potential, thus makes these polymers interesting as hole-injection/hole-transporting materials. The chemical structure of the new alternating copolymers was confirmed by ¹H and ¹³C NMR spectroscopy and elemental analysis and gel-permeation chromatography (GPC; THF, $M_n \approx 15,000$ – $30,000$ g/mol) was conducted. Furthermore, their optical properties were investigated by UV/vis

spectroscopy. The TPA-PPEs exhibit absorption maxima at around 400 nm (π - π^*), except anthracene containing copolymer **3f** ($\lambda_{\max} = 514$ nm in THF) and benzothiadiazole containing one **3g** ($\lambda_{\max} = 503$ nm in THF). The TPA copolymers have oxidation potentials about 1.1 V (Ag/AgCl). They are good photoconducting materials (**3a**: $I_{\text{photo}} = 4 \times 10^{-10}$ A at 425 nm (400 V), **3g**: $I_{\text{photo}} = 1.3 \times 10^{-11}$ A at $\lambda_{\max} = 500$ nm (20 V)) and show emission after excitation at around 450 nm (560 nm **3f**). Their application in nonoptimized polymer solar cells (bulk heterojunction) led to power conversion efficiencies of around 1–1.8% after illumination with 100 mW/cm² of AM1.5. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 1850–1861, 2009

Key words: amino-PPE; TPA-PPE; polycondensation; triphenylamine copolymers; polymer solar cell

INTRODUCTION

Conjugated polymers have recently been the focus of considerable interest because of their potential applications as electroluminescent materials^{1,2} or as molecular wires.³ They can also feature large optical nonlinearities.^{4–6} Moreover, conjugated polymers and fullerene derivatives receive attention for photovoltaic energy conversion.⁷ The concept of “bilayer heterojunction” solar cells (donating and accepting materials in two separate layers),^{8–10} which are based on polymers leads to rather low power efficiencies. Attempts to improve the efficiency lead to the “bulk heterojunction” solar cells, which came out on top. This concept features the blending (mixing)

of the donor polymer and the acceptor (also polymer, but more common: Fullerenes), which results in only one layer between the electrodes.^{11,12} When the solar cell is illuminated a fast photo-induced electron transfer reaction from the conjugated polymer (donor) to the fullerene (acceptor) occurs. Subsequently, the charge carriers are transported to the corresponding electrodes.

State-of-the-art for polymer solar cells, which are prepared on glass substrates, are light power conversion efficiencies about 3.5%¹³ and 4 to 5%,^{14–16} respectively, if the preparation and the following characterization were executed in inert gas atmosphere. Whereas cells on foil substrates with cell preparation and characterization under ambient conditions reach efficiencies of 3%^{17–19} and 3.4%.²⁰ Losses in the photoabsorption, in the fill factor and in the open circuit voltage are the main limitations for the present (photoactive) state-of-the-art material combinations poly(3-hexylthiophene) (P3HT)/[6,6]-phenyl-C61-butyric acid methyl ester (PCBM), and poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV)/PCBM. By realization of 5%,^{14,21,22} and certified 5.2%,²³ 5.4%,²⁴ and in one case 6.7% efficiencies (tandem cell)²⁵ and life

Additional Supporting Information may be found in the online version of this article.

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times about 2000 sun hours (encapsulated in glass) in the meantime the performance is in close contact to the amorphous silicon cells. But there still exist a lot of open questions and problems, which have to be solved to reach higher efficiencies. Therefore, the search for new materials with optimized properties for polymer photovoltaics is still essential combined with a basic understanding of mechanisms and mode of operation.

With this motivation we report the synthesis of new electron-rich alternating aryleneethynylene donor copolymers with triphenylamine (TPA) in the repeating unit and the investigation of their optical, electrochemical, and photovoltaic properties. Poly(phenyleneethynylene)s (PPEs) and accordingly poly(aryleneethynylene)s (PAEs)—a substance class that moved more into the foreground of the interest in the last years—are featured by their good optical characteristics, higher oxidation potentials (versus PPVs), and their rigid rod-like structure of the macromolecules. A comprehensive overview about PAEs and their manifold prepared lower molecular model compounds (oligophenyleneethynylenes) is given in Ref. 26. Because of their rigidity and therefore scheduled better assembling in films this kind of donor polymer is preferred in this article. TPA is an important component of the here described polymers because of the excellent hole-transporting properties. The nitrogen is included in the conjugated system and stabilizes via resonance the positive charges, which are formed by photogeneration or by hole-injection processes. First, results of bulk heterojunction photovoltaic cells based on the new copolymers are reported.

EXPERIMENTAL

Materials

All chemicals were purchased from Merck, Fluka, Acros, and Aldrich. THF and toluene were dried and distilled over sodium/benzophenone. Diisopropylamine and triethylamine was dried over KOH and distilled. All *Sonogashira* reactions were carried out under an inert gas atmosphere (argon) in solvents, which were degassed by bubbling with argon for 1.5 h before use. Silica gel 60 by Merck was used for column chromatography.

4-*tert*-Butyltriphenylamine,^{27–31} 4,4'-dibromotriphenylamine,³² 4,4'-dibromo-4'-*tert*-butyltriphenylamine,³² 4-iodo-(octyloxy)-benzene,^{33,34} 9,10-diiodoanthracene **1e**,^{35–37} 1-methoxy-4-(2-ethylhexyl)oxy-2,5-diiodobenzene **1a**,^{33,38} 2,5-dibromothiophene **1b**,^{39,40} 2,5-dibromo-3-dodecylthiophene **1c**,⁴¹ 1-(trimethylsilylethynyl)-4-iodobenzene,⁴² 1,4-dihexyl-2,5-dibromobenzene **1d**,⁴³ 4,7-dibromo-2,1,3-benzothiadiazole⁴⁴ were synthesized according to literature. The syntheses of the monomers

4,4'-diethynyltriphenylamine **2c** and 4,4'-diethynyl-4'-*tert*-butyltriphenylamine **2a** are described in former publications.^{31,45} For syntheses of the monomer 4,4'-diethynyl-4'-(octyloxy)-triphenylamine **2b** and the model compounds 4,4'-bis(phenyl-ethynyl)-triphenylamine **4a**, and 2-methoxy-5-(2-ethylhexyl)oxy-1,4-bis(triphenylamine-4-yl-ethynyl)benzene **4b** see Supporting information.

Methods

Melting points were measured on a Büchi 530 melting apparatus. The mass spectra were recorded using a SSQ 170, Finnigan MAT, electrospray mass spectra on a Finnigan MAT, MAT 95 XL instrument. ¹H and ¹³C NMR spectra were taken on a Bruker DRX 400 (400 MHz) and a Bruker AC 250 (250 MHz). The absorption spectra were measured in chloroform, 1,4-dioxane, methylene chloride, and THF (HPLC grade, Baker) by using a Perkin-Elmer UV/vis-NIR Spectrometer Lambda 19. Fluorescence excitation and emission spectra were obtained by using a Perkin-Elmer LS 50 luminescence spectrometer in nitrogen-degassed chloroform or 1,4-dioxane. Quinine sulfate in 0.1N sulfuric acid was used as reference ($\phi_f = 0.55$). It was recrystallized twice before use. The luminescence quantum yields were calculated according to Demas and Crosby.⁴⁶ A homemade apparatus served for thermogravimetry measurements. Elemental analyses were performed on a Leco Automat CHNS-932. Molecular weight determinations by gel-permeation chromatography (GPC) were performed on a set of Knauer on Jasco UV 975 and IR 930 (PSS Mainz— 10^3 Å/ 10^4 Å/ 10^6 Å) using THF as eluent at a flow rate of 1 mL/min and polystyrene as standard. Vapor pressure osmometry was carried out in chloroform in a Knauer apparatus. The electrochemical measurements were carried out in a Princeton research PAR 273 with methylene chloride solutions containing $10^{-3}M$ Bu₄NPF₆ using an Ag/AgCl reference electrode and Pt electrode.

Solar cell experiments

For photovoltaic device preparation the substrates (polyester foil coated with indium tin oxide (ITO), surface resistance of 60 Ω/square) were cleaned in an ultrasonic bath in methanol and isopropanol. The area of the substrates was 5 cm × 5 cm. After drying the substrate a thin layer (~ 100 nm) of PEDOT:PSS (poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate)/Baytron P, H.C. Starck GmbH and Co.KG) was spin coated and dried. Subsequently, the photoactive layer was prepared by spin coating from composite solutions: TPA-PPE (**3**)/PCBM (1 : 4 weight ratio) in chlorobenzene on the top of the PEDOT:PSS

layer. PCBM ([6,6]-phenyl-C₆₁-butanoic acid methyl ester) was obtained from the laboratory of J. C. Hummelen at the University of Groningen. The thickness of the photoactive layers was typically in the range of 100–150 nm. The aluminum cathode was thermally deposited (~ 80 nm) through a shadow mask, which defines a device area of 0.25 cm². I/V curves were recorded with a Keithley SMU 2400 Source Meter by illuminating the cells from the ITO side with 100 mW/cm² white light from a Steuernagel solar simulator to realize AM1.5 conditions. All cells were prepared and measured under ambient conditions.

Polycondensation

General procedure

The diethynylene TPA monomers **2a–c** and the dihalogen compounds **1a–f** in equimolar amounts, Pd(PPh₃)₄ (4 or 6 mol%) and CuI (4 or 6 mol%) were added to a degassed solution of dried diisopropylamine or triethylamine and dry toluene or dry THF, respectively. The reaction mixture was degassed for further 30 min and stirred at 50°C (diiodo compound) and 75°C (dibromo derivative), respectively. After a total reaction time of 72 h, the reaction mixture was cooled to room temperature and added dropwise to a tenfold excess vigorously stirred methanol. The precipitated polymer was collected, taken up in a small amount of toluene and filtered if necessary to remove insoluble compounds. The polymer was precipitated again in methanol and purified by Soxhlet extraction with methanol. After dissolving the polymer in a small amount of toluene again, the solution was added dropwise to an excess of vigorously stirred *n*-hexane to precipitate. Soxhlet extraction with *n*-hexane and a final precipitation in methanol yielded the pure polymer, which was dried *in vacuo* at 50°C.

Poly-{triphenylamine-4,4'-diyl-1,2-ethynediyl}[(2-methoxy-5-(2-ethylhexyl)oxy-1,4-phenylene)-1,2-ethynediyl] **3a**: 832 mg (1.70 mmol) 1-methoxy-4-(2-ethylhexyl)oxy-2,5-diiodobenzene **1a**, 500 mg (1.70 mmol) 4,4'-diethynyltriphenylamine **2c**, 79 mg (6.8 × 10⁻⁵ mol) Pd(PPh₃)₄, 13 mg (6.8 × 10⁻⁵ mol) CuI, 30 mL dry diisopropylamine, 70 mL dry toluene. Yield: 740 mg (83%) yellow polymer. ¹H NMR (400 MHz, C₆D₆): δ = 0.97 (6H, m, -CH₃), 1.34–1.75 (9H, m, -CH₂, -CH), 3.28 (0.3H, s, -OCH₃ endgroup/MEH), 3.39 (3H, s, -OCH₃), 3.56 (0.2H, d, ³J = 5.2 Hz, -OCH₂ endgroup/MEH), 3.72 (2H, m, -OCH₂), 6.90–7.63 (15H, m, phenyl) ppm. ¹³C NMR (100 MHz, C₆D₆): δ = 11.7 (-CH₃), 14.5, 23.6, 24.7, 29.7, 31.3, 40.2, 56.0, 71.8, 87.0 (-C≡C-), 95.8 (-C≡C-), 114.5, 114.9, 115.9, 117.5, 118.5, 124.0, 124.1, 124.5, 125.9, 130.0, 133.2, 133.3, 134.1, 135.7,

147.3, 147.8, 154.7, 154.8 ppm. UV/vis (1,4-dioxane): λ_{max} (ε/(l mol⁻¹ cm⁻¹)) = 299 (12,600), 410 (34,800) nm. GPC (THF): M_n = 14,400 g/mol, M_w = 28,200 g/mol, D = 2.0. Anal. calcd. for (C₃₇H₃₅NO₂)_n (525.70)_n: C, 84.54; H, 6.71; N, 2.66. Found: C, 80.74; H, 6.47; N, 2.21; I, 4.08.

Poly-[[4'-tert-butyl]triphenylamine-4,4'-diyl-1,2-ethynediyl}[(2-methoxy-5-(2-ethylhexyl)oxy-1,4-phenylene)-1,2-ethynediyl] **3b**: 279 mg (0.57 mmol) 1-methoxy-4-(2-ethylhexyl)oxy-2,5-diiodobenzene **1a**, 200 mg (0.57 mmol) 4,4'-diethynyl-4'-tert-butyltriphenylamine **2a**, 26 mg (2.28 × 10⁻⁵ mol) Pd(PPh₃)₄, 4 mg (2.28 × 10⁻⁵ mol) CuI, 15 mL dry diisopropylamine, 40 mL dry toluene. Yield: 210 mg (63%) yellow powder. ¹H NMR (400 MHz, C₆D₆): δ = 0.89–1.66 (24H, m, -CH₃, -CH₂, -CH), 3.19 (0.2H, s, -OCH₃ endgroup/MEH), 3.30 (3H, s, -OCH₃), 3.50 (0.15H, d, ³J = 4.8 Hz, -OCH₂ endgroup/MEH), 3.66 (2H, m, -OCH₂), 6.89–7.56 (14H, m, phenyl) ppm. ¹³C NMR (100 MHz, C₆D₆): δ = 11.7 (-CH₃), 14.5, 23.7, 24.6, 29.7, 31.3, 31.6 (tert-butyl-CH₃), 34.6 (tert-butyl-C), 40.2, 56.0, 71.8, 86.9 (-C≡C-), 95.9 (-C≡C-), 114.4, 114.8, 115.8, 117.5, 118.2, 123.7, 123.8, 125.9, 127.0, 133.2, 133.3, 144.7, 147.5, 148.0, 154.7, 154.8 ppm. UV/vis (1,4-dioxane): λ_{max}(ε/(l mol⁻¹ cm⁻¹)) = 411 (57,000) nm. GPC (THF): M_n = 17,200 g/mol, M_w = 34,600 g/mol, D = 2.0. Anal. calcd. for (C₄₁H₄₃NO₂)_n (581.81)_n: C, 84.64; H, 7.45; N, 2.41. Found: C, 81.08; H, 7.41; N, 2.03; I, 3.07.

Poly-{triphenylamine-4,4'-diyl-1,2-ethynediyl}[(2,5-thiophenediyl)-1,2-ethynediyl] **3c**: 247 mg (1.02 mmol) 2,5-dibromothiophene **1b**, 300 mg (1.02 mmol) 4,4'-diethynyltriphenylamine **2c**, 47 mg (4.08 × 10⁻⁵ mol) Pd(PPh₃)₄, 8 mg (4.08 × 10⁻⁵ mol) CuI, 30 mL dry diisopropylamine, 70 mL dry toluene. After 2 h at 75°C the polymer started to fall out. The reaction mixture was cooled down to room temperature and given to 600 mL vigorously stirred methanol. The raw polymer was purified by dropping in *n*-hexane and in methanol twice. Yield: 309 mg (81%) soluble yellow powder. ¹H NMR (400 MHz, C₆D₆): δ = 6.74–7.33 (15H, m, phenyl) ppm. ¹³C NMR (100 MHz, C₆D₆): δ = 82.9 (-C≡C-), 95.2 (-C≡C-), 117.2, 123.5, 123.8, 124.8, 125.5, 126.1, 130.1, 132.3, 133.2, 134.2, 147.1, 148.0 ppm. UV/vis (1,4-dioxane): λ_{max} (ε/(l mol⁻¹ cm⁻¹)) = 303 (9,200), 409 (28,500) nm. GPC (THF): M_n = 12,000 g/mol, M_w = 51,700 g/mol, D = 4.3. Anal. calcd. for (C₂₆H₁₅NS)_n (373.48)_n: C, 83.62; H, 4.05; N, 3.75. Found: C, 80.11; H, 3.94; N, 3.46; Br, 3.07.

Poly-{triphenylamine-4,4'-diyl-1,2-ethynediyl}[(3-dodecyl-2,5-thiophenediyl)-1,2-ethynediyl] **3d**: 2.15 g (5.25 mmol) 2,5-dibromo-3-dodecylthiophene **1c**, 1.54 g (5.25 mmol) 4,4'-diethynyltriphenylamine **2c**, 243 mg (2.10 × 10⁻⁴ mol) Pd(PPh₃)₄, 40 mg (2.10 × 10⁻⁴ mol) CuI, 90 mL dry diisopropylamine, 210 mL dry

THF. Yield: 2.12 g (75%) soluble, thready orange polymer. ^1H NMR (400 MHz, C_6D_6): δ = 0.95 (3H, t, 3J = 6.6 Hz, $-\text{CH}_3$), 1.31 (18H, m, $-\text{CH}_2$), 1.64 (2H, m, $-\text{CH}_2$), 2.39 (0.2H, m, $-\text{CH}_2$ endgroup/thiophene), 2.77 (2H, t, 3J = 7.4 Hz, $-\text{CH}_2$), 6.74–7.33 (14H, m, phenyl) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 14.5 ($-\text{CH}_3$), 23.2, 29.7, 29.9, 30.0, 30.1, 30.2 (2 signals), 30.3, 30.6, 32.5, 82.6 ($-\text{C}\equiv\text{C}-$), 83.4 ($-\text{C}\equiv\text{C}-$), 95.0 ($-\text{C}\equiv\text{C}-$), 97.2 ($-\text{C}\equiv\text{C}-$), 117.3, 117.5, 120.9, 123.7, 123.8, 123.9, 124.1, 124.7, 126.0, 130.0, 133.2, 133.4, 134.2, 135.4, 147.1, 147.8, 147.9, 148.1 ppm. UV/vis (1,4-dioxane): λ_{max} ($\epsilon/(\text{l mol}^{-1} \text{cm}^{-1})$) = 408 (28,400) nm. GPC (THF): M_n = 20,500 g/mol, M_w = 79,500 g/mol, D = 3.9. Anal. calcd. for $(\text{C}_{38}\text{H}_{39}\text{NS})_n$ (541.81) $_n$: C, 84.24; H, 7.26; N, 2.58. Found: C, 81.93; H, 7.29; N, 2.58; Br, 2.22.

Poly-[[4'-*tert*-butyl]triphenylamine-4,4'-diyl-1,2-ethynediyl[2,5-dihexyl-1,4-phenylene]-1,2-ethynediyl] **3e**: 584 mg (1.44 mmol) 1,4-dihexyl-2,5-dibromobenzene **1d**, 505 mg (1.44 mmol) 4,4'-diethynyl-4'-*tert*-butyltriphenylamine **2a**, 67 mg (5.8×10^{-5} mol) $\text{Pd}(\text{PPh}_3)_4$, 11 mg (5.8×10^{-5} mol) CuI , 40 mL dry diisopropylamine, 80 mL dry toluene. Yield: 450 mg (53%) reddish-brown polymer. ^1H NMR (250 MHz, CDCl_3): δ = 0.90–1.69 (31H, m, $-\text{CH}_3$, $-\text{CH}_2$), 2.79 (4H, m, $-\text{CH}_2$), 7.08–7.35 (14H, m, phenyl) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 14.5, 23.1, 29.8, 30.4, 31.7, 32.2, 34.6, 36.1, 89.2 ($-\text{C}\equiv\text{C}-$), 94.9 ($-\text{C}\equiv\text{C}-$), 118.0, 123.8, 133.1, 134.1, 140.1, 142.9, 144.7, 147.9 ppm. UV/vis (1,4-dioxane): λ_{max} ($\epsilon/(\text{l mol}^{-1} \text{cm}^{-1})$) = 387 (34,200) nm. GPC (THF): M_n = 15,400 g/mol, M_w = 34,900 g/mol, D = 2.3. Anal. calcd. for $(\text{C}_{44}\text{H}_{49}\text{N})_n$ (591.89) $_n$: C, 89.29; H, 8.34; N, 2.37. Found: C, 85.72; H, 7.64; N, 2.68; Br, 2.51.

Poly-[[4'-octyloxy]triphenylamine-4,4'-diyl-1,2-ethynediyl[9,10-anthracenediyl]-1,2-ethynediyl] **3f**: 213 mg (0.50 mmol) 9,10-diiodoanthracene **1e**, 209 mg (0.50 mmol) 4,4'-diethynyl-4'-(octyloxy)-triphenylamine **2b** 23 mg (1.98×10^{-5} mol) $\text{Pd}(\text{PPh}_3)_4$, 4 mg (1.98×10^{-5} mol) CuI , 15 mL dry diisopropylamine, 30 mL dry toluene. After stirring for 2 h at 40°C the polymer started falling out. The whole mixture was put into 500 mL vigorously stirred methanol when cooled to room temperature. The red precipitate was collected and purified by soxhlet extraction with methanol. Dissolving the residual in much chloroform, reducing the solution *in vacuo*, and dropping in *n*-hexane followed by the same procedure for dissolving and dropping in methanol–water yielded a red powder, which was dried *in vacuo* at 50°C. Yield: 215 mg (73%) in chloroform soluble polymer. ^1H NMR (250 MHz, CD_2Cl_2): δ = 0.82–1.73 (15H, m, $-\text{CH}_3$, $-\text{CH}_2$), 3.90 (2H, m, $-\text{OCH}_2$), 6.83–8.63 (20H, m, TPA, anth) ppm. ^{13}C NMR (62 MHz, CDCl_3): δ = 14.1 ($-\text{CH}_3$), 22.7, 26.1, 26.3 (2 signals), 29.4, 31.9, 68.3, 86.3 ($-\text{C}\equiv\text{C}-$), 102.8 ($-\text{C}\equiv\text{C}-$), 115.7, 116.7, 118.4, 122.5, 126.7, 127.3, 128.1, 132.0, 132.7, 139.1,

147.8, 156.8 ppm. UV/vis (THF): λ_{max} ($\epsilon/(\text{l mol}^{-1} \text{cm}^{-1})$) = 260 (55,000), 278 (50,000), 306 (25,100), 338 (23,300), 514 (49,200) nm. GPC (THF): M_n = 17,000 g/mol, M_w = 74,400 g/mol, D = 4.4. Anal. calcd. for $(\text{C}_{44}\text{H}_{37}\text{NO})_n$ (595.79) $_n$: C, 88.70; H, 6.26; N, 2.35. Found: C, 85.61; H, 6.41; N, 2.14; I, 2.23.

Poly-[[4'-*tert*-butyl]triphenylamine-4,4'-diyl-1,2-ethynediyl[2,1,3-benzothiadiazole-4,7-diyl]-1,2-ethynediyl] **3g**: 599 mg (2.00 mmol) 4,7-dibromo-2,1,3-benzothiadiazole **1f**, 588 mg (2.00 mmol) 4,4'-diethynyl-4'-*tert*-butyltriphenylamine **2a**, 139 mg (1.2×10^{-4} mol) $\text{Pd}(\text{PPh}_3)_4$, 23 mg (1.2×10^{-4} mol) CuI , 45 mL dry triethylamine, 100 mL dry toluene. After 5 h at 65°C the polymer started to precipitate. The reaction mixture was cooled down to room temperature and dissolved in THF and precipitated from vigorously stirred methanol. The raw polymer was purified by dropping into *n*-hexane. Yield: 560 mg (58%) red polymer. ^1H NMR (250 MHz, CDCl_3): δ = 1.26 (9H, m, $-\text{CH}_3$), 6.92–7.47 (12H, m, phenyl), 7.65 (2H, s, phenyl) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 31.4, 34.5, 85.3 ($-\text{C}\equiv\text{C}-$), 97.9 ($-\text{C}\equiv\text{C}-$), 116.1, 117.1, 123.0, 125.5, 126.6, 132.1, 133.1, 138.0, 143.5, 148.0, 154.4 ppm. UV/vis (chloroform): λ_{max} ($\epsilon/(\text{l mol}^{-1} \text{cm}^{-1})$) = 327 (32,500); 358 (32,500); 503 (30,000) nm. GPC (THF): M_n = 30,000 g/mol, M_w = 52,000 g/mol, D = 1.7. Anal. calcd. for $(\text{C}_{32}\text{H}_{23}\text{N}_3\text{S})_n$ (481.62) $_n$: C, 79.80; H, 4.81; N, 8.72; S, 6.66 Found: C, 78.47; H, 4.86; N, 8.09; S, 5.87; Br, 3.03

RESULTS AND DISCUSSION

The copolymers **3a–g** (Fig. 1) were synthesized by the standard *Sonogashira*-reaction^{47,48} of selected dihalogen arenes **1a–f** with diethynyl triphenylamines **2a–c** in the presence of Pd(0) and CuI, triethylamine or diisopropylamine as base in toluene or tetrahydrofuran (THF) solution. The choice of the aromatic comonomers **1a–f** was motivated by their opto-electronical properties and their assumed influence in the properties of the resulting conjugated polymers, respectively. Alkyl- and even more alkoxy-substituted phenylene comonomers should increase the donor strength. The introduction of thiophene units, in the style of state-of-the-art polymer solar cell material P3HT, should likewise have the same effect. According to Müllen and coworkers,⁴⁹ the incorporation of 9,10-anthrylene structures into conjugated polymers (**1e**) also reduces the bandgap energy. In contrast to the former comonomers the π -deficient benzothiadiazole unit was chosen to shift the absorption in the resulting D/A-polymers drastically to longer wavelengths. The complete series from donor to acceptor comonomers offers the possibility to investigate the influence on the performance in polymer solar cells (electron transfer from donor polymer to PCBM). The side chains in 4 positions

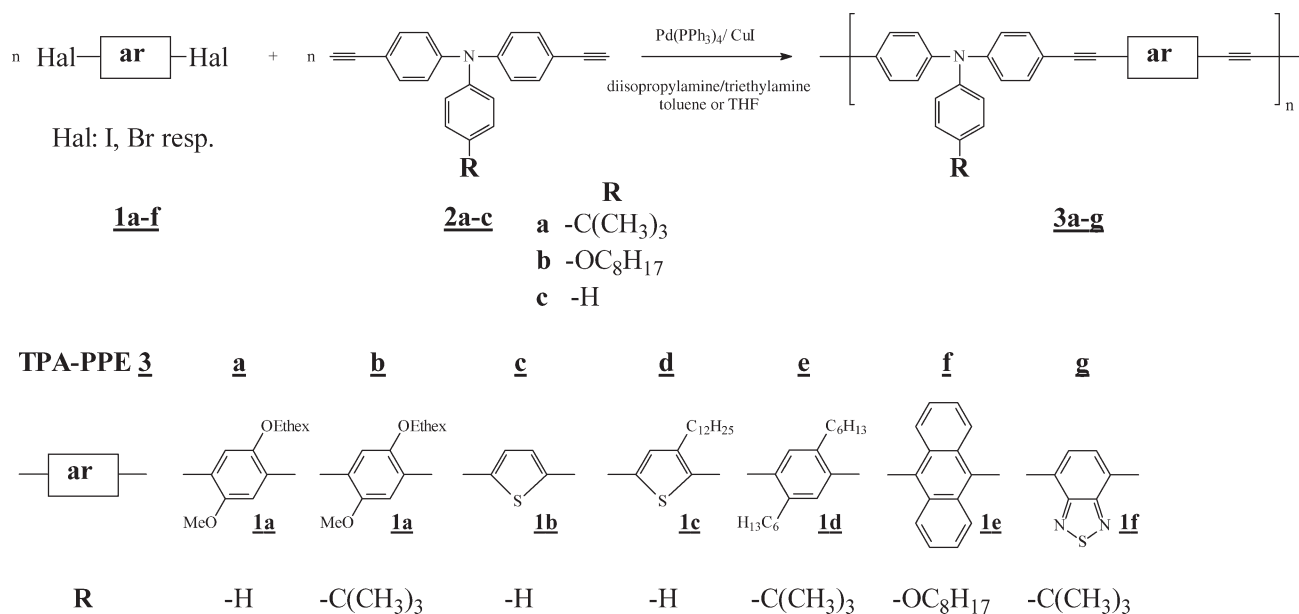


Figure 1 Polycondensation: synthesis of the TPA-PPEs **3a-g**.

of the TPAs should ensure solubility and donor strength as well.

For the Sonogashira cross-coupling the aromatic comonomers **1a-f** were required as diiodo- or dibromo-derivatives. It is known that iodo compounds are more reactive than their bromo pendants in this Pd-catalyzed reaction (oxidative addition), because of the lower bond-dissociation energy (PhX: 81 kcal/mol for X = Br; 65 kcal/mol for X = I).^{50,51} That became evident in the synthesis of **3f** for instance. After stirring for 2 h at 40°C the polymer started already to precipitate. However, coupling of bromo compounds required higher reaction temperatures and longer reaction times (72 h) except for polymer **3g**, which started falling out after stirring for 5 h at 65°C. This can be explained by the acceptor character and therefore higher reactivity of the benzothiadiazole comonomer. After the Sonogashira polycondensation a sequence of precipitations (*n*-hexane, methanol) provided the polymers **3a-e** as

yellow or orange-brown solids in 60 to 80% yield. Polymers **3f+g** are red in color. All shown copolymers are completely soluble in common organic solvents such as chloroform, chlorobenzene, THF, or dioxane. Even the not substituted thiophene-2,5-diethynylene-triphenylamine copolymer **3c** is soluble, but the introduction of additional spacers like dodecyl substituents in **3d** result expectedly in better solubility.

The number average molecular weight (M_n) of the polymers determined by GPC versus polystyrene standards is between 15,000 and 30,000 g/mol, leading to degrees of polymerization (DP) between 25 and 62 (see Table I). The GPC is only a relative method; therefore, the residual halogen values of the polymers (bromine, iodine endgroups) found in elemental analysis were used to calculate also the DP. In analogy with the literature⁵²⁻⁵⁷ the molecular weights determined with GPC are overestimated by a factor of 1.5–3.0 because of the rigid polymer structure.

TABLE I
 M_n and M_w Values of the Copolymers **3a-g**

TPA-PPE 3	M_n^a (g/mol)	M_w^a (g/mol)	DI ^b	DP (M_n)	I/Br (found)	DP ^c (I/Br)
a	14,400	28,200	2.0	26	4.08	11
b	17,200	34,600	2.0	29	3.07	13
c	12,000	51,700	4.3	31	3.07	13
d	20,500	79,500	3.9	37	2.22	13
e	15,400	34,900	2.3	25	2.51	10
f	17,000	74,400	4.4	29	2.23	18
g	30,000	52,000	1.7	62	3.03	10

^a GPC in THF (polystyrene standard).

^b DI = M_w/M_n .

^c Assuming two bromine (iodine) end groups per chain.

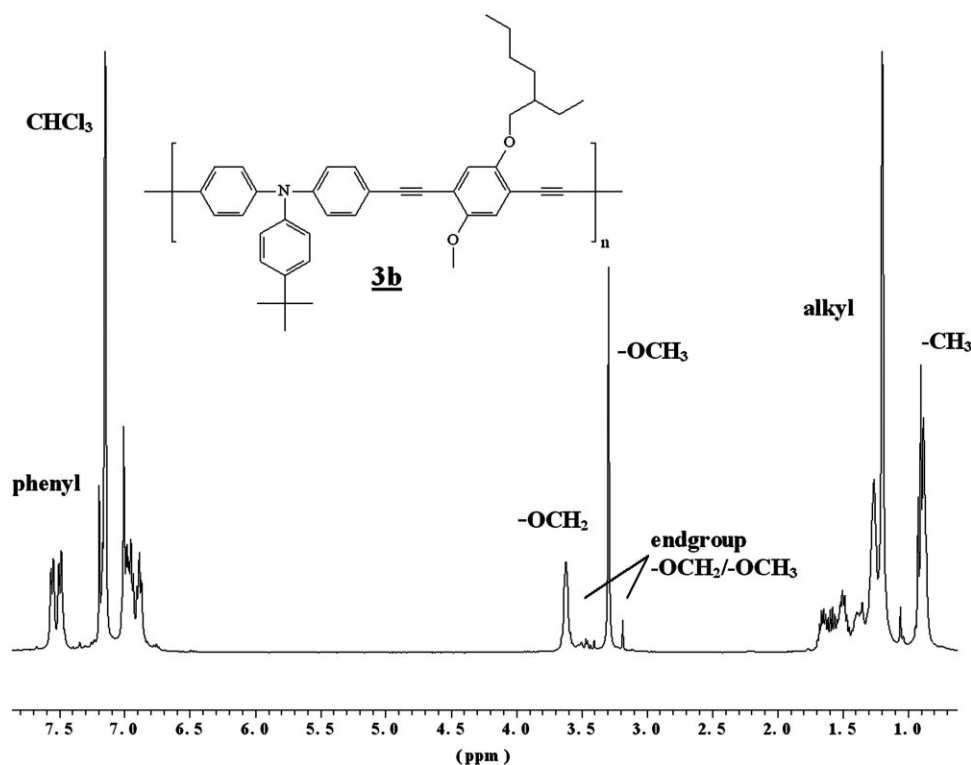


Figure 2 ^1H NMR spectrum of polymer **3b** in CDCl_3 .

The chemical structure of the polymers was confirmed by ^1H NMR and elemental analysis. Figure 2 depicts exemplarily the ^1H NMR spectrum of polymer **3b**. The characteristic signals for the phenyl protons are at 6.9–7.7 ppm. Further the signal for the protons of the alkyl side chain appeared up-field at 0.9–1.7 ppm. The proton signals of the $-\text{CH}_2-$ and $-\text{CH}_3$ group adjacent to the oxygen were detected at 3.3 and 3.6 ppm. Even the signals of the alkyl side chain in the endgroup can be seen. The mentioned assumption of two halogen endgroups per each polymer chain is verified by the ^1H NMR, because no ethynyl termini can be found (for further details, see Experimental section). The rigorous alternating incorporation of the units (1 : 1 ratio) was predetermined by the use of A-TPA-A and B-co-monomer-B in an AA/BB-polycondensation, which can be seen for all the polymers by comparison of the relative areas of the characteristic signals in the ^1H NMR spectrum.

Polymers containing asymmetric substituted comonomers have a random-regularity. Because of typical line broadening in the ^1H NMR spectrum no statement and no differentiation between head-head, head-tail, and tail-tail moieties/ratios could be made.

Optical properties

The optical properties of the copolymers were investigated by UV/vis and photoluminescence spectroscopy

in diluted 1,4-dioxane solutions. Table II gives an overview over the optical properties of the synthesized polymers. All emission data were obtained after excitation in the main absorption band.

The polymers **3a–d** show a prominent absorption at 408–411 nm. Table II shows that the introduction of thiophene or 3-alkyl-thiophene units into the TPA-copolymers has a similar effect on the absorption like the introduction of alkoxy phenylene units. If the phenylene ring is substituted by alkyl groups (**3e**) this absorption shifts to 387 nm, which is mainly caused by the minor donor strength. The integration of anthracenyl groups (**3f**) or benzothiadiazole (**3g**, D/A-polymer) leads to the hoped-for and expected bathochrome shift of approximately 100 nm (see also Fig. 4). By comparing our copolymers **3a–g** with known PPEs, already described in literature,¹ we can notice that the spectroscopic properties are similar, if the same structure elements were incorporated. Therefore, we conclude that the incorporation of the electron-rich amino groups into the PPE backbone does not interrupt the main chain conjugation and the TPA units have no significant influence on the position of the absorption maximum.

Cast films of these amino-PPEs (e.g., **3f+g**) on quartz glass plates show a small red shift of λ_{max} in UV/vis absorption spectrum in contrast to their solutions (Table II). It is quite evident that the polymers are able to form π -stacked structures in the solid state. The effect is less intensive than in alkoxy PPEs

TABLE II
Photophysical Data of the Copolymers 3a–g and Model Compounds 4a–b

	TPA-PPE	$\lambda_{\max, \text{abs.}}^a$ (ϵ [$M^{-1} \text{ cm}^{-1}$])	$E_g^{\text{opt b}}$ (eV)	$\lambda_{\max, \text{em.}}^c$ (Φ_{fl})	$E_g^{0-0 d}$ (eV)
3a		410 nm (34,800) yellow	2.82	443 nm (0.56)	2.85
3b		411 nm (57,000) yellow	2.80	447 nm (0.33)	2.83
3c		409 nm (28,500) yellow	2.79	453 nm (0.55)	2.81
3d		408 nm (28,400) orange	2.77	454 nm (0.22)	2.80
3e		387 nm broad (34,200) reddish-brown	(2.56)	439 (491) nm (0.09)	2.92
3f		514 nm ^e (49,200) (529 nm ^h) red powder	2.23	558 nm ^f (0.40 ^g) (580 nm ^h) (0.02 ^h)	2.32
3g		503 nm (30,000) red powder	2.13	638 nm (0.38)	2.19
4a		366 nm (53,600) light yellow	3.15	401 nm (0.81)	3.20
4b		393 nm (72,700) orange-red	2.91	431 nm (0.96)	2.95

^a In 1,4-dioxane.

^b $E_g^{\text{opt}} = hc/\lambda_{0.1\text{max}}$.

^c Excited in $\lambda_{\max, \text{abs.}}$; in 1,4-dioxane.

^d $E_g^{0-0} = hc/\lambda_{0-0}$.

^e In THF.

^f In CHCl_3 .

^g Rhodamine 6G/sodium fluoresceine in 0.1 M NaOH as standard.

^h Film from chlorobenzene.

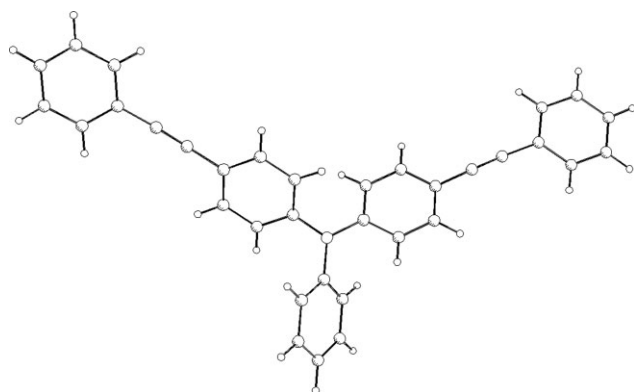


Figure 3 Crystal structure of 4,4'-bis(phenylethynyl)-triphenylamine **4a**.

(shifts around 20–40 nm¹) because of the twisted triphenylamine units. The crystal structure (X-ray) of **4a** (Fig. 3) reveals the planarization of the molecule (sp²) and the propeller-like twisted structure of the phenyl rings with CNC angles of 120.93 ± 0.15° (both substituted), 119.53 ± 0.07°, and 119.5 ± 0.07° (not substituted and substituted).

Upon comparing the optical properties of the low molecular model compounds 4,4'-bis(phenylethynyl)triphenylamine **4a** and 2-methoxy-5-(2-ethylhexyl)oxy-1,4-bis(triphenylamine-4-ylethynyl)benzene **4b** with the appropriate copolymer **3a**, we observed the expected significant red shift of the absorption band of about 20 nm by increasing the conjugation length (Fig. 4).

Furthermore, the novel TPA-based amino-PPEs are highly photoconducting materials (**3a**: $I_{\text{Photo}} = 4.0 \times 10^{-10}$ A at $\lambda_{\text{max}} = 425$ nm (400 V); film from chlorobenzene, 20 μW/0.2 mm; **3g**: $I_{\text{Photo}} = 1.3 \times 10^{-11}$ A at $\lambda_{\text{max}} = 500$ nm (20 V); film from chlorobenzene, 20 μW/0.2 mm). The photocurrent of **3g** is four orders of magnitude larger than for the well-known photoconductor polyvinylcarbazole ($I_{\text{Photo}} = 1.0 \times 10^{-13}$ A at $\lambda_{\text{max}} = 450$ nm (800 V)).

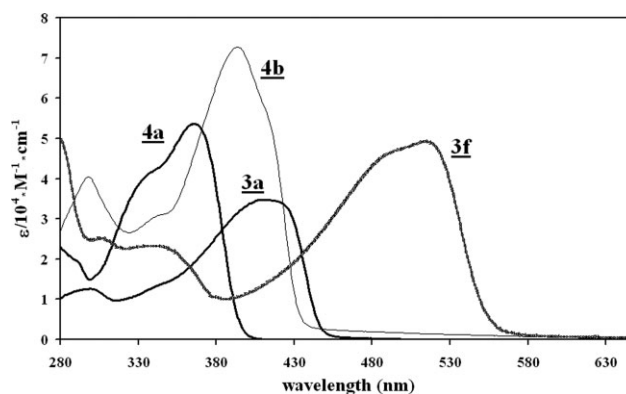


Figure 4 UV/vis spectra of polymers **3a**, **3f** and model compounds **4a**, **4b** in 1,4-dioxane.

Electrochemical studies

The electrochemical properties of the polymers were characterized by cyclic voltammetry (CV) and difference pulse polarography (DPP) of either dichloromethane solutions or cast films on a Pt plate in CH₃CN (Table III). Figure 5 depicts the CV curve of polymer **3a** in solution. The electrochemical oxidation gives one reversible oxidation step at 1.03 V (Ag/AgCl). In DPP measurements, the polymer **3a** shows also only one oxidation peak at about 1.05 V (methylene chloride solution) and 1.17 V (film from chlorobenzene, Fig. 5) (Ag/AgCl). In no CV curve a second oxidation step appeared.

The electron, which is remaining on the TPA unit after the electrochemical oxidation to a radical cation, is delocalized to two thirds into the phenyl rings and is not restricted to the central nitrogen atom.⁵⁸ In principle, two radical cations are able to recombine which will result in a new bond between the two 4-positions of the phenyl rings. The formation of such *N,N,N',N'*-tetraphenylbenzidines are well described in literature for TPAs.^{59–62} However, no indication for this was found in the electrochemical investigations of the described polymers. The double

TABLE III
Oxidation Potentials of Selected TPA-PPEs

Compound	E_{Ox} (DPP/ solution) ^a (V vs. Ag/AgCl)	E_{Ox} (CV/ solution) ^b (V vs. Ag/AgCl)	E_{Ox} (DPP/film) ^c (V vs. Ag/AgCl)	E_{Ox} (CV/film) ^d (V vs. Ag/AgCl)
3a	1.05	1.03	1.17	1.34
3b	0.99	–	–	–
3c	–	–	1.29	1.30
3d	1.04	1.05	–	1.37
3f	–	–	–	1.16
3g	1.24	1.23	1.35	–

^a In methylene chloride, TBAPF₆, Pt electrode, 0.02 V/s.

^b In methylene chloride, TBAPF₆, Pt electrode, 0.167 V/s.

^c Film from chlorobenzene in acetonitrile (“–” not determined).

^d Film from methylene chloride in acetonitrile (“–” not determined).

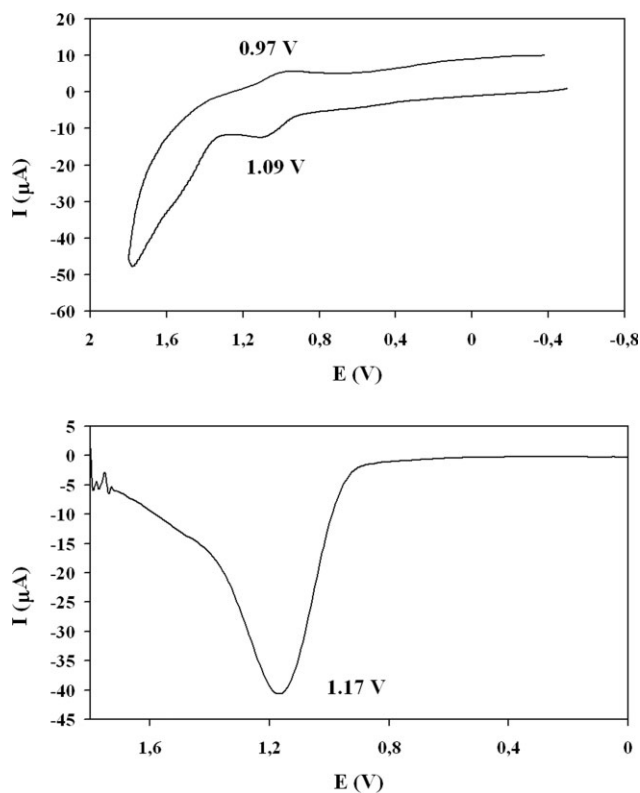


Figure 5 CV of polymer **3a** (Ag/AgCl) in methylene chloride (above) and DPP of polymer **3a** (Ag/AgCl) in film (below).

or triple substitution of the TPA units in 4,4',4'-position prevents recombinations apparently completely. Even after repeated CV cycles of the same solutions of model structures or polymers no evidence for tetraphenylbenzidine structures were found. Also the formation of dicationic structures inside one polymer chain that is known from TPA-PPVs (two reversible oxidation steps, two repeating units involved) could not be observed.

For photovoltaics the HOMO and LUMO energy levels of the polymers are very important in performance and energetic considerations. From the E_{onset} values of CV measurements in film the energy of HOMO levels of the polymers could be obtained. In addition with known bandgap energies (E_g^{opt}) a complete band diagram with HOMO/LUMO levels of the TPA-PPEs was created (Fig. 6).

Photovoltaics

The incorporation of triphenylamine into the polymer backbone leads to a decreasing effect on the oxidation potential of the copolymers **3a–g** and makes these polymers interesting as hole-injection/hole-transporting materials.

Charge carrier mobilities and hole conductivities, respectively, of **3g** could be measured by using an organic field-effect transistor (OFET) set-up. Thereby

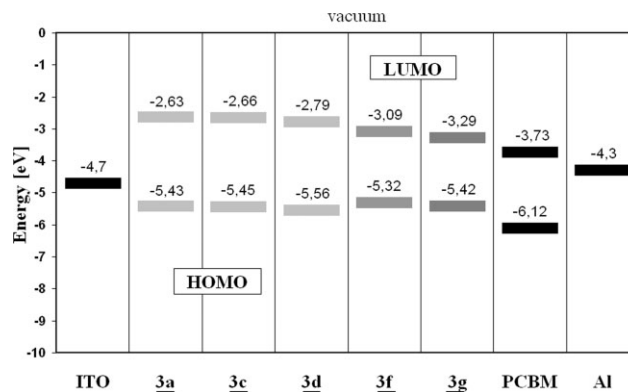


Figure 6 Band diagram with HOMO/LUMO levels of the TPA-PPEs **3a**, **3c**, **3d**, **3f**, **3g** and the acceptor PCBM in relation to ITO and Al. $E_{\text{HOMO}} = [-(E_{\text{onset}}(\text{versus Ag/AgCl}) - E_{1/2}(\text{Fc/Fc}^+ \text{ versus Ag/AgCl}))] - 4.8 \text{ eV}$; $E_{\text{LUMO}} = E_{\text{HOMO}} + E_g^{\text{opt}}$.

good lateral mobilities $\mu_{||}$ were determined $2.0 \times 10^{-4} \text{ cm}^2/\text{versus}$ (bottom-contact/Au-S/D-contacts) and $2.2 \times 10^{-4} \text{ cm}^2/\text{versus}$ (top-contact/Au-S/D-contacts). Considering values of MDMO-PPV in the same experiment $\mu_{||} = 5.9 \times 10^{-4} \text{ cm}^2/\text{versus}$ (top-contact/Au-S/D-contacts) and $8.5 \times 10^{-4} \text{ cm}^2/\text{versus}$ (top-contact/Au-S/D-contacts) the TPA-PPEs mobilities are in the same range like those of the PPV material often used in bulk heterojunction polymer solar cells. The vertical mobilities were rather low. They could not be determined exactly so far. Deeper theoretical and also instrumental work would be necessary to differentiate certain effects (contact, possible traps, enhancement zone, and bulk) from each other. But at least the range of μ_{\perp} could be estimated: 10^{-8} to $10^{-6} \text{ cm}^2/\text{volt} \times \text{second}$.

Some of the new polymers were tested in polymer solar cells. They were applied in bulk heterojunction cells (for literature overview see ref. 63) on polyester foil covered by ITO and PEDOT:PSS, PCBM (electron acceptor in the bulk with the photoactive polymer), and an Al electrode on top (for further details see Experimental section). Power conversion efficiencies of around 0.5 to 1.8% after illumination with $100 \text{ mW}/\text{cm}^2$ of AM1.5 could be reached without any optimization of concentration of the solutions, the ratio of the polymer to PCBM, the spin coating process itself or annealing. The characteristic parameters are given in Table IV.

TABLE IV
Photovoltaic Performance Parameters for the Studied Solar Cells Obtained under AM1.5 Conditions

Solar cells	I_{SC} (mA/cm ²)	V_{OC} (mV)	FF	$\eta_{\text{AM1.5}}$ (%)
3a /PCBM	2.82	474	0.38	0.51
3c /PCBM	3.81	628	0.37	0.89
3d /PCBM	3.70	658	0.37	0.89
3f /PCBM	4.65	665	0.39	1.21
3g /PCBM	5.22	891	0.40	1.85

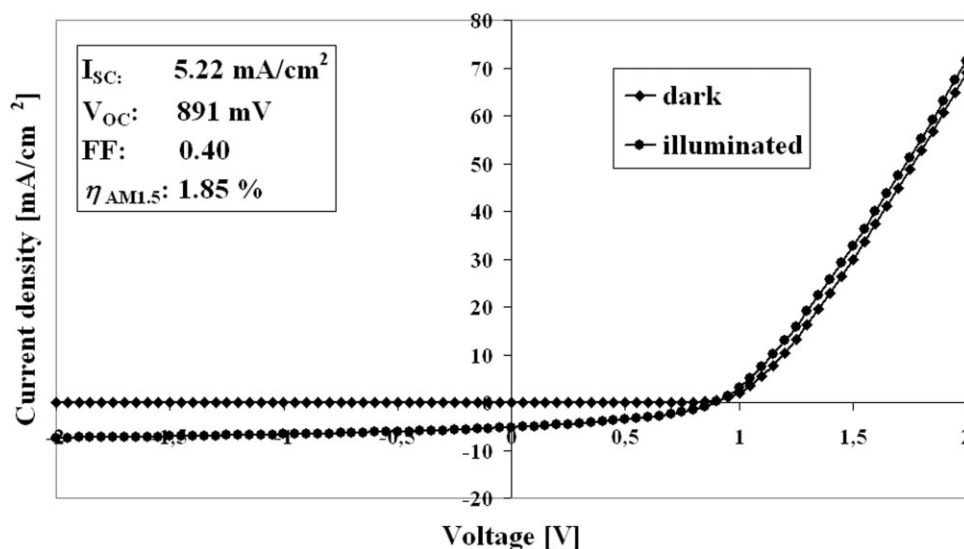


Figure 7 I–V characteristic of a PET/ITO/PEDOT:PSS/3g:PCBM/Al cell ($A = 0.25 \text{ cm}^2$) under illumination AM1.5 (100 mW/cm^2).

For calculation: $\eta_{AM1.5} = I_{SC} \times V_{OC} \times FF \times 100 / P_{in}$ and $FF = P_{max} / (I_{SC} \times V_{OC})$ were used.

We have to point out, that the reached efficiencies are really high for PPEs and set-ups on foil. The anthrylene and especially the benzothiadiazole polymer have high values of the open circuit voltage (V_{OC}). This can be explained by the known effect, that V_{OC} directly depends on the difference between the HOMO of the donating polymer and the LUMO of the acceptor. So, $V_{OC} \approx 850\text{--}900 \text{ mV}$ of **3g** is a result of the low position of its HOMO at -5.42 eV (see Fig. 6; for comparison: P3HT $-5.2 \text{ eV}/\approx 650 \text{ mV}$; MDMO-PPV $-5.3 \text{ eV}/\approx 750 \text{ mV}$). In contrast to this observation, the polymers **3a**, **3c**, and **3d** show lower values of the V_{OC} , even though having lower HOMO level. This is contradictory to the mentioned correlation between V_{OC} and the difference between $HOMO_{donor}$ and $LUMO_{acceptor}$ and reveals the demand of further investigations. We have grounds to believe that not only the distance between the HOMO-LUMO levels is responsible for the measured open circuit voltages, but also, for instance, the rotation speed in the spin coating process. Not only the chemical structure of the polymers itself is important, also the nanomorphology has to be considered. Currently we study this phenomenon further and will report in subsequent publications. Although the fill factors (FF) of all polymers do not differ, the higher short circuit currents (I_{SC}) of the polymers **3f** and **3g** lead to the best power conversion efficiency ($\eta_{AM1.5}$) with 1.2% and 1.8% (Fig. 7). All substrates were built under the same conditions. We propose, that the higher $\eta_{AM1.5}$ of **3f** and **3g** are caused by the bathochromic shift of their absorption in the visible region (lower bandgap energy) in comparison to the

other polymers. Thereby the solar spectrum (light from sun simulator) can be better exploited, more charge carriers are generated and the ultra-fast photo-induced electron transfer plus following charge transport by hopping can take place better. The highest light power conversion efficiency could be obtained with **3g** in which the π -excessive TPA and the π -deficient benzothiadiazole unit (D/A-system) are combined leading to the mentioned bathochromic shifted absorption.

The electron poor benzothiadiazole seems not to reduce significantly the electron donating behavior and the electron transfer to the fullerene acceptor can take place (no competition between PCBM and benzothiadiazole as electron acceptor). So, polymer **3g** can still be considered as donor (electron-donor) polymer in photovoltaic aspects. This means that both conjugated D- and also D/A-polymers like **3g** are promising candidates for high efficiency photovoltaic devices.

CONCLUSIONS

New well-defined high molecular PPE-based copolymers containing triphenylamine as hole-conducting donor were successfully synthesized by using the Sonogashira reaction for polycondensation. The incorporation of electron-rich amino groups in the backbone does not interrupt the main-chain conjugation. Electrochemical measurements show the expected higher oxidation potential for TPA-PPEs in comparison with TPA-PPVs but no indication for a two-step oxidation process, that is known for TPA-PPVs, forming dicationic structures between adjacent

repeating units could be observed. The amino-PPEs are interesting as hole-injection/hole-transporting materials in photovoltaic applications and in light emitting devices. The focus in this work was on photovoltaic application, which is the first example of investigations of TPA-PPEs. In first nonoptimized tests with heterojunction solar cells in combination with ITO, PEDOT:PSS, PCBM remarkable and even very high power conversion efficiencies of around 0.5% to 1.8% could be reached. The highest value of 1.85% could be achieved by a promising D/A-polymer, containing TPA and benzothiadiazole moieties, working as electron-donor polymer in blend with the PCBM-acceptor in the photoactive layer. The described new type of copolymer combining light absorption, conjugation by triple bonds and enhanced hole transport by TPA-units demonstrates the huge potential of such polymers in the field of OPV.

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References

- Bunz, U. H. F. *Chem Rev* 2000, 100, 1605.
- Friend, R. H. *Pure Appl Chem* 2001, 73, 425.
- Schumm, J. S.; Pearson, D. L.; Tour, J. M. *Angew Chem* 1994, 106, 1445.
- Yamamoto, T.; Yamada, W.; Tagaki, N.; Kizu, K.; Maruyama, T.; Ooba, N.; Tomaru, S.; Kurihara, T.; Kaino, T.; Kubota, K. *Macromolecules* 1994, 27, 6620.
- Wautelet, P.; Moroni, M.; Oswald, L.; Le Moigne, J.; Pham, A.; Bigot, J.-Y.; Luzzati, S. *Macromolecules* 1996, 29, 446.
- Nalwa, H. S. In *Handbook of Organic Conductive Molecules and Polymers*, Nalwa, H. S., ed.; Wiley: Chichester, 1997, Vol. 4, p 261.
- Brabec, C. J.; Sariciftci, N. S. In *Semiconducting Polymers*, Hadziioannou, G., van Hutten, P. F., eds.; Wiley-VCH: Weinheim, 2000, p 515.
- Sariciftci, N. S.; Braun, D.; Zhang, C.; Srđanov, V. I.; Heeger, A. J.; Stucky, G.; Wudl, F. *Appl Phys Lett* 1993, 62, 585.
- Jenekhe, S. A.; Yi, S. *Appl Phys Lett* 2000, 77, 2635.
- Janssen, R. A. J.; Hummelen, J. C.; Sariciftci, N.S. *MRS Bull* 2005, 30, 33.
- Halls, J. J. M.; Walsh, C. A.; Greenham, N. C.; Marseglia, E. A.; Friend, R. H.; Moratti, S. C.; Holmes, A. B. *Nature* 1995, 376, 498.
- Yu, G.; Gao, J.; Hummelen, J. C.; Wudl, F.; Heeger, A. J. *Science* 1995, 270, 1789.
- Padinger, F.; Rittberger, R. S.; Sariciftci, N. S.; *Adv Funct Mater* 2003, 11, 1.
- Brabec, C. J.; Hauch, J. A.; Schilinsky, P.; Waldauf, C. *MRS Bull* 2005, 30, 50.
- Li, G.; Shrotriya, V.; Huang, J.; Yao, Y.; Moriarty, T.; Emery, K.; Yang, Y. *Nat Mater* 2005, 4, 864.
- Kim, Y.; Cook, S.; Tuladhar, S.M.; Choulis, S.A.; Nelson, J.; Durrant, J. R.; Bradley, D. D. C.; Giles, M.; McCulloch, I.; Ha, C.-S.; Ree, M. *Nat Mater* 2006, 5, 197.
- Al-Ibrahim, M.; Roth, H.-K.; Sensfuss, S.; *Appl Phys Lett* 2004, 85, 1481.
- Al-Ibrahim, M.; Konkin, A.; Roth, H.-K.; Egbe, D. A. M.; Klemm, E.; Zhokhavets, U.; Gobsch, G.; Sensfuss, S.; *Thin Solid Films* 2005, 474, 201.
- Sensfuss, S.; Al-Ibrahim, M. In *Organic Photovoltaics: Mechanisms, Materials and Devices*; Sun, S.-S., Sariciftci, N. S.; CRC Press: Boca Raton, FL, 2005; p 529.
- Al-Ibrahim, M.; Sensfuss, S.; Gobsch, G.; Ambacher, O. *Appl Phys Lett* 2005, 86, 201120.
- Ma, W.; Yang, C.; Gong, X.; Lee, K.; Heeger, A. J. *Adv Funct Mater* 2005, 15, 1617.
- Reyes-Reyes, M.; Kim, K.; Carroll, D. L. *Appl Phys Lett* 2005, 87, 083506.
- Brabec, C. *Proceedings of the OEC'07, Frankfurt, 2007 (Day1/Track:Three)*.
- Press relation 2007. Available at: http://idtechex.com/printe-delectronicsworld/articles/plextronics_organic_solar_cell_technology_breaks_world_record_00000664.asp (accessed, August 10, 2007).
- Kim, J. Y.; Lee, K.; Coates, N. E.; Moses, D.; Nguyen, T.-Q.; Dante, M.; Heeger, A. J. *Science* 2007, 317, 222.
- Weder, C. (ed.); Blankenburg, L.; Bunz, U. H. F.; Klemm, E.; Moore, J. S.; Pautzsch, T.; Ray, C. R.; Swager, T. M.; Voskerician, G.; Yamaguchi, I.; Yamamoto, T.; Yasada, T.; Zheng, J. *Adv Polym Sci* 2005, 177.
- Hartwig, J. F.; Kawatsura, M.; Hauck, S. J.; Shaughnessy, K. H.; Alcazar-Roman, L. M. *J Org Chem* 1999, 64, 5575.
- Wolfe, J. P.; Buchwald, S. L. *J Org Chem* 1996, 61, 1133.
- Harris, M. C.; Buchwald, S. L. *J Org Chem* 2000, 65, 5327.
- Yamamoto, T.; Nishiyama, M.; Koie, Y.; *Tetrahedron Lett* 1998, 39, 2367.
- Pautzsch, T.; Blankenburg, L.; Hager, M.; Egbe, D. A. M.; Klemm, E. *Proc of SPIE* 2004, 5215, 161.
- Kim, S. W.; Shim, S. C.; Kim, D. Y.; Kim, C. Y.; *Synt Met* 2001, 122, 363.
- Weder, C.; Wrighton, M. S.; *Macromolecules* 1996, 29, 5157.
- Swager, T. M.; Gil, C. J.; Wrighton, M. S. *J Phys Chem* 1995, 99, 4886.
- Duerr, B. F.; Chung, Y.-S.; Czarnik, A. W. *J Org Chem* 1988, 53, 2120.
- Heilbron, I. M.; Heaton, J. S. *Organic Syntheses*; Wiley: New York, 1941, Vol. 1, p 207.
- Jones, S.; Atherton, J. C. C. *Synth Commun* 2001, 31, 1799.
- Egbe, D. A. M.; Roll, C. P.; Birckner, E.; Grummt, U.-W.; Stockmann, R.; Klemm, E. *Macromolecules* 2002, 35, 3825.
- Blicke, F. F.; Burckhalter, J. H. *J Am Chem Soc* 1942, 64, 477.
- D'Auria, M. *J Chem Soc Perkin Trans 1* 1987, 1777.
- Sato, M.; Tanaka, S.; Kaeriyama, K.; *J Chem Soc Chem Commun* 1986, 873.
- Grosshenny, V.; Romero, F. M.; Ziesel, R.; *J Org Chem* 1997, 62, 1491.
- Steffen, W.; Koehler, B.; Altmann, M.; Scherf, U.; Stitzer, K.; zur Loye, H.-C.; Bunz, U. H. F. *Chem Eur J* 2001, 7, 117.
- Pilgram, K.; Zupan, M.; Shiles, R. *J Heterocycl Chem* 1970, 7, 629.
- Pautzsch, T.; Blankenburg, L.; Klemm, E. *J Polym Sci Part A: Polym Chem* 2004, 42, 722.
- Demas, J. N.; Crosby, G. A. *J Phys Chem* 1971, 75, 991.
- Sonogashira, K.; Tohda, Y.; Hagihara, N.; *Tetrahedron Lett* 1975, 16, 4467.
- Sonogashira, K. *J Organomet Chem* 2002, 653, 46.
- Garay, R. O.; Naarmann, H.; Müllen, K. *Macromolecules* 1994, 27, 1922.
- Grushin, V. V.; Alper, H. In *Activation of Unreactive Bonds and Organic Synthesis*, Springer: Berlin, 1999, p 193.
- Grushin, V. V.; Alper, H. *Chem Rev* 1994, 94, 1047.
- Francke, V.; Mangel, T.; Müllen, K. *Macromolecules* 1998, 31, 2447.

53. Kloppenburg, L.; Jones, D.; Claridge, J. B.; zur Loye, H.-C.; Bunz, U. H. F. *Macromolecules* 1999, 32, 4460.
54. Watanabe, Y.; Mihara, T.; Koide, N. *Macromol Chem Phys* 1998, 199, 977.
55. Kloppenburg, L.; Jones, D.; Bunz, U. H. F. *Macromolecules* 1999, 32, 4194.
56. Cotts, P. M.; Swager, T. M.; Zhou, Q. *Macromolecules* 1996, 29, 7323.
57. Ricks, H. L.; Choudry, U. H.; Marshall, A. R.; Bunz, U. H. F. *Macromolecules* 2003, 36, 1424.
58. Neugebauer, F. A.; Bamberger, S.; Groh, W. R. *Chem Ber* 1975, 108, 2406.
59. Sumiyoshi, T. *Chem Lett* 1995, 645.
60. Creason, S. C.; Wheeler, J.; Nelson, R. F. *J Org Chem* 1972, 37, 4440.
61. Zhang, T.; Brajter-Toth, A. *Anal Chem* 2000, 72, 2533.
62. Marcoux, L. S.; Adams, R. N.; Feldberg, S. W. *J Phys Chem* 1969, 73, 2611.
63. Frechet, J. M. J.; Thompson, B. C. *Angew Chem Int Ed* 2007, 46, 2.