Chem. Mater. **2007,** *19,* 5194−5199

Synthesis and Characterization of a Fullerene Bearing a Triazole Group

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Received June 24, 2007. Revised Manuscript Received August 14, 2007

A soluble fullerene, TAZC60, bearing an electron transport moiety (triazole) is synthesized and characterized. TAZC60 possesses a band gap of 2.2 eV, and HOMO and LUMO energy levels of 5.9 and 3.7 eV, respectively. Thin films of TAZC60 exhibit an electron mobility of 2.2×10^{-8} m^2/V s, as determined from the current−voltage characteristics that fit with a space-charge limited current (SCLC). These properties are similar to those of [6,6]-phenyl C61 butyric acid methyl ester, PCBM, a soluble fullerene widely used in organic photovoltaics. The strategy of modifying fullerenes with a solublizing electron transport moiety may open avenues for the design of more specific polymers for controlling the morphology and transport properties of polymer-fullerene blends for polymer solar cells.

Introduction

There is great interest in the study of organic molecules and polymers that transport electronic charge. In the field of polymer photovoltaic (PV) devices,[1] π-conjugated polymers (πCPs) are actively studied because of their p-type charge transport properties and favorable absorption cross section. Despite recent advances in n-type πCPs,[2−4] fullerene derivatives remain the current electron acceptor of choice because of their high electron mobility, low LUMO energy level, and efficient photoinduced electron-accepting properties.[5] Recent directions in the search for high-efficiency organic PVs have adopted films of bulk heterojunctions,[2,6] prepared by solution processing blends of a p-type πCP, such as poly(3-alkylthiophene), and a soluble fullerene derivative, such as [6,6]-phenyl C61 butyric acid methyl ester (PCBM).[7,8] The device power conversion efficiency strongly depends on the morphology of the donor−acceptor blend, which is controlled by the interaction and compatibility of the donor and acceptor components.[1,9] In stark contrast to numerous reports on the synthesis and study of p-type conjugated polymers, the number of reports of soluble fullerene derivatives designed for polymer PV work are relatively few,[10−12] partly because modification of the fullerene to impart solubility in casting solvents and miscibility with polymers often results in a significant lowering of electron mobility. In contrast, there are many studies of small molecule, organic electron transport compounds incorporated into polymers or polymer blends and studied either as electron-transporting materials and/or exciton blocking materials.[13−15] Electron

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(1) Brabec, C. J.; Sariciftci, N. S.; Hummelen, J. C. *Adv. Funct. Mater.* **2001**, *11*, 15.

(2) 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.

(3) (a) Granstrom, M.; Petritsch, K.; Arias, A. C.; Andersson, M. R.; Friend, R. H. *Nature* **1998**, *395*, 257. (b). Halls, J. J. M.; Arias, A. C.; Mackenzie, J. D.; Wu, W. S.; Inbasekaran, M.; Woo, E. P.; Friend, R. H. *Adv. Mater.* **2000**, *12*, 498.

(4) Jenekhe, S. A.; Yi, S. J. *Appl. Phys. Lett.* **2000**, *77*, 2635.

(5) (a) Sariciftci, N. S.; Smilowitz, L.; Heeger, A. J.; Wudl, F. *Science* **1992**, *258*, 1474. (b) Nierengarten, J. F. *Sol. Energy Mater. Sol. Cells* **2004**, *83*, 187. (c) Nierengarten, J. F. *New J. Chem.* **2004**, *28*, 1177. (d) Segura, J. L.; Martin, N.; Guldi, D. M. *Chem. Soc. Rev.* **2005**, *34*, 31. (e) Figueira-Duarte, T. M.; Gegout, A.; Nierengarten, J. F. *Chem. Commun*. **2007**, 109.

(6) Yu, G.; Gao, J.; Hummelen, J. C.; Wudl, F.; Heeger, A. J. *Science* **1995**, *270*, 1789.

(7) Padinger, F.; Rittberger, R. S.; Sariciftci, N. S. *Adv. Funct. Mater.* **2003**, *13*, 85.

(8) Hummelen, J. C.; Knight, B. W.; Lepeq, F.; Wudl, F.; Yao, J.; Wilkins, C. L. *J. Org. Chem.* **1995**, *60*, 532.

(9) Shaheen, S. E.; Brabec, C. J.; Sariciftci, N. S.; Padinger, F.; Fromherz, T.; Hummelen, J. C. *Appl. Phys. Lett.* **2001**, *78*, 841.

(10) (a) Popescu, L. M.; van't Hof, P.; Sieval, A. B.; Jonkman, H. T.; Hummelen, J. C. *Appl. Phys. Lett.* **2006**, *89*, 213507. (b) Wienk, M. W.; Kroon, J. M.; Verhees, W. J. H.; Knol, J.; Hummelen, J. C. van Hal, P. A.; Janssen, R. A. J. *Angew. Chem., Int. Ed.* **2003**, *42*, 3371. (c) Drees, M.; Hoppe, H.; Winder, C.; Neugebauer, H.; Sariciftci, N. S.; Schwinger, W.; Schaffler, F.; Topf, C.; Scharber, M. C.; Zhu, Z.; Gaudiana, R. *J. Mater. Chem.* **2005**, *15*, 5185. (d). Kooistra, F. B.; Knol, J.; Kastenberg, F.; Popescu, L. M.; Verhees, W. J. H.; Kroon, J. M.; Hummelen, J. C. *Org. Lett.* **2007**, *9*, 551. (e). Backer, S. A.; Sivula, K.; Kavulak, D. F.; Frechet, J. M. J. *Chem. Mater*. **2007**, *19*, 2927.

(11) Riedel, I.; von Hauff, E.; Parisi, J.; Martin, N.; Giacalone, F.; Dyakonov, V. *Adv. Funct. Mater.* **2005**, *15*, 1979.

(12) (a) Wang, X.; Perzon, E.; Delgado, J. L.; de la Cruz, P.; Zhnag, F.; Langa, F.; Andersson, M.; Inganas, O. *Appl. Phys. Lett*. **2004**, *85*, 5081. (b) Gadisa, A.; Wang, X.; Admassie, S.; Perzon, E.; Oswald, F.; Langa, F.; Andersson, M. R.; Inganas, O. *Org. Electron*. **2006**, *7*, 195.

(13) (a) Adachi, C.; Tsutsui, T.; Saito, S. *Appl. Phys. Lett.* **1989**, *55*, 1489. (b) Kido, J.; Ohtaki, C.; Hongawa, K.; Okuyama, K.; Nagai, K. *Jpn. J. Appl. Phys.* **1993**, *32*, L917. (c) Tanaka, D.; Sasabe, H.; Li, Y. J.; Su, S. J.; Takeda, T.; Kido, J. *Jpn. J. Appl. Phys.* **2007**, *46*, L10. (d) O'Brien, D. F.; Balo, M. A; Thompson, M. E.; Forrest, S. R. *Appl. Phys. Lett.* **1999**, *74*, 442. (e) Adamovich, V. I.; Cordero, S. R.; Djurovich, P. I.; Tamayo, A.; Thompson, M. E.; D', Andrade, B. W.; Forrest, S. R. *Org. Electron*. **2003**, *4*, 77. (f). Xiao, L.; Lan, H;, Kido, J. *Chem. Lett.* **2007**, *6*, 802.

(14) (a) Strukelj, M.; Papadimitrakopoulos, F.; Miller, T. M.; Rothberg, L. J. *Science* **1995**, *267*, 1969. (d) Grice, A. W.; Tajbakhsh, A.; Burn, P. L.; Bradley, D. D. C. *Adv. Mater.* **1997**, *9*, 1174. (e) Peng, Z.; Bao, Z.; Galvin, M. E. *Adv. Mater.* **1998**, *10*, 680.

(15) (a) Lee, Y. Z.; Chen, X.; Chen, S. A.; Wei, P. K.; Fann, W. S. *J. Am. Chem. Soc.* **2001**, *123*, 2296. (b). Yu, L. S.; Chen, S. A. *Adv. Mater*. **2004**, *16*, 744.

10.1021/cm071686y CCC: $37.00

mobilities as high as 10^{-7} m^2/V s have been reported for oxadiazoles,[16] which is higher than the SCLC hole mobility of regioregular P3HT.[17] Forrest et al.[18] used 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) as an exciton block layer and electron transport layer in organic solar cells, and this concept has been applied to other materials.[19] Organic electron transport materials have also been used in their n-doped form in light-emitting devices and photovoltaics.[19a,20] Inorganic counterparts, including titanium oxide, have also been investigated as electron transport and/or exciton blocking layers in polymer solar cells.[21]

The exploration of organic electron transport materials such as triazole for polymer PV applications has been relatively unexplored.[22] We herein report the design; synthesis; characterization; and physical, optical, and electronic transport properties of a novel soluble fullerene modified with an electron transport moiety, triazole, and discuss how modification of the acceptor may assist in the design of polymer−acceptor blends with controlled morphology.

Experimental Section

Materials. C$_{60}$ (99%) was received from MER Corp., and PCBM was purchased from American Dye Source, Inc. Other chemicals were obtained from Aldrich unless otherwise stated. ω-Bromo-*p*-hexyloxy)benzaldehyde[23] and 1-(4-methoxybenzoyl)-2-(4-*tert*-butylbenzoyl)hydrazide[15b] were synthesized using literature methods.

3-(4′-Anisyl)-4-(4′-*n*-butylphenyl)-5-(4′-*tert*-butylphenyl)-1,2,4-triazole (1). A solution of 4-*n*-butylaniline (66.0 g, 0.44 mol) in *o*-dichlorobenzene (100 mL) was stirred under nitrogen, and a solution of phosphorus chloride (19.6 g, 0.14 mol) in *o*-dichlorobenzene (80 mL) was added dropwise. The mixture was stirred at 100 °C for 1 h. 1-(4-Methoxybenzoyl)-2-(4-*tert*-butylbenzoyl)-hydrazide (42.6 g, 0.13 mol) and *o*-dichlorobenzene (100 mL) were added to the solution, and the mixture was refluxed at 180 °C for 3 h. The resulting mixture was concentrated under reduced pressure and the residual solvent removed by distillation with water. The solid was filtered and dried. Recrystallization from ethyl acetate gave 24.5 g of a white solid (yield 42.9%). ^{1}H NMR (500 MHz, DMSO-d_6): 7.26−7.35 (m, 8H), 7.175 (d, 2H), 6.679 (d, 2H), 3.78 (s, 3H), 2.634 (t, 2H), 1.656 (quintet, 2H), 1.232 (s, 9H), 1.20−1.27 (m, 2H), 0.871 (t, 3H).

3-(4′-Phenoyl)-4-(4′-*n*-butylphenyl)-5-(4′-*tert*-butylphenyl)-1,2,4-triazole (2). A solution of boron tribromide (4.3 mL, 46 mmol) in 10 mL of dichloromethane was added dropwise to a suspension of **1** (13.5 g, 30.7 mmol) in dichloromethane (100 mL) at −78 °C under nitrogen. The mixture was allowed to warm to room temperature and stirred overnight. The clear solution was added to water and the precipitate filtered and dried under vacuum to yield 13.0 g of product (yield 100%). ^{1}H NMR (500 MHz, DMSO-d_6): 9.934 (s, 1H), 7.29−7.37 (m, 8H), 7.198 (d, 2H), 6.706 (d, 2H), 2.632 (t, 2H), 1.555 (quintet, 2H), 1.20−1.27 (m, 2H), 1.230 (s, 9H), 0.869 (t, 3H).

4-(6-(4-(5-(4-*tert*-Butylphenyl)-4-(4-butylphenyl)-4*H*-1,2,4-triazol-3-yl)phenoxy)hexyloxy)benzaldehyde (3). A mixture of **2** (5.97 g, 14.0 mmol), ω-bromo-*p*-hexyloxy)benzaldehyde (4.0 g, 14.0 mmol), and potassium carbonate (5.5 g, 28 mmol) in 100 mL of DMF was heated at 140 °C for 2 days. The mixture was cooled and diluted with water, and the product was extracted with ethyl acetate. The crude was purified on a silica gel column to provide 7.9 g (yield 37%) of a white solid. ^{1}H NMR (500 MHz, CD$_2$Cl$_2$): 9.856 (s, 1H), 7.822 (d, 2H), 7.30−7.36 (m, 6H), 7.251 (d, 2H), 7.089 (d, 2H), 7.000 (d, 2H), 6.798 (d, 2H), 4.057 (t, 3H), 3.958 (t, 2H), 2.681 (t, 2H), 1.76−1.88 (m, 4H), 1.627 (quintet, 2H), 1.287 (s, 9H), 1.24−1.40 (m, 2H), 0.937 (t, 3H). Anal. Calcd for C$_{41}$H$_{47}$N$_3$O$_3$: C, 78.19; H, 7.52; N, 6.67. Found: C, 77.95; H, 7.73; N, 6.40.

Fullerene Modified with a Triazole (TAZC60). A mixture of **3** (500 mg, 0.79 mmol), C$_{60}$ (1.14 g, 1.59 mmol), and sarcosine (*N*-methylglycine) (141 mg, 1.59 mmol) was dissolved in 200 mL of chlorobenzene under nitrogen. The mixture was refluxed for 5 h and then the solvent was removed by vacuum distillation. The solid was dissolved in a mixture of chloroform and carbon disulfide and absorbed with silica gel. The absorbed gel was packed on top of a silica gel column. C$_{60}$ was eluted first using carbon disulfide, and the product (620 mg, yield 57.0%) was collected by eluting with a mixture of carbon disulfide and ethyl acetate. The retention factor, R_f, is 0.1 for a 1:9 mixture of carbon disulfide and ethyl acetate. ^{1}H NMR (600 MHz, CDCl$_3$): 7.692 (s, br, 2H), 7.345 (d, J = 8.4, 2H), 7.326 (d, J = 9.0, 2H), 7.276 (d, J = 9.0, 2H), 7.216 (d, J = 8.4, 2H), 7.054 (d, J = 8.4, 2H), 6.934 (d, J = 7.8, 2H), 6.762 (d, J = 9.0, 2H), 4.974 (d, J = 9.6, 1H), 4.822 (s, 1H), 4.241 (d, J = 9.6, 2H), 3.960 (t, J = 6.6, 2H), 3.925 (t, J = 6.6, 2H), 2.788 (s, 3H), 2.679 (t, J = 7.8, 2H), 1.786 (m, 4H), 1.625 (quintet, J = 7.8, 2H), 1.510 (m, 2H), 1.341 (quintet, J = 7.2, 2H), 1.275 (s, 9H), 0.938 (t, J = 7.2, 3H). ^{13}C NMR (150 MHz, CDCl$_3$): 159.923, 159.054, 156.325, 154.599, 154.473, 154.067, 153.615, 152.559, 147.259, 146.772, 146.488, 146.351, 146.266, 146.234, 146.173, 146.117, 146.086, 146.060, 145.901, 145.885, 145.746, 145.506, 145.449, 145.412, 145.302, 145.272, 145.239, 145.199, 145.168, 145.101, 144.665, 144.561, 144.506, 144.357, 143.103, 142.943, 142.637, 142.542, 142.519, 142.504, 142.237, 142.216, 142.126, 142.096, 142.060, 142.049, 141.998, 141.949, 141.931, 141.767, 141.647, 141.492, 140.118, 140.080, 139.851, 139.516, 136.758, 136.515, 135.753, 135.721, 134.956, 132.950, 130.109, 129.815, 128.200, 127.661, 125.266, 124.111, 119.258, 114.195, 83.134, 77.306, 69.909, 68.912, 67.749, 67.696, 39.977, 35.211, 33.145, 31.104, 29.680, 29.200, 29.067, 25.860, 22.156, 13.959. Anal. Calcd for C$_{103}$H$_{52}$N$_4$O$_2$: C, 89.80; H, 3.80; N, 4.07. Found: C, 90.02; H, 3.93; N, 4.20.

4-(2′-Ethyl)hexyloxybenzaldehyde (4). 4-Hydroxybenzaldehyde (6.00 g, 49.1 mmol) was dissolved in butanone (300 mL). Potassium carbonate (27.0 g, 197 mmol), potassium iodide (0.6 g), and 2-ethylhexyl bromide (11.4 g, 58.9 mmol) were added, and the mixture was heated to reflux under nitrogen for 48 h. Upon cooling, water (500 mL) was added and the organic layer extracted with CH$_2$Cl$_2$. The combined organic extracts were washed with 5% aqueous NaOH and water, dried over MgSO$_4$, filtered, and

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(16) (a) Tokuhisa, H.; Era, M.; Tsutsui, T. *Adv. Mater.* **1998**, *10*, 404. (b) Zhang, M.; Hu, Z.; He, T. *J. Phys. Chem. B* **2004**, *108*, 19198.

(17) (a) Mihailetchi, V. D.; Xie, H. X.; de Boer, B.; Koster, L. J. A.; Blom, P. W. M. *Adv. Funct. Mater.* **2006**, *16*, 699. (b) Goh, C.; Kline, R. J.; McGehee, M. D.; Kadnikova, E. N.; Frechet, J. M. J. *Appl. Phys. Lett.* **2005**, *86*, 122110.

(18) (a) Peumans, P.; Bulovic, V.; Forrest, S. R. *Appl. Phys. Lett.* **2000**, *76*, 2650. (b) Rand, B. P.; Li, J; Xue, J.; Holmes, R. J.; Thompson, M. E.; Forrest, S. R. *Adv. Mater.* **2005**, *17*, 2714.

(19) Chan, M. Y.; Lai, S. L; Lau, K. M.; Lee, C. S; Lee, S. T. *Appl. Phys. Lett.* **2006**, *89*, 163515.

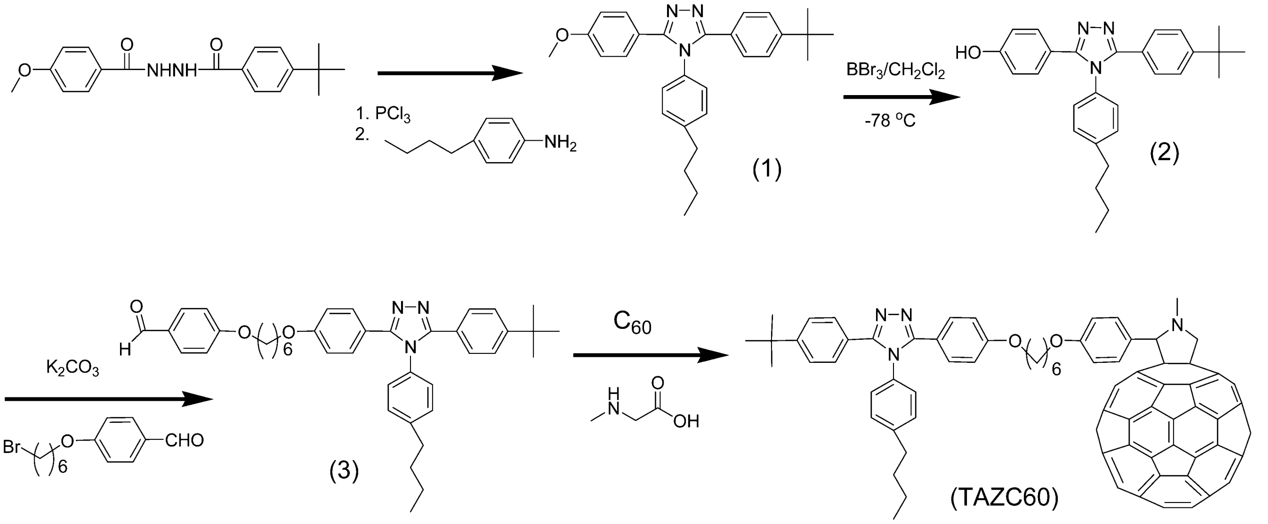
(20) Walzer, K.; Maennig, B.; Pfeiffer, M.; Leo, K. *Chem. Rev.* **2007**, *107*, 1233.

(21) (a) Kim, J. Y.; Kim, S. H.; Lee, H. H; Lee, K.; Ma, W.; Gong, X.; Heeger, A. J. *Adv. Mater.* **2006**, *18*, 572. (b) Hayakawa, A.; Yoshikawa, O.; Fujieda, T.; Uehara, K.; Yoshikawa, S. *Appl. Phys. Lett.* **2007**, *90*, 163517. (c). Kim, J. Y.; Lee, K.; Coates, N. E.; Moses, D.; Nguyen, T. Q.; Dantte, M.; Heeger, A. J. *Science* **2007**, *317*, 222.

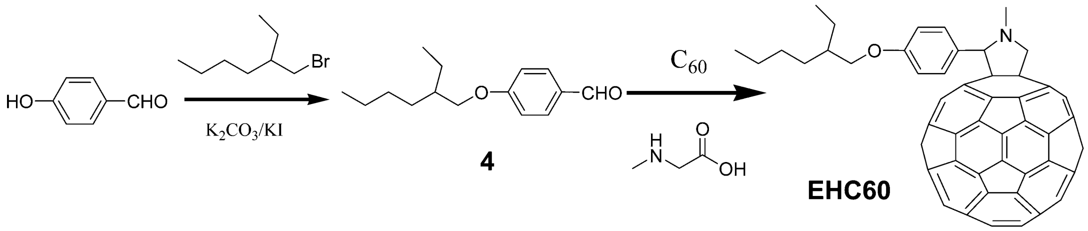
(22) Huang, S. P.; Liao, J. L.; Tseng, H. E.; Jen, T. H.; Liou, J. Y.; Chen, S. A. *Synth. Met.* **2006**, *156*, 949.

(23) Wen, L.; Li, M.; Schlenoff, J. B. *J. Am. Chem. Soc.* **1997**, *119*, 7726.

Scheme 1. Synthetic Route for an Electron Transport Moiety Modified Fullerene (TAZC60)



Scheme 2. A Model Fullerene (EHC60) without the Triazole Moiety



evaporated to give a yellow oil (11.1 g, yield 96.5%). ^{1}H NMR (CD_2Cl_2): 9.876 (1 H, s), 7.836 (2 H, d), 7.036 (2 H, d), 3.962 (2 H, d), 1.797 (1 H, m), 1.3−1.6 (8 H, m), 0.90−0.99 (6 H, m).

EHC60. A mixture of 4-(2′-ethyl)hexyloxybenzaldehyde (**4**) (100 mg, 0.42 mmol), C_{60} (615 mg, 0.84 mmol), and sarcosine (74 mg, 0.84 mmol) was dissolved in 160 mL of chlorobenzene under nitrogen. The mixture was refluxed for 5 h and then concentrated. The concentrated solution was loaded onto a silica gel column. Excess C60 was removed by first eluting with CS_2 and the desired brown solid product (0.23 g, 56% yield) was obtained by eluting with a mixture of toluene/CS_2. ^{1}H NMR ($CD_2Cl_2 + CS_2$): 7.698 (2 H, br, s), 6.933 (2 H, d), 4.990 (1 H, d), 4.907 (1 H, s), 4.276 (1 H, d), 3.849 (2 H, d), 2.805 (3 H, s), 1.722 (1 H, m), 1.3−1.6 (8 H, m), 0.90−0.98 (6 H, m).

Instrumentation. ^{1}H NMR spectra were recorded using a 500 MHz Varian Inova500 or a Bruker Avance 600 QNP cryoprobe. The latter was also used for ^{13}C NMR spectroscopy. Elemental analyses were performed using a Carlo Erba model 1106 C, H, N analyzer. Absorption spectra were collected using Cary 3EI spectrophotometers. Photoluminescence (PL) spectra and absolute quantum yield measurements were recorded using a Photon Technology International QuantumMaster model QM-4 equipped with an extra sample compartment containing an integrating sphere. Samples for fluorescent measurements were excited with 280 nm irradiation. The *relative* quantum efficiency was determined using the same spectrophotometric configuration. The quantum yield of an unknown solution is related to that of a standard through the equation $\Phi_u = (A_s F_u n^2)/(A_u F_s n_0^2)\Phi_s$, where the subscripts u and s refer to the unknown and standard, respectively, Φ is the quantum yield, A is absorbance at the excitation wavelength; F is the integrated emission, and n and n_0 are the refraction indices of the solutions containing unknown and standard. Cyclic voltammetry was carried out on a potentiostat/galvanostat Model 263A (Princeton Applied Research). A one-compartment, three-electrode cell was used with glassy carbon disk working electrode and a platinum wire counter electrode. A Pt wire in a solution of 0.1 M Bu_4NI/0.05 M I_2 in acetonitrile, separated from the working electrode compartment by a glass frit, served as the reference electrode. The materials were dissolved in the electrolytes. The electrolyte was 0.1 M Bu_4NClO_4 in dry toluene and acetonitrile (3:1 v/v). Solutions were deoxygenated using nitrogen gas, and ferrocene served as an internal standard for calibrating the potential of the reference electrode. Current−voltage characteristics of the electron-transport-only devices were measured using a Keithley power supply (model 238), computer-controlled using Labview. The thickness and active area of the films were measured using a Tencor P-10 surface profiler. Impedance spectroscopy was carried out on a Solartron 1260, at a frequency ranging from 100 Hz to 1 MHz, a DC bias of 0 V, and an ac amplitude of ±100 mV at room temperature. Transmission electron microscope (TEM) images were collected with an Hitachi H7600 TEM using an accelerating voltage of 80 kV. Thin films were spin-cast from 25 mg/mL chlorobenzene onto glass coated with poly(styrene sulfonic acid)-doped poly(ethylenedioxythiophene), and the films, floated on water, were picked up on Cu grids. Staining was performed for 60 min using RuO_4 vapor prepared in situ by 0.5% ruthenium(III) chloride in a sodium hypochlorite solution (containing ≥4% chlorine).

Device Fabrication. Cleaned, patterned indium−tin oxide (ITO) glass (Merck) was exposed to oxygen plasma for 5 min at a power of 50 W and a pressure of 200 mTorr. A layer of poly(styrene sulfonic acid)-doped poly(ethylenedioxythiophene) (PEDOT, AI4083, Bayer Corp.) (25 nm) was spin-coated on top of the ITO. TAZC60 in chlorobenzene (25 mg/mL) was filtered through a 5 μm filter and spin-coated at 800 rpm on top of the PEDOT layer inside a glove box. A layer of LiF (3 nm) followed by a layer of aluminum (40 nm) was thermally deposited in a vacuum chamber at 2×10^{-6} Torr pressure through a shadow mask. This device was used to measure the electron mobility of TAZC60. A device for measuring the capacitance of TAZC60 was made in a similar way, except no PEDOT or LiF layers were deposited, and the area and the thickness

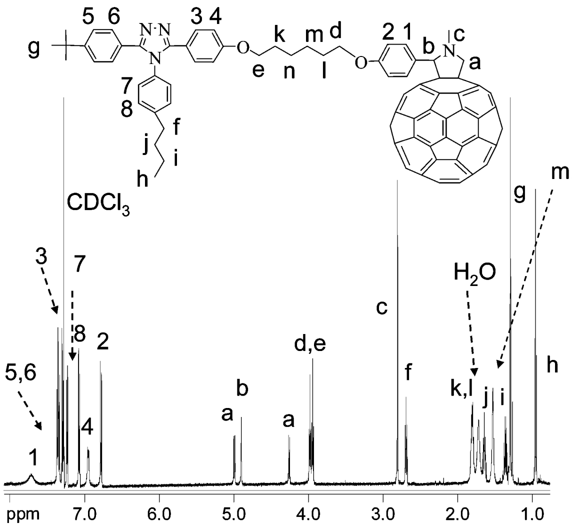


Figure 1. ^{1}H NMR spectrum of TAZC60.

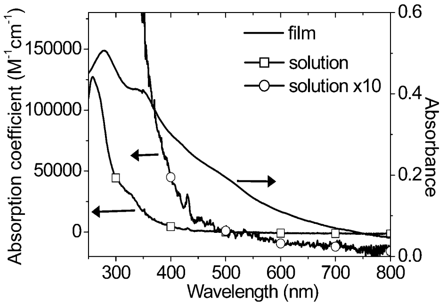


Figure 2. UV−vis absorption spectra of TAZC60 (2 mg/L) in chloroform solution and as a film spin-cast from 5 mg/mL toluene solution.

of the TAZC60 layer were 0.13 cm^2 and 90 nm, respectively. A capacitance of 5.70 × 10^{-9} F was obtained using impedance analysis, and a relative dielectric constant (ϵ_r) of 4.3 for TAZC60 was obtained using the equation $C = \epsilon_0\epsilon_r A/d$, where ϵ_0 is the vacuum permittivity, A is the area, and d is the thickness.

Results and Discussion

The synthetic route for the synthesis of the soluble, triazole-containing C60 (TAZC60) is depicted in Scheme 1. The pyrrolidinofullerene was obtained by a 1,3-dipolar cycloaddition of an azomethine ylide to C60, the former was formed in situ from the aldehyde compound **3** and sarcosine.[24] The assignment of the proton NMR signals are shown in Figure 1. TAZC60 is readily soluble in solvents, such as carbon disulfide, dichloromethane, chloroform, THF, toluene, and chlorobenzene. For comparative purposes, a pyrrolidinofullerene derivative in which the triazole moiety is absent, EHC60 (*N*-methyl-2-(4′-(2′′-ethyl)hexyloxyphenylpyrrolidinofullerene), was prepared according to Scheme 2 and found to be much less soluble than TAZC60. Note that the chiral centers on the pyrrolidine and/or the alkyl chain means that the product is a mixture of diastereoisomers.

The UV−vis absorption spectrum of TAZC60 in chloroform (Figure 2) is characterized by a strong absorption peak at 256 nm, a shoulder at 323 nm, and weak absorption peak at 432 nm. The triazole-free model, EHC60, possesses the same three absorption peaks (Figure 3). The peak at 432 nm can only be observed when the spectrum is expanded (not shown), which is typical for a pyrrolidinofullerene.[24] The triazole compound **3** (see Scheme 1) exhibits an absorption peak at 282 nm, assigned to the triazole moiety. The additive absorption spectrum of EHC60 and **3** is very similar to that of TAZC60, indicating that the absorption spectrum of TAZC60 is the superimposition of individual components of fullerene and triazole and that no significant ground state interaction exists between the fullerene and the triazole. The absorption spectrum of spin-cast films of TAZC60 is characterized by having absorption peaks at 277 and 349 nm, and a shoulder at ~470 nm. The onset of absorption, at 572 nm, yields an estimated band gap of 2.17 eV. This is similar to the value of 2.4 eV reported for PCBM and in the range of values reported for C_{60} films (1.6−2.6 eV).[25]

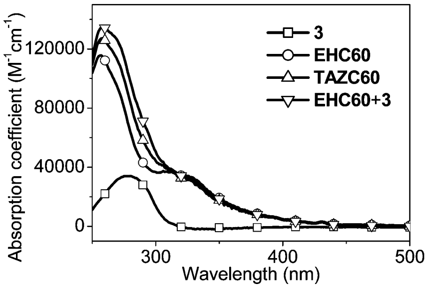


Figure 3. UV−vis absorption spectra of TAZC60, EHC60, and **3** (2 mg/L) in chloroform solutions, along with an additive spectrum of **3** + EHC60.

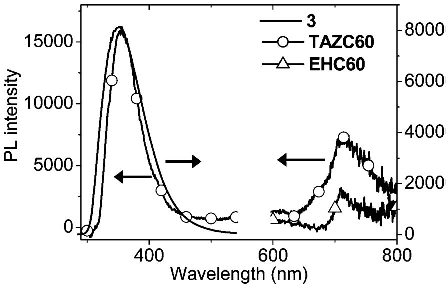


Figure 4. Photoluminescent spectra of **3**, TAZC60, and EHC60 in 2 mg/L chloroform solutions.

The PL of triazole compound **3** in chloroform (2 mg/L) is shown in Figure 4 and is characterized as possessing a PL peak at 354 nm due to emission from TAZ. Irradiation of EHC60 gave rise to a weak signal at 712 nm (Figure 4) due to emission from C60. The PL of a solution of TAZC60 in chloroform (2 mg/L), obtained using identical spectrophotometric parameters, is also shown in Figure 4. The PL spectrum shows peaks at 354 and 712 nm due to emission from the TAZ and C60 component, respectively. Qualitatively, the emission at 354 nm due to the TAZC60 is observed to be at least an order of magnitude lower than that of compound **3**. The absolute quantum yield of **3** obtained using an integrating sphere is found to be 5.2%, whereas the quantum yields for TAZC60 and EHC60 are too low to measure. The *relative* quantum yields of TAZC60 to EHC60 were calculated according to the method described in the Experimental Section. It was found that the *relative*

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(24) Maggini, M.; Scorrano, G.; Prato, M. *J. Am. Chem. Soc.* **1993**, *115*, 9798.

(25) Ren, S. L.; Wang, Y.; Rao, A. M.; McRae, E.; Holden, J. M.; Hager, T.; Wang, K. A.; Lee, W. T.; Ni, H. F.; Selegue, J.; Eklund, P. C. *Appl. Phys. Lett.* **1991**, *59*, 2678.

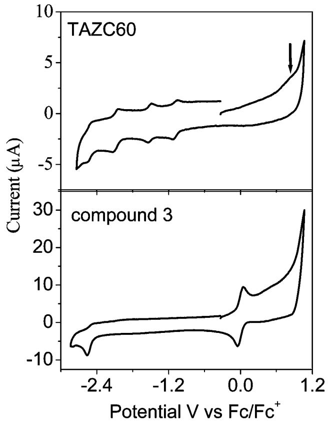

Figure 5. Cyclic voltammogram of TAZC60 and **3** (+ferrocene) in 0.1 M Bu_4NClO_4 in toluene/acetonitrile (3:1 v/v) at a scan rate of 50 mV/s at room temperature.

quantum yield of TAZC60 to EHC60 in chloroform solution due to emission from the C60 component is ~1.9 when excited with 280 nm. At 280 nm, light is absorbed by both the TAZ and C60 groups in TAZC60 and solely by C60 in EHC60. Coupled with the fact that TAZ emission is quenched, this indicates that energy transfer from TAZ to C60 occurs in TAZC60 to some extent. It also indicates that photoinduced electron transfer from TAZ to C60 is not significant, since this would lead to a reduced emission from C60. Energy transfer not electron transfer has also been found in fullerene−oligophenylenevinylenes.[26]

The electrochemistry of the TAZC60 in 0.1 M Bu_4NClO_4 in toluene/acetonitrile (3:1 v/v) was studied by cyclic voltammetry (CV). Four pairs of quasireversible redox peaks with $E_{1/2}$ at −1.09, −1.52, −2.09, and −2.53 V vs Fc/Fc$^+$ were found at room temperature (Figure 5). The potentials of these four redox processes are very similar to those reported for *N*-methylpyrrolidinofullerene (−1.13, −1.52, −2.08, and −2.49 V vs Fc/Fc$^+$), obtained at low temperature.[27] The C60-free triazole compound, **3**, exhibited an irreversible cathodic current at −2.49 V, which overlaps with the fourth cathodic peak of the fullerene. For the anodic scan of TAZC60, there is a weak oxidation peak at ~0.9 V on top of a rising background current. The observation that TAZC60 may be oxidized or reduced may indicate ambipolar charge transport for this molecule—a phenomenon that has been reported for both PCBM and single crystals of C_{60} using time-of-flight and field effect transistor measurements.[28]

From the cathodic redox peak at −1.09 V, the LUMO energy level of TAZC60 was estimated to be 3.7 eV, assuming that the Fc/Fc$^+$ redox couple is 4.8 eV with respect to an electron in vacuum.[29] TAZC60 thus possesses a similar LUMO energy to PCBM. In conjunction with the band gap estimated from the onset of absorption (2.17 eV), the HOMO energy level for TAZC60 is estimated to be 5.9 eV. Similarly, for the C60-free triazole compound, **3**, the LUMO and HOMO levels are estimated to be ~2.4 and ~6.3 eV, respectively.

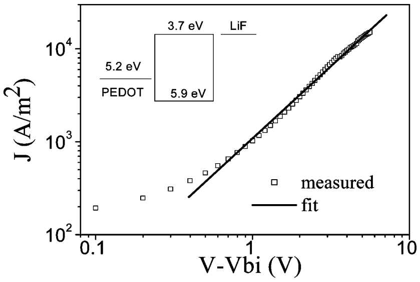

Figure 6. Experimental (open squares) and calculated (line) *J*−*V* characteristics for an ITO/PEDOT/TAZC60(100 nm)/LiF/Al device. V_{bi} ~1.4 eV. Inset, device energy band diagram.

The electron mobility in TAZC60 was measured using an electron-only device, ITO/PEDOT/TAZC60/LiF/Al, similar to that used to determine the electron mobility of PCBM.[30] As TAZC60 possesses a similar LUMO energy level to PCBM and it has been shown that LiF/Al forms an Ohmic contact for electron injection into PCBM, it is reasonably assumed that an Ohmic contact is formed between LiF/Al and TAZC60. PEDOT possesses a work function of ~5.0−5.2 eV, and given that the HOMO energy level of TAZC60 is 5.9 eV, a barrier height of >0.7 eV prevents hole injection from PEDOT into TAZC60. A band diagram for this structure is shown as an inset in Figure 6. The current density, *J*, versus applied internal voltage was analyzed by using eq 1, which describes the space-charge limited current:[31]

$$J = \frac{8}{9}\epsilon_0\epsilon_r\mu_e\frac{V_{\mathrm{int}}^{\ 2}}{L^3} \tag{1}$$

where μ_e is the zero-field electron mobility, ϵ_0 is the vacuum permittivity, ϵ_r is the relative dielectric constant, V_{int} is the applied voltage, and *L* is the film thickness. A dielectric constant of 4.3 was measured for TAZC60 by determining the capacitance of a TAZC60 film. This value falls between the range of reported data for C60 (3.6−4.6)[25] and is similar to that of PCBM (~3.9).[30]

The *J*−*V* characteristic of the electron-only device is shown in Figure 6. V_{bi} represents the built-in potential that is formed as a result of the film being in contact with an anode and cathode having significantly different work functions. An opposite bias must be exceeded for current to flow in the forward direction. A V_{bi}, of 1.4 V was used as previously reported.[30] The linear fit of the *J*−*V* curve provided an electron mobility value of 2.5 × 10^{-8} m^2/V s. For comparison, a typical electron mobility for PCBM based on SCLC measurements is reported to be ~2 × 10^{-7} m^2/V s.[30] The electron mobility of TAZC60 is therefore an order of magnitude lower than that of PCBM[30] but comparable to

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(26) Armaroli, N.; Barigelletti, F.; Ceroni, P.; Eckert, J. F.; Nicoud, J. F.; Nierengarten, J. F. *Chem. Commun.* **2000**, 599.

(27) Prato, M.; Maggini, M.; Giacometti, C.; Scorrano, G.; Sandonh, G.; Farnia, G. *Tetrahedron* **1996**, *52*, 5221.

(28) (a) Tuladhar, S. M.; Poplavskyy, D.; Choulis, S. A.; Durrant, J. R.; Bradley, D. D. C.; Nelson, J. *Adv. Funct. Mater.* **2005**, *15*, 1171. (b) Frankevich, E.; Maruyama, Y.; Ogata, H. *Chem. Phys. Lett.* **1993**, *214*, 39. (c) Anthopoulos, T. D.; Tanase, C.; Setayesh, S.; Meijer, E. J.; Hummelen, J. C.; Blom, P. W. M.; de Leeuw, D. M. *Adv. Mater.* **2004**, *16*, 2174.

(29) Pommerehne, J.; Vestweber, H.; Guss, W.; Mahrt, R. F.; Bassler, H.; Porsch, M.; Daub, J. *Adv. Mater.* **1995**, *7*, 551.

(30) Mihailetchi, V. D.; van Duren, J. K. J.; Blom, P. W. M.; Hummelen, J. C.; Janssen, R. A. J.; Kroon, J. M.; Rispens, M. T.; Verhees, W. J. H.; Wienk, M. M. *Adv. Funct. Mater.* **2003**, *13*, 43.

(31) Lampert, M. A.; Mark, P. *Current Injection in Solids*; Academic Press: New York, 1970.

or an order of magnitude higher than that of other fullerenes described in the literature.[10a,12b] Note that charge mobilities measured by the SCLC technique are orders of magnitude lower that those measured by the field effect transistor technique.[32]

Judging from difference between LUMO energy levels of triazole and fullerene (2.4 and 3.7 eV, respectively), it would appear that triazole is unable to contribute to electron transport through TAZC60 films because the barrier to electron injection from C60 to TAZ is as high, 1.3 eV. However, it is worth noting that in the case of organic light-emitting devices (OLEDs) TAZ may serve as an electron transport material because the emissive materials employed possess LUMOs that are closer in energy to TAZ. Furthermore, it has been reported that triazole incorporated into the side chain of poly(phenylene vinylene) (PPV) improves its performance in light-emitting diodes, even though the LUMO level of TAZ (2.4 eV) lies higher than that of PPV (2.8 eV). LEDs based on TAZ-PPV show increased electron flux and decreased hole flux, thus providing a more balanced charge transport.[15b] A higher built-in potential (1.2 V versus 0.9 V) than triazole-free PPV devices was also observed using a Al cathode.[15b] Similarly, a MEH-PPV [poly(2-methoxy-5-ethylhexyl-phenylene vinylene)] device (ITO/MEH-PPV/LiF/Al) that incorporates LiF between the Al and the polymer exhibits a higher built-in potential than ITO/MEH-PPV/Al devices (1.4 versus 1.0 V).[33] It was concluded that triazoles attached to the side chains of PPV perform a similar function to LiF layers introduced between the polymer and Al by reducing the barrier to electron injection from Al to the conjugated polymer,[15b] as do the organic materials, such as BCP.[34,18] This leads to the speculation that the actual energy level for electron transport of triazole at the interfaces of triazole/electrode, triazole/PPV, and triazole/fullerene might thus be lower relative to the reported LUMO value.

A preliminary TEM study of TAZC60 spin-cast sample indicates that the film possesses a bicontinuous, nanophase morphology (Figure 7), that two electron transport channels may potentially exist for TAZC60, and that both could potentially contribute to the overall rate of electron transport. The exact nature of this morphology is uncertain: the darker domain might be due to the C60 component, since it possesses more double bonds than TAZ and TEM contrast is induced by staining by reaction of double bonds with ruthenium tetraoxide. However, it may be that if the TAZC60 possesses both amorphous and crystalline domains and if staining predominantly occurs in the former, then TEM simply distinguishes between amorphous and crystalline domains. Similarly, a TEM image of a PCBM film, spin-cast also from chlorobenzene, shows a nanophase structure after staining. It is speculated that TEM contrast might arise from the nanocrystal nature of PCBM spin-cast film.[35] In order to elucidate the morphology of TAZC60 further, its crystal structure will be determined in order to investigate to see if the modification of C60 by triazole disrupts the favorable crystal structure of fullerene, which is essential for the high mobility of PCBM.[36]

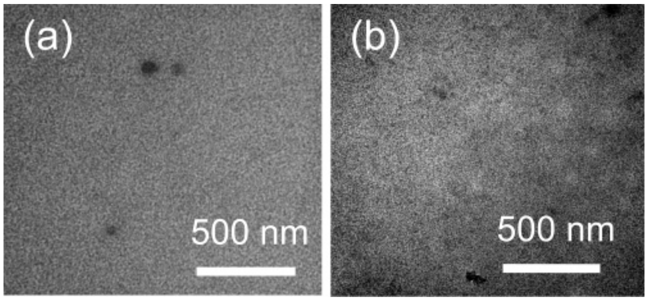

Figure 7. TEM images of TAZC60 (a) and PCBM (b) as spin-cast films from chlorobenzene solution, staining with RuO_4.

In summary, a novel, soluble fullerene possessing an electron transport moiety was synthesized and characterized. The optical and electronic properties are similar to those of PCBM, except the electron mobility, which is large but 1 order of magnitude lower. This work provides a preliminary study of materials in which electron transport moiety is attached to a fullerene. If the LUMO energies of the attached electron transport moiety and fullerene are not too dissimilar and if a bicontinous percolation pathway exists, then new and interesting electron transport materials for a variety of applications may be developed. In the case of TAZC60, a bicontinous morphology is present, and although the difference between the LUMO energy levels of TAZ and C60 appears too large for cooperative electron transport, the presence of TAZ may assist in electron injection in device applications, as has been observed for TAZ-PPV systems. Experiments are underway to evaluate these materials in organic electronic devices. Future work will be directed to attaching electron transport moieties that more closely match the LUMO of fullerenes.

Acknowledgment. We thank financial support from the Natural Sciences and Engineering Research Council of Canada and the National Science Council of Republic of China (Project No. 95-2752-E-007-005 and 008-PAE). We thank Dr. Ken Shi of Institute for Fuel Cell Innovation, National Research Council Canada, Vancouver, BC V6T 1W5, Canada, for assistance in obtaining TEM images.

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(32) Nierengarten, J. F.; Gu, T.; Aernouts, T.; Geens, W.; Poortmans, J.; Hadziioannou, Tsamouras, D. *Appl. Phys. A* **2004**, *79*, 47.

(33) Yang, X.; Mo, Y.; Yang, W.; Yu, G.; Cao, Y. *Appl. Phys. Lett.* **2001**, *79*, 563.

(34) O'Brien, D. F.; Baldo, M. A.; Thompson, M. E.; Forrest, S. R. *Appl. Phys. Lett.* **1999**, *74*, 442.

(35) Yang, X.; van Duren, J. K. J.; Rispens, M. T.; Hummelen, J. C.; Janssen, R. A. J.; Michels, M. A. J.; Loos, J. *Adv. Mater.* **2004**, *16*, 802.

(36) Rispens, M. T.; Meetsma, A.; Rittberger, R.; Brabec, C. J.; Sariciftci, N. S.; Hummelen, J. C. *Chem. Commun.* **2003**, 2116.