



Material Matters™

Chemistry Driving Performance

2007
VOLUME 2
NUMBER 3



Organic Electronics



Organic Materials
For Thin Film
Transistors

Polymers for
Plastic Electronics

Fullerene-Based
Semiconductors

Organic
Light-Emitting
Devices

Light-Emitting
Polymers

*Printed circuits for a
cleaner and brighter future.*



Introduction

Welcome to the third installment of *Material Matters*™ for 2007 focusing on Organic Electronics. Started over 30 years ago with the discovery that organic molecules can act as electrical conductors, this field is on the verge of the first commercially successful applications. Low-cost manufacturing methods and compatibility with flexible substrates are two of the exciting features of plastic electronics. One day soon, these attributes may enable disposable RFID tags made from interconnected organic field-effect transistors (OFETs), or large-area photovoltaic cells (PVs) painted on building roofs and economically replaced every other year to match color preferences of homeowners. Bright, high-resolution flat-screen displays made from organic light-emitting diodes (OLEDs) are closest to commercial success, but remain expensive and power-hungry relative to the entrenched technologies. Steady advances in the quality and variety of available organic conductors, as well as a fundamental understanding of materials physics and device engineering, enabled progress from early polymer conductors to the present day OFETs and OLEDs.

In this issue, Professor Zhenan Bao (Stanford University) describes organic materials essential for making better OFETs. The article is accompanied by a selection of p-type and n-type semiconductors as well as polymer dielectrics available from Sigma-Aldrich. Scientists from TDA Research, Inc. describe novel intrinsically conductive polymers and n-type semiconductors that are now available from Sigma-Aldrich and could enhance performance of many plastic electronic devices. Researchers from the University of Groningen (Netherlands) write about methanofullerenes, a class of compounds widely used as n-type semiconductors in organic PVs. Sigma-Aldrich is pleased to offer an entire library of soluble n-type methanofullerene semiconductors that will help you explore materials and processing parameters toward improved device performance. Eugene Polikarpov and Professor Mark Thompson (USC) discuss strategies for improving the efficiency of small molecule OLEDs. The article is accompanied by a list of Sigma-Aldrich OLED materials classified by device function. Finally, Professor Qibing Pei (UCLA) writes about the chemistry of light-emitting polymers (LEPs). Sigma-Aldrich offers many chemical families of LEPs, as well as monomers and reagents essential for making new LEP molecules.

Commencing with this issue, we are pleased to introduce a new "Your Materials Matter" feature (page 3) to *Material Matters*. Our goal at Sigma-Aldrich Materials Science is to provide innovative materials that meet your needs. Tell us what materials will accelerate your research, and we will carefully consider adding them to our portfolio of products. We hope that the articles and Sigma-Aldrich products featured in this issue will help you in your work. Please contact the Sigma-Aldrich Materials Science Team at matsci@sial.com if you need a material that you cannot find in our catalog.

Ilya Koltover, Ph.D.
Materials Science
Sigma-Aldrich Corporation

About Our Cover

Organic electronic devices can be fabricated on many substrates, including glass, flexible plastics, and even building roofs. Soluble organic semiconductors, such as the TDCV-TPA featured on our cover and described in the new "Your Materials Matter" feature on page 3, will enable economical processing of organic circuits by techniques of high-throughput printing. Resulting technologies will include ultra-thin television sets delivering crisper pictures than today's LCDs, inexpensive RFID tags, and low-cost solar panels integrated into buildings, cars, and clothing fabrics.

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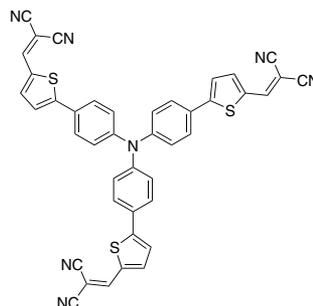
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(1) Roquet, S.; Cravino, A.; Leriche, P.; Alévêque, O.; Frère, P.; Roncali, J., *J. Am. Chem. Soc.* **2006**, *128*, 3459. (2) Cravino, A.; Leriche, P.; Alévêque, O.; Roncali, J., *Adv. Mater.* **2006**, *18*, 3033.

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Materials for Organic Electronics Featured in This Issue

Materials Category	Content	Page	Also See Page
p-Type Semiconductors	p-type small molecules, oligomers and polymers	7	10, 20, 24
n-Type Semiconductors	n-type molecules and polymers	8	14, 20
Dielectric Materials	Polymers and cross-linking agents for dielectric layers	9	
Conducting Thin Film Materials	Inherently conducting materials for deposition of thin films and hole-injection layers	15	
Materials for Organic Photovoltaics	n-type (PCBMs) and p-type (PPV, P3HT) materials for OPVs	20	2, 7–8, 29
OLED Materials	Hole transport, electron transport, host, and emitter/dopant materials.	24–25	15, 31
Light-Emitting Polymers	PPV, CN-PPV, PFO, and water-soluble LEPS	29–30	7, 20
Substrates and Electrodes	ITO substrates, high-purity metals	31	9

For questions, product data, or new product suggestions, please contact the Materials Science team at matsci@sial.com.



Prof. Zhenan Bao
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Introduction

Flexible electronic circuits, displays, and sensors based on organic active materials will enable future generations of electronics products that may eventually enter the mainstream electronics market. The motivations in using organic active materials come from their ease in tuning electronic and processing properties by chemical design and synthesis, low cost processing based on low temperature processes and reel-to-reel printing methods, mechanical flexibility, and compatibility with flexible substrates.^{1,2}

Organic thin film transistors (OTFTs) are the basic building blocks for flexible integrated circuits and displays. A schematic structure is shown in **Figure 1**. During the operation of the transistor, a gate electrode is used to control the current flow between the drain and source electrodes. Typically, a higher applied gate voltage leads to higher current flow between drain and source electrodes. The semiconductor material for a fast switching transistor should have high charge carrier mobility and on/off current ratio. For pixel switching transistors in liquid crystal displays, mobility greater than 0.1 cm²/Vs and on/off ratio greater than 10⁶ are needed.

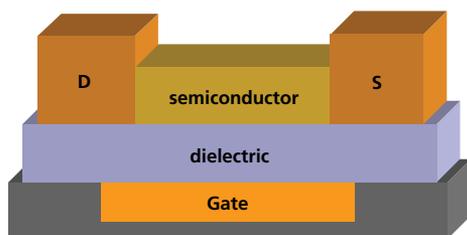


Figure 1. Schematic structure of an organic thin film transistor (OTFT). S: source; D: drain.

To make OTFTs, materials ranging from conductors (for electrodes), semiconductors (for active channel materials), to insulators (for gate dielectric layers) are needed. This article will discuss the basic requirements for these materials and give examples of some representative materials.

Organic Semiconductors

There are two types of organic semiconductors based on the type of majority charge carriers: p-type (holes as major charge carriers) and n-type (electrons as major charge carriers). To facilitate charge transport, the organic semiconductor layer usually consists of π -conjugated oligomers or polymers, in which the π - π stacking direction should ideally be along the current flow direction. This requires the semiconductor molecules to self-assemble into a certain orientation upon either vapor or solution deposition. It is also important that the semiconductor thin film has large, densely packed and well-interconnected grains. Most small molecule, high performance organic semiconductors tend to have the long axes of the molecules oriented close to normal to the dielectric surface (**Figure 2a**) with the typical grain size in the order of at least a few micrometers. In case of solution processed semiconducting polymers, it is preferred for the π -conjugated plane to adapt an edge-on orientation on the surface (**Figure 2b**).

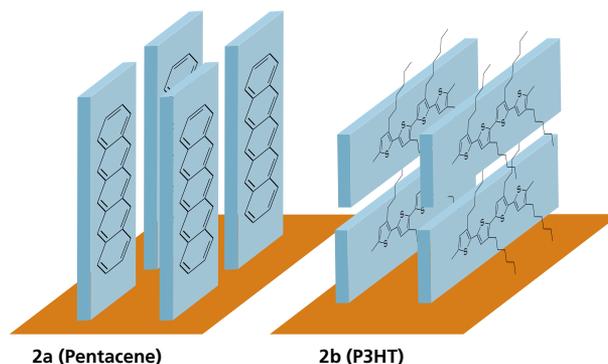


Figure 2. Molecular orientation of high-performance organic semiconductors. (a) Pentacene molecules assemble with the long axis oriented perpendicular to the dielectric surface. (b) Molecules of regioregular poly(3-hexylthiophene) (P3HT) spontaneously assemble into ordered structures with edge-on orientation. The π - π stacking between polymer chains facilitates charge transport.

The morphology of the semiconductor film is highly dependent on the chemical and physical nature of the dielectric surface. Patterning of dielectric surface can lead to selective patterning of the organic semiconductor in desired locations, which is important to reduce cross talk between devices. With proper control of the dielectric surface, arrays of organic semiconductor single crystals can be patterned over a large area for high performance transistors.³

Great progress has been made in the development of organic semiconductor materials. The initial demonstration of transistor activity in these films was with a narrow group of p-channel thiophene oligomers and polymers. The reported mobilities were on the order of 0.01–0.1 cm²/Vs.^{4,5} During the last few years, a much broader selection of molecular solids and polymers has been developed, all with mobilities above 0.1 cm²/Vs and achievable on/off ratios greater than 10⁵.¹ The chemical structures of some representative materials are shown in **Figure 3**. p-Channel compounds in this category include substituted thiophene oligomers, pentacene, acenes, and their derivatives, phthalocyanine- and thiophene-based fused ring compounds, and fluorene oligomer derivatives. Regioregular poly(3-hexylthiophene) is one of the few polymer semiconductors that spontaneously assembles into well ordered structures upon solution deposition by drop casting or spin coating⁶ (Figure 3) and gives a mobility greater than 0.1 cm²/Vs.^{7,8} More recently, a few new polythiophene derivatives have been reported and show improved mobility and air stability (Figure 3, g,h).^{9,10}

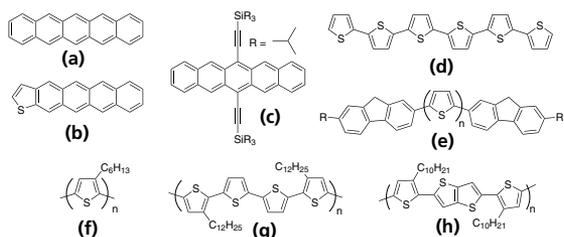


Figure 3. Chemical structures of some representative p-channel organic semiconductors. (a) pentacene;^{11,12} (b) tetraceno[2,3-b]thiophene;¹³ (c) TIPS-pentacene;¹⁴ (d) α -sexithiophene;^{4,5} (e) oligothiophene-fluorene derivative;¹⁵ (f) regioregular(poly(3-hexylthiophene));⁷ (g) poly(3,3''-didodecylquaterthiophene);¹⁶ (h) poly(2,5-bis(3-decylthiophen-2-yl)thieno[3,2-b]thiophene).¹⁰

Complementary metal oxide semiconductor (CMOS) circuits are desirable because of their ease in circuit design and low power consumption. CMOS inverters usually consist of a p- and an n-channel transistor. Several classes of organic materials have displayed good n-channel activity, including C₆₀, perfluoro-copper phthalocyanine, and naphthalene and perylene-based compounds.^{17,18,19,20} **Figure 4** shows the chemical structures of some representative high performance air-stable n-channel semiconductors. More recently, ambipolar behavior for certain organic semiconductors has also been reported.²¹ This type of material can be used for the fabrication of complementary circuits without the need to pattern the p- and n-channel semiconductors separately.

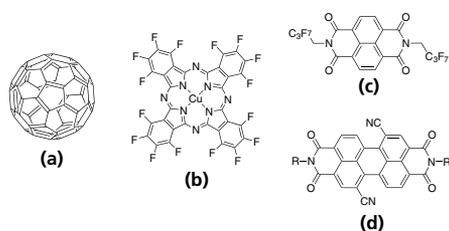


Figure 4. Chemical structures of some representative n-channel organic semiconductors. (a) C₆₀;²² (b) hexadecafluoro copper phthalocyanine (F₁₆CuPc);²⁰ (c) naphthalene diimide derivative;¹⁹ (d) perylene diimide derivative.¹⁸

Dielectric Materials

The dielectric layer for organic transistors should be as thin as possible, pinhole-free, and ideally with a high dielectric constant for low voltage operation. Inorganic, organic, and inorganic/organic hybrid materials have been investigated as the gate dielectric materials. Promising materials include poly(methyl methacrylate) (PMMA), poly(styrene), poly(vinyl phenol), silsesquioxane (glass resin), and benzocyclobutene (BCB), etc. (**Figure 5a**).^{23,24,25} Crosslinked polymers generally are more robust as ultrathin dielectric materials.²⁶ Examples of cross-linkers used to make dielectric materials are shown in **Figure 5b**. Even a well-ordered densely packed self-assembled monolayer (SAM) may be used as the thinnest possible high quality dielectric layer.²⁷ Incorporation of high dielectric constant inorganic nanoparticles into a polymer matrix boosts the overall dielectric constant of the thin film.²⁸

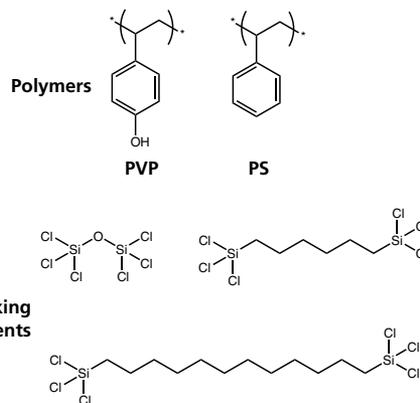


Figure 5. Examples of dielectric materials and cross-linkers. Siloxane cross-linkers can be used to enhance stability of PVP (polyvinylphenol) and PS (polystyrene) gate insulating layers.²¹

Surface treatment of the dielectric layer is an important method to improve organic transistor performance. Most of the charge carriers induced in the semiconductor layer are confined to the first 5 nm of the organic semiconductor film adjacent to the semiconductor/dielectric interface. Thus, the chemical and physical characteristics of the dielectric surface have a significant effect on the charge carrier transport. For example, Si-OH groups on SiO₂ surface (a typical dielectric material) are known to trap electrons. Capping SiO₂ surfaces with octadecyl trichlorosilane (OTS, Aldrich Prod. No. **104817**) molecules can significantly reduce electron traps and improve mobility of n-channel semiconductors (electrons are the major charge carriers).²³

Additionally, dielectric surface treatment with SAMs also affects the nucleation and growth of organic semiconductors.²⁹ For example, pentacene is an organic semiconductor with the highest reported thin film charge carrier mobility. Its charge carrier mobility changes significantly depending on the types of hydrophobic SAM surface treatment of the dielectric. This difference is related to the morphological difference of the first pentacene monolayer formed on different surfaces.²⁹

Electrode Materials

For organic transistors to function properly, charge injection from the electrode needs to be efficient. This requires the work function of the electrode to match well with the energy level of the organic semiconductor such that the energy barrier for charge injection is low. Typically high work function electrodes (Au, Pd, or indium tin oxide) have been used for p-channel organic transistors. Electrode surface modification with a self-assembled monolayer can be used to improve the charge injection into the organic semiconductor.³⁰ When the organic semiconductor is deposited onto the source and drain electrodes, the morphology of organic semiconductors is significantly different when deposited on SAM-modified Au compared to bare Au. This observation has been used to tune the morphology of the organic semiconductor at the Au/organic interface to improve its charge injection.³¹

Solution processable electrode materials are desirable for low cost production. To that end, a few groups have developed Au or Ag nanoparticle inks that can be cured at below 200 °C to be compatible with low cost plastic substrates.³² Carbon nanotube dispersion and conducting polymer solutions are among other promising electrode candidates.

In summary, organic materials are promising candidates for flexible electronic devices. Significant progress has already been made in this field. Nevertheless, better understanding of the structure property relationship is still needed so that we can rationally design materials to achieve desired device performance parameters.

References:

- (1) *Organic Field Effect Transistors*; Bao, Z.; Locklin, J., Eds.; Taylor and Francis Group, LLC, **2007**.
- (2) Ling, M. M.; Bao, Z. N. *Chemistry of Materials* **2004**, *16*, 4824–4840.
- (3) Briseno, A. L.; Mannsfeld, S. C. B.; Ling, M. M.; Liu, S. H.; Tseng, R. J.; Reese, C.; Roberts, M. E.; Yang, Y.; Wudl, F.; Bao, Z. N. *Nature* **2006**, *444*, 913–917.
- (4) Garnier, F.; Hajlaoui, R.; Yassar, A.; Srivastava, P. *Science* **1994**, *265*, 1684–1686.
- (5) Dodabalapur, A.; Torsi, L.; Katz, H. E. *Science* **1995**, *268*, 270–271.
- (6) McCullough, R. D. *Advanced Materials* **1998**, *10*, 93–116.
- (7) Bao, Z.; Dodabalapur, A.; Lovinger, A. *J. Appl. Phys. Lett.* **1996**, *69*, 4108–4110.
- (8) Sirringhaus, H.; Tessler, N.; Friend, R. H. *Science* **1998**, *280*, 1741–1744.
- (9) Pan, H.; Li, Y.; Wu, Y.; Liu, P.; Ong, B. S.; Zhu, S.; Xu, G. *J. Am. Chem. Soc.* **2007**, *129*, 4112–4113.
- (10) McCulloch, I.; Heeney, M.; Bailey, C.; Genevicius, K.; Macdonald, I.; Shkunov, M.; Sparrowe, D.; Tierney, S.; Wagner, R.; Zhang, W. M.; Chabynyc, M. L.; Kline, R. J.; McGehee, M. D.; Toney, M. F. *Nature Materials* **2006**, *5*, 328–333.
- (11) Klauk, H.; Jackson, T. N. *Solid State Technology* **2000**, *43*, 63.
- (12) Kelley, T. W.; Baude, P. F.; Gerlach, C.; Ender, D. E.; Muires, D.; Haase, M. A.; Vogel, D. E.; Theiss, S. D. *Chemistry of Materials* **2004**, *16*, 4413–4422.
- (13) Tang, M. L.; Okamoto, T.; Bao, Z. N. *J. Am. Chem. Soc.* **2006**, *128*, 16002–16003.
- (14) Anthony, J. E.; Brooks, J. S.; Eaton, D. L.; Parkin, S. R. *J. Am. Chem. Soc.* **2001**, *123*, 9482–9483.
- (15) Meng, H.; Zheng, J.; Lovinger, A. J.; Wang, B. C.; Van Patten, P. G.; Bao, Z. N. *Chemistry of Materials* **2003**, *15*, 1778–1787.
- (16) Ong, B. S.; Wu, Y. L.; Liu, P.; Gardner, S. *J. Am. Chem. Soc.* **2004**, *126*, 3378–3379.
- (17) Chikamatsu, M.; Nagamatsu, S.; Yoshida, Y.; Saito, K.; Yase, K.; Kikuchi, K. *Applied Physics Letters* **2005**, *87*.
- (18) Jones, B. A.; Ahrens, M. J.; Yoon, M. H.; Facchetti, A.; Marks, T. J.; Wasielewski, M. R. *Angew. Chem. Int. Ed.* **2004**, *43*, 6363–6366.
- (19) Katz, H. E.; Lovinger, A. J.; Johnson, J.; Kloc, C.; Siegrist, T.; Li, W.; Lin, Y. Y.; Dodabalapur, A. *Nature* **2000**, *404*, 478–481.
- (20) Bao, Z. A.; Lovinger, A. J.; Brown, J. *J. Am. Chem. Soc.* **1998**, *120*, 207–208.
- (21) Yoon, M. H.; Kim, C.; Facchetti, A.; Marks, T. J. *J. Am. Chem. Soc.* **2006**, *128*, 12851–12869.
- (22) Haddon, R. C.; Perel, A. S.; Morris, R. C.; Palstra, T. T. M.; Hebard, A. F.; Fleming, R. M. *Appl. Phys. Lett.* **1995**, *67*, 121–123.
- (23) Chua, L. L.; Zaumseil, J.; Chang, J. F.; Ou, E. C. W.; Ho, P. K. H.; Sirringhaus, H.; Friend, R. H. *Nature* **2005**, *434*, 194–199.
- (24) Bao, Z. N.; Kuck, V.; Rogers, J. A.; Paczkowski, M. A. *Adv. Funct. Mater.* **2002**, *12*, 526–531.
- (25) Liu, P.; Wu, Y. L.; Li, Y. N.; Ong, B. S.; Zhu, S. P. *J. Am. Chem. Soc.* **2006**, *128*, 4554–4555.
- (26) Yoon, M. H.; Yan, H.; Facchetti, A.; Marks, T. J. *J. Am. Chem. Soc.* **2005**, *127*, 10388–10395.
- (27) Halik, M.; Klauk, H.; Zschieschang, U.; Schmid, G.; Dehm, C.; Schutz, M.; Maisch, S.; Effenberger, F.; Brunnbauer, M.; Stellacci, F. *Nature* **2004**, *431*, 963–966.
- (28) Maliakal, A.; Katz, H.; Cotts, P. M.; Subramoney, S.; Mirau, P. *J. Am. Chem. Soc.* **2005**, *127*, 14655–14662.
- (29) Yang, H. C.; Shin, T. J.; Ling, M. M.; Cho, K.; Ryu, C. Y.; Bao, Z. N. *J. Am. Chem. Soc.* **2005**, *127*, 11542–11543.
- (30) Gundlach, D. J.; Jia, L. L.; Jackson, T. N. *IEEE Electr. Dev.* **2001**, *22*, 571–573.
- (31) Kymissis, I.; Dimitrakopoulos, C. D.; Purushothanman, S. *IEEE Trans. Elec. Dev.* **2001**, *48*, 1060–1064.
- (32) Wu, Y. L.; Li, Y. N.; Ong, B. S. *J. Am. Chem. Soc.* **2007**, *129*, 1862–1863.

Aldrich Adjustable Sublimation Apparatus

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Molecular Semiconductors

Sigma-Aldrich offers many molecular semiconductors for applications in organic electronics. The following tables list some of the available p-type and n-type conductors. For a complete list, please visit us at sigma-aldrich.com/organelectronics.

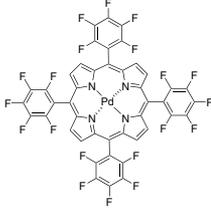
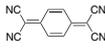
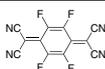
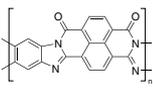
p-Type Semiconductors

Description	Structure	*Mobility (cm ² /Vs) On/Off ratio	Prod. No.
Benz[<i>b</i>]anthracene, (tetracene) 98%		0.4 cm ² /Vs	B2403-100MG B2403-500MG B2403-1G
Pentacene		0.4–3 cm ² /Vs	P1802-100MG P1802-1G P1802-5G
Pentacene, sublimed, > 99.9%		10 ⁵ –10 ⁸	684848-1G
Also see p. 10 for Soluble Pentacene Precursors.			
5,5'-Dihexyl-2,2'-bithiophene, (DH-2T), 96%			632953-1G 632953-5G
α -Quaterthiophene, (4T), 96%		0.006 cm ² /Vs 10 ⁴	547905-1G
α -Sexithiophene, (6T)		0.075 cm ² /Vs 10 ⁴	594687-1G
α,ω -Dihexylsexithiophene, (DH-6T)		0.13 cm ² /Vs 10 ⁴	633216-500MG
Bis(ethylenedithio)tetrathiafulvalene, (BEDT-TTF), 98%			362026-100MG 362026-500MG
Bis(4,5-dihydronaphtho[1,2- <i>d</i>])tetrathiafulvalene, 98%			366269-250MG 366269-1G
Copper (II) phthalocyanine, sublimed, 99%		0.01–0.02 cm ² /Vs 4x10 ⁵	546674-1G
Platinum octaethylporphyrin, 98%		2.2x10 ⁻⁴ cm ² /Vs 10 ⁴ –10 ⁵	673625-100MG
Poly(3-hexylthiophene-2,5-diyl), (P3HT), regioregular, electronic grade, 99.995%		10 ⁻⁴ –10 ⁻¹ cm ² /Vs 10 ⁴	669067-300MG 669067-1G
Poly(3-octylthiophene-2,5-diyl), (P3OT), regioregular, electronic grade, 99.995%		10 ⁻⁴ –10 ⁻¹ cm ² /Vs 10 ⁴	682799-250MG
Poly(3-dodecylthiophene-2,5-diyl), (P3DDT), regioregular, electronic grade, 99.995%		10 ⁻⁴ –10 ⁻¹ cm ² /Vs 10 ⁴	682780-250MG

More polythiophenes are available in other purity grades, regiorandom configuration, and with additional alkyl substituents.

*Literature values for carrier mobility and On/Off ratios from: Shirota, Y; Kageyama, H. *Chem. Rev.* **2007**, *107*, 953; Murphy, A.; Frechet, J. *ibid.* 1066.

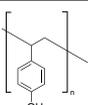
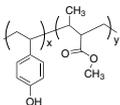
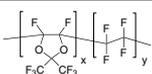
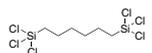
n-Type Semiconductors

Description	Structure	*Mobility (cm ² /Vs) On/Off ratio	Prod. No.
Fullerene-C ₆₀ , sublimed, 99.9%		0.3 cm ² /Vs 10 ⁶	572500-500MG
Fullerene-C ₇₀ , 99%			482994-10MG 482994-50MG
Fullerene-C ₈₄ , 98%		1.1 X 10 ⁻³ cm ² /Vs	482986-5MG
Hexadecafluoro copper phthalocyanine, (F ₁₆ CuPc), 80% dye content		0.03 cm ² /Vs 10 ⁴	446653-1G
Pd(II) meso-Tetra(pentafluorophenyl)porphine, 95% dye content			673587-100MG
1,4,5,8-Naphthalenetetracarboxylic dianhydride, (NTCDA)		0.003 cm ² /Vs	N818-5G N818-25G N818-100G
Perylene-3,4,9,10-tetracarboxylic dianhydride, (PTCDA), 97%		10 ⁻⁴ cm ² /Vs	P11255-25G P11255-100G
<i>N,N'</i> -Dipentyl-3,4,9,10-perylenedicarboximide, (PTCDI-C5), 98%			663921-500MG
<i>N,N'</i> -Dioctyl-3,4,9,10-perylenedicarboximide, (PTCDI-C8), 98%		1.7 cm ² /Vs 10 ⁶	663913-1G
<i>N,N'</i> -Diphenyl-3,4,9,10-perylenedicarboximide, (PDCDI-Ph), 98%		10 ⁻⁵ cm ² /Vs	663905-500MG
7,7,8,8-Tetracyanoquinodimethane, (TCNQ), 98%		10 ⁻⁵ cm ² /Vs 10 ³	157635-1G 157635-5G 157635-10G
2,3,5,6-Tetrafluoro-7,7,8,8-tetracyanoquinodimethane, (F4TCNQ), 97%			376779-5MG 376779-25MG
Poly(benzimidazobenzophenanthroline), (BBL)		0.1 cm ² /Vs 10 ³ -10 ⁵	667846-1G

*Literature values for carrier mobility and On/Off ratios from: Shirota, Y; Kageyama, H. *Chem. Rev.* **2007**, *107*, 953; Murphy, A.; Frechet, J. *ibid.* 1066.

Dielectric Materials

Sigma-Aldrich carries many polymers useful as gate-insulators (dielectrics) in OTFTs. A selection of representative materials is given in the following table. Please visit us at sigma-aldrich.com/polymers for a complete list of high-quality polymer products. You will also find many silsesquioxane materials (glass resins) useful in organic electronics at sigma-aldrich.com/nanomaterials.

Description	Structure	Property/Purity	Prod. No.
Poly(methyl methacrylate) (PMMA)		Avg. M_w ~93,000	370037-25G
		Avg. M_w ~996,000	182265-25G 182265-500G 182265-1KG
Polystyrene (PS)		Avg. M_w ~280,000	182427-25G 182427-500G 182427-1KG
Poly(4-vinylphenol) (PVP)		Avg. M_w ~20,000	436224-5G 436224-25G
Poly(4-vinylphenol-co-methyl methacrylate) (PVP-co-PMMA)		x:y = 1.8:1 Avg. M_w ~10,000	474576-50G 474576-250G
Polyisobutylene		Avg. M_w ~500,000	181455-100G 181455-250G
Poly[4,5-difluoro-2,2-bis(trifluoromethyl)-1,3-dioxole-co-tetrafluoroethylene]		65 mol % dioxole	469610-1G
		87 mol % dioxole	469629-1G
Hexachlorodisiloxane		96%	368334-5ML 368334-25ML
1,2-Bis(trichlorosilyl)ethane		97%	447048-5ML 447048-25ML
1,6-Bis(trichlorosilyl)hexane		97%	452246-1G 452246-10G

Electrode Materials

Sigma-Aldrich offers a complete line of:

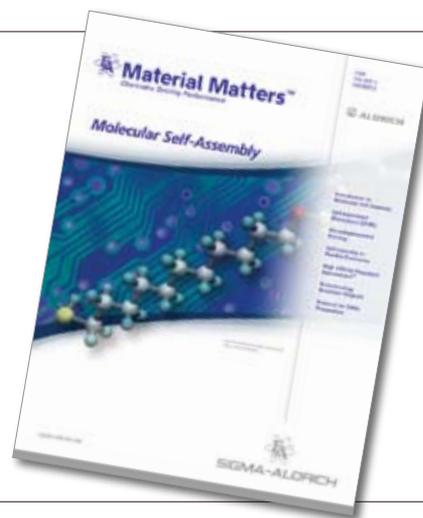
- gold and ITO substrates
- self-assembling silane and thiol molecules

for substrate modification.

These products, as well as research advances in the field of molecular self-assembly, were featured in *Material Matters*™ Vol. 1, No. 2.

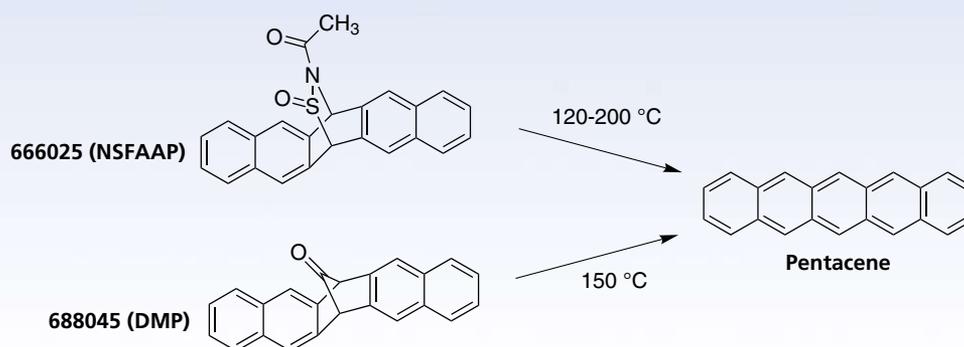
We invite you to visit us at sigma-aldrich.com/matsci to read this and other recent issues of *Material Matters*—or subscribe for free to *Material Matters* at sigma-aldrich.com/mm and receive latest issue notifications by e-mail!

Also see p. 31 for a list of available ITO substrates and representative high-purity materials for evaporative electrode deposition.



Soluble Pentacene Precursors

Pentacene is one of the best performing molecular conductors that forms excellent p-type semiconducting channels with field-effect mobilities $> 1\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. One of its main drawbacks is insolubility in solvents compatible with low-cost, large-area processing methods (printing, stamping, curtain-coating) that are essential to the commercial success of organic electronics. A successful approach to overcome this problem is to use soluble pentacene precursor molecules that can be solution-processed and then thermally converted to high-quality pentacene films.¹ Sigma-Aldrich is pleased to offer two soluble pentacene precursors.



666025 13,6-*N*-Sulfinylacetamidopentacene (NSFAAP) is highly soluble ($> 50\text{ mg/mL}$) in apolar solvents (halogenated solvents, THF). In thin films, **666025** is converted to pentacene by heating under N_2 atmosphere for 5–15 minutes at 120–200 °C. Organic thin-film transistors fabricated by solution processing of this precursor afforded highest mobilities—up to $0.8\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ —reported for a solution-processed organic semiconductor.²

688045 6,13-Dihydro-6,13-methanopentacene-15-one (DMP) is quantitatively converted to pentacene by heating at 150 °C. It is sparingly ($\sim 0.7\text{ mg/mL}$) soluble in apolar solvents (chloroform, toluene, THF), but has the advantage of only generating CO gas as the by-product of the thermal conversion.³

Chemists at Sigma-Aldrich are continuing their efforts to make additional soluble pentacene precursors available to researchers in organic electronics. Please visit us often at sigma-aldrich.com/organicelectronics for up-to-date news of latest products.

13,6-*N*-Sulfinylacetamidopentacene, (NSFAAP), 97%

666025-200MG	200 mg
666025-1G	1 g

6,13-Dihydro-6,13-methanopentacene-15-one, (DMP), 97%

688045-100MG	100 mg
688045-500MG	500 mg

References:

(1) Menard, E.; Meitl, M.; Sun, Y.; Park, J.; Shir, D.; Nam, Y.; Jeon, S.; Rogers, J. *Chem. Rev.* **2007**, *107*, 1117. (2) Afzali, A.; Dimitrakopoulos, C.; Breen, T. J. *Am. Chem. Soc.* **2002**, *124*, 8812. (3) Chen, K.; Hsieh, H.; Wu, C., Hwang, J.; Chow, T. *Chem. Comm.* **2007**, 1065.

New Conducting And Semiconducting Polymers For Plastic Electronics



Dr. Silvia Luebben and Dr. Shawn Sapp
TDA Research, Inc.

Introduction

In the emerging field of organic printable electronics, such as OLEDs and organic photovoltaics (OPVs), there is a significant need for improved organic conducting and semiconducting materials. This paper reports our recent progress in two fields: 1) the development of solvent-based dispersions of the intrinsically conducting polymer (ICP) poly(3,4-ethylenedioxythiophene) (PEDOT) and 2) the synthesis of new electron-deficient (n-type) semiconducting polymers.

PEDOT Copolymers in Organic Solvent Dispersions

ICPs are polymers with extended π conjugation along the molecular backbone, and their conductivity can be changed by several orders of magnitude from a semiconducting state to a metallic state by doping. p-Doping is achieved by partial oxidation of the polymer by a chemical oxidant or an electrochemical method, and causes depopulation of the bonding π orbital (HOMO) with the formation of "holes".¹

Despite the promise of ICPs since their discovery in the 1970s, relatively few commercial products have succeeded, primarily because of their limited performance and poor solubility, which makes processing difficult. PEDOT is one of the most commonly used ICPs because of its good electrical conductivity, environmental stability in the doped (conducting) form, and reasonable optical transparency when used as a thin film.² A common way to apply a PEDOT coating is to use a water dispersion consisting of a blend of PEDOT and the polyanion poly(styrene sulfonate) or PEDOT-PSS. Several grades of conductive PEDOT-PSS blends are available from Sigma-Aldrich (Aldrich Prod. No. **655201**, **483095**, **560596**). A low-conductivity grade has been successfully employed as the hole injection layer in OLEDs and OPVs and the high conductivity grades are being evaluated as transparent conductors with work functions of ca. 5.1 eV.^{3,4}

Despite the success of the PEDOT-PSS blends, it has been shown that the presence of the strongly acidic and hygroscopic PSS can sometimes degrade device lifetime and performance.⁵⁻⁷ With recent advances in flexible, printed electronic devices, there is increasing interest in optically transparent conducting polymer materials that can be processed from non-hygroscopic solvents and that will wet hydrophobic plastic substrates.

TDA Research, Inc. (TDA) developed and manufactures solvent-dispersible forms of PEDOT under the trademark Aedotron™ polymers. Selected grades of these materials

are available through Sigma-Aldrich. Our approach is to synthesize block copolymers of doped PEDOT and a flexible, soluble polymer such as poly(ethylene glycol) (PEG).⁸ We have developed several block copolymer geometries (**Figure 1**) and methods to purify and process them to form stable colloidal dispersions in organic solvents. **Figure 2** shows the chemical structure of a multi-block Aedotron™ P-NM and a tri-block Aedotron™ C3-NM copolymers; **Table 1** summarizes some of the important properties of two representative materials. By carefully controlling block composition, molecular weight, block ratio, and dopant type, we can vary the bulk conductivity of the copolymers from 10^{-4} S/cm to 60 S/cm. The Aedotron™ materials are neither acidic nor corrosive and can be used to spin cast or otherwise apply non-hygroscopic thin films of the copolymers on a variety of inorganic and organic substrates. These colloidal dispersions are stabilized by the highly solvated PEG chains which sterically limit the aggregation of the PEDOT blocks. Our copolymers easily disperse in polar aprotic solvents; we have selected propylene carbonate for applications that require a high boiling solvent, and nitromethane for applications that require a volatile solvent. Other solvents are being explored, especially for the low conductivity materials.

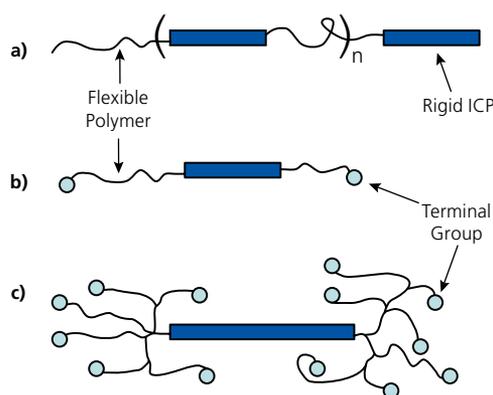


Figure 1. Schematic structures of TDA block copolymers: linear triblock (a), linear triblock (b), and hyperbranched (c); the dark blue rectangles represent the rigid blocks of doped PEDOT, and the curvy lines represent blocks of PEG.

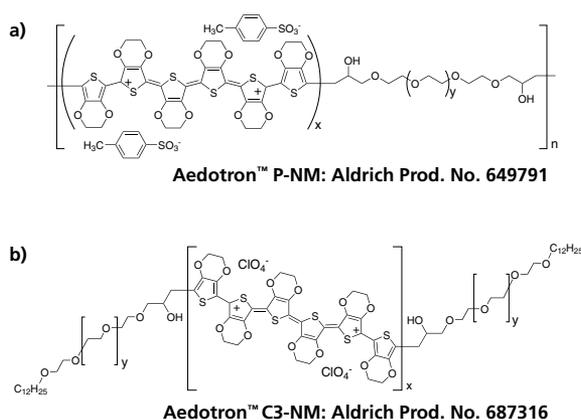


Figure 2. Chemical structure of TDA's multi-block (a) and tri-block (b) PEDOT-PEG block copolymers.

Table 1. Comparison of two Aedotron™ Conducting Polymers.

Material	Particle Size in suspension (nm)	Bulk conductivity (S/cm)	*Sheet Resistance (Ω /square)	**Average Transmittance (%T)	RMS Roughness of spin cast thin films (nm)
Aedotron™ C-NM 649805	600–1000	0.1–2	10^4 – 10^5	70–85%	40
Aedotron™ C3-NM 687316	200–600	10–60	600–3000	70–85%	10

*Typically 1–3 layers spun at 1000 rpm or higher.

**%T averaged from 400–800 nm, background to Corning Glass

Since the colloidal stabilization mechanism in our products is independent from the polymer doping, the dopant can be controllably varied to tune the bulk conductivity and the work function of our copolymers. Typically, *para*-toluenesulphonate (PTS) doped copolymers (Aedotron™ P **649791**) have a lower conductivity, making them useful for antistatic dissipation applications and as an electrode interface layer in OLEDs. Aedotron™ P polymers usually have larger particle sizes in suspension and are somewhat amenable to being dispersed in less polar solvents. Perchlorate-doped copolymers (Aedotron™ C **649805**, **649783**) typically have a higher conductivity with thin films that are more transparent. With the improved tri-block copolymer (Aedotron™ C-3 **687316**, **Figure 2b**) we can spin cast thin films with 1000 Ohms/square sheet resistance at 80% transmittance (400–800 nm average) with good wetting properties on polycarbonate and other plastic films. **Figure 3** shows the UV-vis transmission spectra for 1-, 2-, and 3-layer films spun on glass at 1000 RPM, and each data trace is labeled with the measured sheet resistance for that film. These properties meet requirements for a transparent conductor that can be used in touch sensitive displays and electroluminescent lamps and displays. The tri-block copolymer has smaller particle size (290 nm) in suspension than our multi-block copolymers, and form thin films with lower surface roughness (<10 nm), as determined by contact-mode Atomic Force Microscopy.

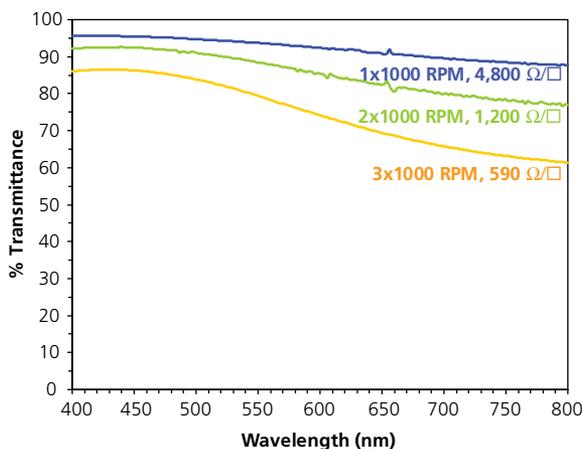


Figure 3. UV-visible spectra of TDA's new, high-conductivity, tri-block copolymer spin cast at 1000 rpm; 1, 2, & 3-layer films are shown and labeled with the corresponding sheet resistance.

Relative electronic band energies of materials in different layers are important to consider in designing multilayer devices. The work functions of our multi-block copolymers, measured using x-ray photoelectron spectroscopy, were found to be lower than the work function of PEDOT-PSS blends (~4.2 eV for Aedotron™ P polymers and 4.3 eV for Aedotron™ C polymers).⁹ This lower work function must be taken into account when fabricating thin film electronic devices in which the alignment or overlap of electronic bands is crucial.

New n-Type Polymeric Semiconductors

The unifying basic requirement of most thin-film, organic electronic devices like OLEDs and OPVs is that they contain at least two semiconducting materials with offsets in their molecular orbital (HOMO-LUMO) energy levels. In the organic semiconductor world, one can create such an energy offset by forming an interface between a more electron-rich (p-type) semiconductor and an electron-poor (n-type) material. It is at this interface that charge separation or recombination typically occurs. Moreover, the extent of the offset and the proper alignment of the HOMO-LUMO bands of the p-type and n-type semiconductors are critical to the efficient operation of the device. It is, therefore, important to have a wide variety of p-type and n-type materials to choose from. There are a number of available classes of relatively electron-rich, p-type semiconducting molecules and polymers. In contrast, there are few electron-poor, n-type semiconducting molecules, like metalloporphyrins and methanofullerenes. Even rarer are the n-type semiconducting, π -conjugated polymers like cyano-derivatives of poly(*p*-phenylenevinylenes).

Our group has been working to develop and produce new n-type semiconducting, π -conjugated polymers and oligomers. Our approach is quite similar to what has been done for many years to produce electron-rich, p-doped conducting polymers: we introduce a heteroatom to the π -conjugated backbone that can alter the electron density of the overall polymer. The heteroatom that we add is boron, whose vacant p orbitals are conjugated to the π electronic system of unsaturated repeat units of the polymer. Because of the absence of electrons in the boron p orbitals, the overall π electronic system of the polymer becomes inherently electron deficient and, therefore, the polymer has n-type electronic properties.

Several different synthetic methods are available to prepare air stable π -conjugated organoboron polymers.^{10–15} Our group has prepared a number of both new and previously reported π -conjugated organoboron polymers and oligomers. **Figure 4** shows representative chemical structures of the polymers we have been studying. Over the past few years we have refined their synthesis and purification, characterized their properties as organic semiconductors, and evaluated their performance in thin film devices. TDA just began manufacturing selected π -conjugated organoboron polymers and oligomers under the trade name of Boramer™ materials, which are now available from Sigma-Aldrich (**688010** and **688002**) Additional π -conjugated organoboron structures are under development and investigation.

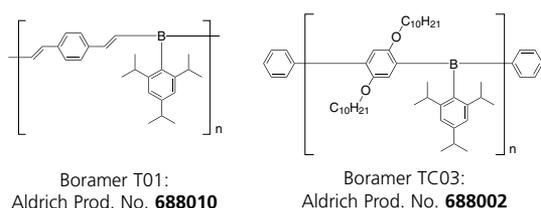


Figure 4. Chemical structure of TDA's boron-containing, n-type polymers.

We have found that careful purification of the polymers is critical to preserve the solubility of these materials. Chloroform and chlorobenzene are preferred solvents for most of these polymers. All the prepared organoboron polymers are colored and the majority are strongly photoluminescent in the blue to green region of the visible spectrum (**Figure 5**). Air-stability has not been fully assessed yet, but preliminary evidence indicates that it varies with the polymer structure: Boramer™ T01 polymer is more sensitive to air than Boramer™ TC03 polymer. We recommend handling both materials under an inert atmosphere.

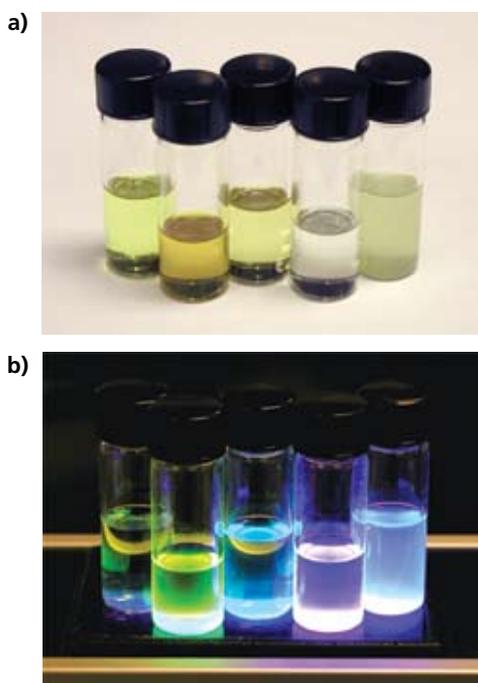


Figure 5. Chloroform solutions of TDA's Boramer™ polymers under ambient (a) and ultraviolet (b) lighting.

The electronic band structure of selected Boramer™ materials was characterized via ultraviolet photoelectron spectroscopy (UPS) at Colorado State University (Fort Collins, CO). UPS gives a direct measure of the electron energies of the HOMO level to Fermi level gap at the low binding energy end of the spectrum. UPS results conclusively prove that our polymers are in fact n-type semiconductors and that their valence band (VB) resides at a similar energy to the VB of common n-type organic semiconductors including methanofullerenes (PCBM) and cyano-PPV. The polymer bandgap was estimated from UV-Vis spectra and was found to be in the range of 2.6–2.9 eV. **Figure 6** shows the HOMO-LUMO levels of two of our boron-containing, π -conjugated polymers (orange) along with familiar p-type (blue) and other n-type organic materials (green). The energy level data clearly indicate their n-type character, with Boramer™ T01 having the lowest lying work function and HOMO-LUMO levels.

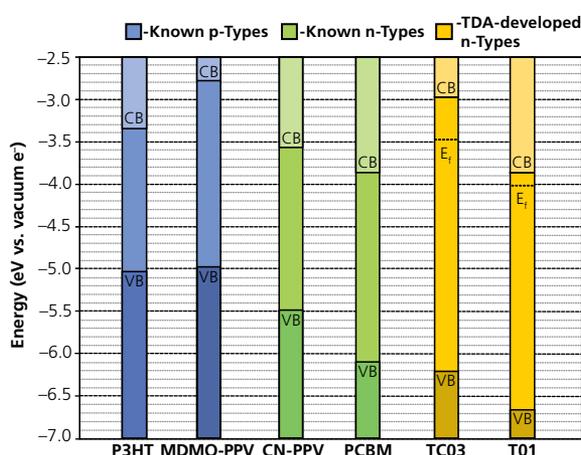


Figure 6. Energy level diagram of HOMO-LUMO levels for known p-type and n-type semiconducting materials, including TDA's new n-type Boramer™ materials.

During our work on these n-type materials we collaborated with the National Renewable Energy Laboratory (NREL, Golden, CO) to evaluate the properties of our polymers for use in OPV prototypes. NREL carried out photoluminescence quenching (PLQ) experiments and built OPV devices with two of the materials supplied by TDA. Results from PLQ indicated that our polymers efficiently quench the excited state of a typical p-type semiconductor (MDMO-PPV) with efficiencies up to 83%. This indicates that, in fact, efficient electron transfer occurs from this p-type semiconductor to our material. One of the prepared polymers was also used as the electron-transporting and light-emitting layer for the fabrication of an OLED prototype. Bright green light emission was observed (similar in color to the solid-state luminescence of our polymer) at a turn-on voltage of approximately 6 V.

Acknowledgements

We would like to thank Emily Chang, Raechelle D'Sa, Cory Kruetzer, and Carolina Wilson at TDA Research, Inc. for the synthetic work, Profs. Anthony Caruso and Doug Schulz at North Dakota State University for the work function measurements, Prof. Bruce Parkinson and Dr. Bengt Jaekel at Colorado State University for the UPS measurements, and Dr. Sean Shaheen, Dr. Muhammet Kose, Dr. Don Selmarten, and Cary Allen at NREL for characterizing the n-type materials in organic photovoltaics. This work was carried out in part with funding from the National Science Foundation (contracts DMI-0319320, OII-0539625, DMI-0110105) and the Office of the Secretary of Defense (contract N00164-06-C-6042).

References:

- (1) MacDiarmid, A. G. *Angew. Chem. Int. Ed.* **2001**, *40*, 2581–2590.
- (2) Groenendaal, L.; Dhaen, J.; Manca, J.; Van Luppen, J.; Verdonck, E.; Louwet, F.; Leenders, L. *Synth. Met.* **2003**, *135–136*, p.115–117.
- (3) Granström, M.; Petritsch, K.; Arias, A. C.; Lux, A.; Andersson, M. R.; Friend, R. H. *Nature* **1998**, *395*, 257–260. (4) Cao, Y.; Yu, G.; Zhang, C.; Menon, R.; Heeger, A. J. *Synth. Met.* **2003**, *87*, 171–174. (5) Kawano, K.; Pacios, R.; Poplavskyy, D.; Nelson, J.; Bradley, D.; Durrant, J. R. *Solar Energy Materials & Solar Cells* **2006**, *90*, 3520–3530. (6) Danier Van Der Gon, A. W.; Birgerson, J.; Fahlman, M.; Salaneck, W. R. *Org. Electr.* **2002**, *3*, 111–118. (7) Greczynski, G.; Kugler, T.; Keil, M.; Osikowicz, W.; Fahlman, M.; Salaneck, W. R. *J. Elec. Spectr. & Rel. Phenom.* **2001**, *121*, 1–17.
- (8) Luebben, S.; Elliott, B.; Wilson, C. "Poly(heteroaromatic) Block Copolymers with Electrical Conductivity," U.S. Patent Application US 2003/0088032 A1. (9) Sapp, S.; Luebben, S.; Jeppson, P.; Shulz, D. L.; Caruso, A. N. *Appl. Phys. Lett.* **2006**, *88*, 152107(1–3). (10) Chujo, Y.; Miyata, M.; Matsumi, N. *Polymer Bulletin* **1999**, *42*, 505–510. (11) Chujo, Y.; Miyata, M.; Matsumi, N. *Macromolecules* **1999**, *32*, 4467–4469. (12) Chujo, Y.; Naka, K.; Matsumi, N. *J. Am. Chem. Soc.* **1998**, *120*, 10776–10777. (13) Chujo, Y.; Umeyama, T.; Matsumi, N. *Polymer Bulletin* **2002**, *44*, 431–436. (14) Jäkle, F.; Sundararaman, A.; Victor, M.; Varughese, R. *J. Am. Chem. Soc.* **2005**, *127*, 13748–13749. (15) Parab, K.; Venkatasubbaiah, K.; Jäkle, F. *J. Am. Chem. Soc.* **2006**, *128*, 12879–12885.

n-Type Polymers

Sigma-Aldrich now offers three semiconducting polymer categories known to show n-type behavior:

- BBL ladder polymer (Aldrich Prod. No. **667846**, page 8)
- the Boramer™ polymers featured on this page
- organo-PPV (CN-PPV) polymers (page 29)

We will continue to expand this offer; visit us at sigma-aldrich.com/matsci for the latest product releases.

Boramer™ n-Type Conducting Polymers

Product Name	Structure	HOMO/LUMO	Prod. No.
Poly[(1,4-divinylphenylene)(2,4,6-triisopropylphenylborane)], Boramer-T01		-6.65 eV/-3.85 eV	688010-250MG
Poly[(2,5-didecyloxy-1,4-phenylene)(2,4,6-triisopropylphenylborane)], diphenyl terminated, Boramer-TC03		-6.2 eV/-3.0 eV	688002-250MG

Materials for Conducting Thin Films and Hole-Injection Layers

This table is a selection of commonly used and new materials. For a complete list go to sigma-aldrich.com/organicelectronics.

Product Name*	Product Description	Conductivity S/cm	Prod. No.
Polyethylenedioxythiophene (PEDOT)			
PEDOT-block-PEG solution, 1 wt. % dispersion in nitromethane, contains p-toluenesulfonate as dopant (Aedotron™ P-NM)	Material for hole injection layers and low conductivity applications	10 ⁻³ –10 ⁻⁴ (bulk)	649791-25G
PEDOT-block-PEG solution, 1 wt. % dispersion in nitromethane, contains perchlorate as dopant (Aedotron™ C-NM)	General purpose, moderate conductivity ICP dispersion in volatile solvent	0.1–2 (bulk)	649805-25G
PEDOT-block-PEG solution, 1 wt. % dispersion in propylene carbonate, contains perchlorate as dopant (Aedotron™ C-PC)	General purpose, moderate conductivity ICP dispersion in volatile solvent	0.1–2 (bulk)	649783-25G
C ₁₂ -PEG- <i>b</i> -PEDOT- <i>b</i> -PEG-C ₁₂ solution, 0.7% dispersion in nitromethane, contains perchlorate as dopant (Aedotron™ C3-NM)	High transparency and good conductivity dispersion in volatile solvent	10–60 (bulk)	687316-25G
PEDOT, tetramethacrylate end-capped, 0.5% dispersion in propylene carbonate with p-toluenesulfonate dopant (Oligotron™-PC)	Reactive oligomer in non-volatile solvent. Can be crosslinked or blended with reactive acrylate and methacrylate compounds to make polymer blends.	0.1–0.5 (bulk)	649813-25G
PEDOT, tetramethacrylate end-capped, 0.5% dispersion in nitromethane with p-toluenesulfonate dopant (Oligotron™-NM)	Reactive oligomer in volatile solvent. Can be crosslinked or blended with reactive acrylate and methacrylate compounds to make polymer blends.	0.1–0.5 (bulk)	649821-25G
PEDOT-PSS formulation, 2.8 wt. % dispersion in H ₂ O, low-conductivity grade	Low-conductivity polymer blend, contains 0.14 wt.% PEDOT and 2.6 wt.% PSS. Reduced particle size allows to create smooth spin-coated films on ITO useful as charge injection layers for OLEDs and OPVs.	~10 ⁻⁵	560596-25G 560596-100G
PEDOT-PSS formulation, 1.3–1.7 wt. % dispersion in H ₂ O	Conductive polymer blend. Suitable for OTFT applications.	~10 ⁻³ (18 μm film)	655201-5G 655201-25G
PEDOT-PSS formulation, 1.3 wt. % dispersion in H ₂ O, conductive grade	Conductive polymer blend, contains 0.5 wt.% PEDOT and 0.8 wt.% PSS. Useful for antistatic coating applications	~1	483095-250G
PEDOT nanoparticles, 1% (w/v) in H ₂ O	Aqueous dispersion of < 300 nm PEDOT nanoparticles. Contains dodecylbenzene sulfonic acid (DBSA) as dopant	1–50 (pellet)	675288-25ML
PEDOT nanotubes, > 97%	PEDOT nanotube powder O.D. x I.D. x length 272.4 nm x 416 nm x 11.5 μm (TEM)		678392-500MG
Polyaniline (PANI)			
Polyaniline (emeraldine salt), 0.5 wt. % dispersion in mixed solvents	Conductive polymer suitable for dip-coating applications. Doped with organic sulfonic acid.	~1 (film)	649996-10ML 649996-50ML
Polyaniline (emeraldine salt), 2–3 wt. % dispersion in xylene	Conductive polymer suitable for spin-coating applications. Doped with organic sulfonic acid.	10–20 (film)	650013-10ML 650013-50ML
Polyaniline (emeraldine salt), average M _w > 15,000, powder, 3–100 μm particle size	Additive in polymer blends and liquid dispersions for electromagnetic shielding, charge dissipation, electrodes, batteries and sensors. Doped with organic sulfonic acid.	2–4 (pellet)	428329-5G 428329-25G
The three listed PANI materials are representative of our offerings. For a complete list of PANI products, including base form (undoped) materials, visit sigma-aldrich.com/organicelectronics .			

*PEDOT=Poly(3,4-ethylenedioxythiophene); PEG=poly(ethylene glycol); PSS=poly(styrenesulfonate); PANI=Polyaniline.

For questions, product data, or new product suggestions, please contact the Materials Science team at matsci@sial.com.

Fullerene-Based n-Type Semiconductors in Organic Electronics



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Introduction

Since the first publication in 1995 describing a bulk heterojunction photodiode incorporating a methanofullerene,¹ significant progress has been made in improving device performance and the scope of device research has broadened widely. The most commonly used fullerene derivative in organic electronics is the methanofullerene **Phenyl-C₆₁-Butyric-Acid-Methyl-Ester** ([60]PCBM).² Various analogues (termed here PCBMs) have been made and tested as n-type semiconductors. The use in organic photovoltaics, photodetectors³ and organic field effect transistors (OFETs)⁴ among other applications, has been investigated and is under active development. After more than a decade of research, it appears that PCBMs have proven to be effective solution processable organic n-type semiconductors in a variety of thin film organic electronics applications.

Figure 1 is a schematic showing a typical bulk heterojunction organic photovoltaic device (OPV) architecture and performance characteristics. Fabrication of bulk heterojunction OPVs requires soluble fullerene derivatives in order to form blends with p-type polymer semiconductors. PCBMs preserve important electronic and optical properties of the parent fullerenes while providing a significant increase in solubility and processability. Some of these properties are fast electron transfer, an adequate dielectric constant, isotropic (in the case of C₆₀ derivatives) or relatively isotropic (in the case of C₇₀ and C₈₄ derivatives) electron accepting due to the symmetry of the fullerene acceptor, and good electron mobilities. Coupling these properties of the parent fullerenes with improved solubility in common organic solvents and the observed desirable precipitation kinetics of the PCBMs provides robust formation of uniform nanoparticulate n-type domains in the final film.

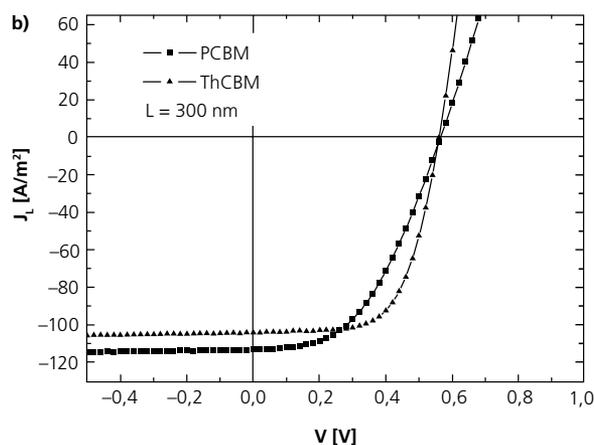
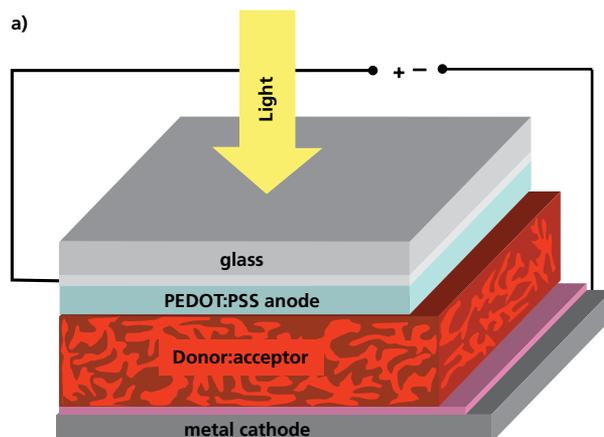


Figure 1. a) Present day standard architecture for bulk heterojunction OPV devices. The unnamed layers are a transparent conducting oxide (TCO, e.g. ITO; top) and an ultra-thin protective layer (e.g. LiF; bottom); b) I/V curves of optimized regioregular P3HT:methanofullerene (1:1) PV cells under AM1.5 illumination, 1 sun intensity. Current density values are corrected for spectral mismatch and real active area. (Presented at MRS spring meeting 2007; devices by Lacramioara Popescu, Univ. of Groningen). It can be seen that a relatively minor change in molecular structure of the n-type semiconductor influences the performance of the final device.

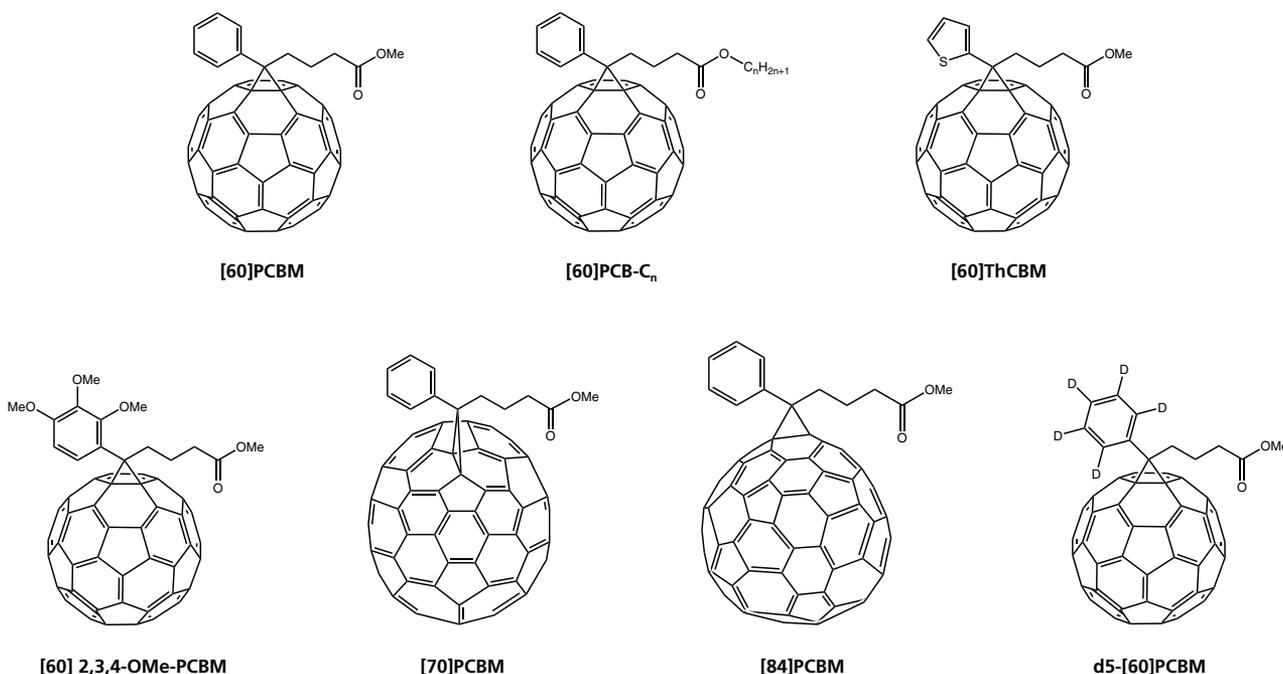


Figure 2. Library of the [60]PCBM analogues (PCBM)s

Analogues of [60]PCBM based on higher fullerenes (C_{70} and C_{84}) have been synthesized and tested in devices, and [60]PCBM analogues based on alterations of the addend moiety to vary miscibility/solubility and electronic properties have also been developed and tested. **Figure 2** shows the more commonly used and best performing PCBM. Since the formation of thin film organic electronics devices is highly complex, especially due to morphology considerations, it is hard to generalize or extrapolate trends and predict which PCBM will give the best performance in a given device or architecture. These molecules do however represent a library available for the experimental researcher to explore optimization, and each has shown in different devices and architectures to provide advantages. Different purity grades have also been developed allowing for significantly lower prices and the availability of commercial scale volumes.

Overview of PCBM as n-Type Semiconductors in Organic Electronics Applications

Organic Photovoltaics (OPV)

[60]PCBM is still by far the most commonly used n-type component in organic photovoltaics. Over at least the last 6 years, the published world record power conversion efficiency (η) for an organic photovoltaic device to our knowledge has been continuously held by devices incorporating [60]PCBM, save for a period in which a device containing [70]PCBM held the record. MDMO-PPV:PCBM devices were thoroughly studied and characterized, eventually leading to $\eta=3.0\%$ ⁵ when [70]PCBM was substituted for [60]PCBM, which earlier had given $\eta=2.5\%$.⁶ The increase was due to the higher optical absorption of [70]PCBM in visible wavelengths compared to [60]PCBM. [84]PCBM has an even stronger absorption in the visible wavelengths, though the better electron accepting ability led to a diminished performance in OPV, because it was used in combination with a relatively strongly electron

donating donor polymer.⁷ More recently, researchers and developers have transitioned to polythiophene/PCBM systems, and η 's of 4.4%–6% have been published by several groups.^{8,9} Careful control of morphology, either by annealing or slow evaporation, provides a significant improvement in performance.

The state of the art roadmap for research and development to achieve η of 10% focuses on improving morphology and polymer characteristics¹⁰ leading to an inference that [60]PCBM is largely adequate as the n-type semiconductor for improved devices. However, improvements in morphology control with polythiophenes, where more extensive demixing of the PCBM and polymer phase has been observed, is also desired. This has led to the design and testing of a new molecule, [60]ThCBM, which in preliminary results does appear to give a slightly more advantageous morphology with P3HT.¹¹ [60]ThCBM also preserves the electronic properties (LUMO and mobility) of [60]PCBM. Increases in LUMO level of the n-type have also been long sought by OPV developers and a recently synthesized molecule, 2,3,4-OMe-PCBM, shows a modest though significant increase in LUMO. This molecule has been shown to give a higher open circuit voltage (V_{oc}) in combination with MDMO-PPV¹² but has not yet been fully characterized in OPV devices.

Organic Field Effect Transistors (OFETs)

Relatively high mobilities for an organic semiconductor have been demonstrated for [60]PCBM devices (1×10^{-2} – $2 \times 10^{-1} \text{ cm}^2/\text{Vs}$),⁴ as well as ambipolar transport which allowed for the construction of inverters.¹³ Stability has been an issue, though efficient passivation has been reported. [70]PCBM thus far has shown about an order of magnitude lower electron mobilities but allows for shorter annealing times and higher stability. [84]PCBM has shown very good stability, in combination with an electron mobility up to 3×10^{-3} and a hole mobility of 10^{-5} – $10^{-4} \text{ cm}^2/\text{Vs}$.¹⁴ Blends of conjugated polymers with PCBM

can also be used for ambipolar OFETs.¹⁵ Less work has been done with OFET devices using PCBM's compared to OPV, and it can be expected that mobility improvements can be obtained applying similar control of film morphology (optimal solvents and evaporation/annealing) as has been demonstrated with OPV.

Organic Photodetectors

Concurrent with the early development of OPV devices, bulk heterojunction organic photodetectors based on similar photodiodes were also developed.¹⁶ Performance adequate for commercial application was realized, with low dark currents, high external quantum efficiencies (80%), and fast transient behavior.³ Significantly, large area applications are envisioned due to the cost advantages of organic thin films over silicon-based devices.

Properties of the Individual Members of the PCBM Library

[60]PCBM (Aldrich Prod. Nos. **684430**, **684449**, **684457**)

[60]PCBM is present as a single isomer. An interesting feature of [60]PCBM which may correlate with its performance is that it preserves to a high degree the electronic and physical properties of C_{60} . Single crystal structure analysis shows that intermolecular spacing is essentially identical to C_{60} , with the shortest ball-to-ball spacing curiously being slightly smaller in PCBM than C_{60} .¹⁷ It has been consistently demonstrated that deviation to too great of a degree from the compact structure of [60]PCBM (and thus from the parent fullerene) leads to diminished performance.

The >99.5% grade of [60]PCBM (Aldrich Prod. No. **684449**) has been and is still most extensively used by researchers, but testing has shown that in some devices and architectures >99% grade (Aldrich Prod. No. **684430**) is acceptable. However, it must be cautioned that since precipitation/crystallization behavior of the PCBM has a strong influence on morphology and small amounts of impurities may have a strong influence on precipitation/crystallization kinetics, the different grades must be examined to determine optimal performance.

[70]PCBM (Aldrich Prod. No. **684465**)

The motivation for the first synthesis of [70]PCBM was to take advantage of the increased optical absorption in the visible region compared to [60]PCBM. This can be especially advantageous in combination with relatively large bandgap donors like MDMO-PPV. It is prepared as a mixture of 1 major and 2 minor isomers and it is used as such. Since the LUMO energies of [70]PCBM and [60]PCBM are very close,⁵ it offers the opportunity for improvement in light harvesting where the film absorption is a function of the n-type as well as the p-type while preserving the electronic performance of [60]PCBM.

It should be noted that though the measured amount of [70]PCBM easily dissolved in common solvents is somewhat higher than [60]PCBM, the precipitation behavior in solution processed thin film devices is different (and consistent with behavior that would be expected for a less soluble molecule). This led to the necessity for the use of a stronger fullerene solvent ortho-dichlorobenzene (ODCB) for optimal performance, at least in combination with MDMO-PPV,⁵ as using chlorobenzene resulted in extensive de-mixing and large [70]PCBM domains. We speculate that the reduced symmetry of the C_{70} molecule and mixed isomer form induces differences in precipitation kinetics compared to [60]PCBM.

[84]PCBM (Aldrich Prod. No. **684473**)

[84]PCBM comes as a mixture of mainly three isomers and it is used as such.⁷ [84]PCBM shows panchromatic absorption (extending into the NIR), in combination with a 350 mV lower LUMO level, compared to that of [60]PCBM. This lower LUMO led to a diminished performance in the OPV system in combination with MDMO-PPV, but it is most likely an important factor in the much better air stability of the single component OFET.¹⁸

[60]PCB-C_n esters (Aldrich Prod. Nos. **685321** (C₄) and **684481** (C₈))

One strategy for morphology control has been to use stronger fullerene solvents, which reduces the precipitation driving force for the PCBM, thus leading to smaller PCBM domains and smoother films. Similarly, the solubility of [60]PCBM has been improved upon by replacing the methyl group by larger alkyl moieties. It has been demonstrated that for certain solvent systems (poorer solvents), higher solubility provides performance advantages, which improvements diminish with larger increases in solubility.¹⁹ Depending on solvent choice and device architecture, these higher solubility versions may provide advantages in forming the desired morphology. Alkyl chain lengths of n=4, 8, 12, 16, and 18 have been synthesized. [60]PCB-C₄ shows only a moderate increase in solubility, while n=8 and higher are significantly more soluble. It is likely that the crystal structure of the derivatives with longer chain lengths deviates from that of the compact structure of PCBM, and it is thought that this may lead to reduced mobilities. It may also influence recombination via lowering the dielectric constant.

[60]ThCBM (Aldrich Prod. No. **688215**)

Phase separation has been shown to be more extensive in polythiophene:PCBM systems, and so to increase miscibility a thieryl group was substituted for the phenyl of [60]PCBM. Though not yet fully characterized in devices, [60]ThCBM may offer more controllable morphology with polythiophenes due to improved miscibility. The LUMO and pure thin-film mobilities are very similar to those of [60]PCBM.¹¹

2,3,4-OMe-PCBM

The V_{OC} in OPV has been shown to be a function of the HOMO of the donor and LUMO of the acceptor, which has led to efforts in increasing the LUMO relative to [60]PCBM. 2,3,4-OMe-PCBM has been synthesized for this purpose and does demonstrate a higher LUMO while moderately preserving the processability of [60]PCBM. Preliminary work shows an increased V_{OC} in combination with MDMO-PPV,¹² though the overall device characteristics have yet to be optimized.

d₅-PCBM (Aldrich Prod. No. **684503**)

As thin film organic electronics device performance is such a strong function of film morphology, information regarding the structure of donor-acceptor blends can be crucial. Dynamic secondary ion mass spectroscopy (SIMS) can be used with blends where PCBM is replaced by the deuterated version d₅-PCBM to provide a detailed elemental analysis of film morphology in three dimensions. This technique successfully elucidated the 3-D morphology of MDMO-PPV:PCBM OPV devices.²⁰

Practical Use

In solution processing of organic electronic device layers containing PCBM, care should be taken to ensure complete dissolution of the PCBM. Incomplete dissolution can lead to seeding of the precipitation, leading to larger PCBM domain sizes and even in some cases micron-scale crystallite formation. Typically stirring for 8 hours or more at concentrations well below the solubility limits is adequate. Filtration should also be used. Sonication alone does not ensure adequate mixing and may leave sub-micron or nano-scale suspended particulates not visible to the naked eye.

PCBMs are relatively stable; though fullerenes typically form epoxides upon exposure to light and air, the process is slow. Storage in sealed, opaque containers is adequate, though for longer storage (> 6 months), purging with an inert gas (N₂ or Ar) may be desired. In practice we find that device performance in OPV applications does not degrade using PCBM that has been stored sealed in an opaque container (without inert gas purging or storage in a glovebox) for up to a year.

Conclusions and Outlook

PCBMs have shown to be broadly applicable as solution processable organic n-type semiconductors. The variations available represent opportunities for optimization in various devices and architectures. Volume and cost considerations have also been adequately addressed, allowing for commercial use of these materials. Further optimization of molecules is likely, though it appears that the compact structure of the PCBMs is a desirable property in preserving the inherently desirable properties of the parent fullerenes, while still providing adequate solution processability. The presently available library of PCBMs allows the researcher to vary a number of important parameters governing the action of the various molecular electronics devices. The present choice is in terms of miscibility, solubility, optical absorption, air stability, and LUMO energy. A likely experimental strategy to minimize R&D time and cost is the use of [60]PCBM for basic understanding and preliminary optimization, and the testing of various PCBM variations when undertaking fine tuning of the system.

References:

- (1) Hummelen, J. C.; Yu, G.; Gao, J.; Wudl, F.; Heeger, A. J. *Science* **1995**, *270*, 1789–1791. (2) Hummelen, J. C.; Knight, B. W.; LePeq, F.; Wudl, F. *J. Org. Chem.* **1995**, *60*, 532–538. (3) Rauch, T.; Henseler, D.; Schilinsky, P.; Waldauf, C.; Hauch, J.; Brabec, C. J. *4th IEEE Conf. on Nanotechnology* **2004**, 632–634. (4) Anthopoulos, T. D.; de Leeuw, D. M.; Cantatore, E.; van't Hof, P.; Alma, J.; Hummelen, J. C. *J. Appl. Phys.* **2005**, *98*, 503. (5) Wienk, M. M.; Kroon, J. M.; Verhees, W. J. H.; Knol, J.; Hummelen, J. C.; van Hal, P. A.; Janssen, A. J. *Angew. Chem. Int. Ed.* **2003**, *42*, 3371. (6) Shaheen, S. E.; Brabec, C. J.; Padinger, F.; Fromherz, T.; Hummelen, J. C.; Sariciftci, N. S. *Appl. Phys. Lett.* **2001**, *78*, 841. (7) Kooistra, F. B.; Mihailtchii, V. D.; Popescu, L. M.; Kronholm, D.; Blom, P. W. M.; Hummelen, J. C. *Chem. Mat.* **2006**, *18*, 3068–3073. (8) Li, G.; Shrotriya, V.; Huang, J.; Yao, Y.; Moriarty, T.; Emery, K.; Yang, Y. *Nat. Mat.* **2005**, *4*, 864–868. (9) Kim, K.; Liu, J.; Namboothiry, M. A. G.; Carroll, D. L. *App. Phys. Lett.* **2007**, *90*, 163511. (10) Scharber, M. C.; Muehlbacher, D.; Koppe, M.; Denk, P.; Waldauf, C.; Heeger, A. J.; Brabec, C. J. *Adv. Mater.* **2006**, *18*, 789–794. (11) Popescu, M.; van't Hof, P.; Sieval, A. B.; Jonkman, H. T.; Hummelen, J. C. *App. Phys. Lett.* **2006**, *89*, 213507. (12) Kooistra, F. B.; Knol, J.; Kastenber, F.; Popescu, L. M.; Verhees, W. J. H.; Kroon, J. M.; Hummelen, J. C. *Org. Lett.* **2007**, *9*, 551–554. (13) Anthopoulos, T. D.; de Leeuw, D. M.; Cantatore, E.; Setayesh, S.; Meijer, E. J.; Tanase, C.; Hummelen, J. C.; Blom, P. W. M. *App. Phys. Lett.* **2004**, *85*, 4205–4207. (14) Anthopoulos, T. D.; de Leeuw, D. M.; Cantatore, E.; van't Hof, P.; Alma, J.; Hummelen, J. C. *J. Appl. Phys.* **2005**, *98*, 054503. (15) Meijer, E. J.; de Leeuw, D. M.; Setayesh, S.; van Veenendaal, E.; Huisman, B.-H.; Blom, P. W. M.; Hummelen, J. C.; Scherf, U.; Klapwijk, T. M. *Nat. Mat.* **2003**, *2*, 678–682. (16) Yu, G.; Yong, C. U.S. Patent App. 20020017612, 2002. (17) Rispens, M. T.; Meetsma, A.; Rittberger, R.; Brabec,

- C. J.; Sariciftci, N. S.; Hummelen, J. C. *Chem. Commun.* **2003**, 2116–2118. (18) Anthopoulos, T. D.; Kooistra, F. B.; Wondergem, H. J.; Kronholm, D.; Hummelen, J. C.; de Leeuw, D. M. *Adv. Mat.* **2006**, *18*, 1679–1684. (19) Zheng, L.; Zhou, Q.; Deng, X.; Yuan, M.; Yu, G.; Cao, Y. *J. Phys. Chem. B* **2004**, *108* (32), 11921–11926. (20) Bulle-Lieuwma, C. W. T.; van Duren, J. K. J.; Yang, X.; Loos, J.; Sieval, A. B.; Hummelen, J. C.; Janssen, R. A. J. *App. Surf. Sci.* **2004**, *213–232*, 274–277.

Properties of PCBMs

Electronic

Table 1 gives a summary of the first reduction potentials of various methanofullerenes. [60]PCBM, [70]PCBM, and [60]ThCBM are very close in value. [84]PCBM shows a significantly lower LUMO energy, while that of 2,3,4-OMe-PCBM is slightly raised.

Table 1. *First Reduction Potentials of Several PCBMs

	E _{1st} , 1st Reduction Potential (V)
[60]PCBM	-1.078 ⁷
[70]PCBM	-1.089 ⁷
[84]PCBM	-0.730 ⁷
[60]ThCBM	-1.08 ¹¹
2,4,6-OMe-PCBM	-1.13 ¹²

*Values taken from references (superscripts) cited in this article.

Physical

Table 2 gives a summary of practical dissolution guidelines for various methanofullerenes. Choice of solvent exerts a strong influence on film morphology due to the influence on precipitation.

Table 2. *Practical Dissolution Guidelines for Several PCBMs (mg/ml)

Solvent	[60]PCBM	[70]PCBM	[60]ThCBM
toluene	10	20	5
p-xylene	5	10	5
o-xylene	15	30	10
chlorobenzene	25	40	10
chloroform	25	30	20
o-dichlorobenzene	30	70	20

*Determined by HPLC analysis of liquid phase after stirring with excess solid for three days at 25°. It should be cautioned that these values do not necessarily reflect thermodynamic solubilities, as verification of thermodynamic equilibrium was not performed, but are rather concentration values representing what is easily dissolved with stirring at room temperature.

Table 3 gives molar extinction coefficients for [60]PCBM, [70]PCBM, and [84]PCBM. As molecular weight of the parent fullerene increases, absorption increases significantly in the visible wavelengths.

Table 3. *Molar Extinction Coefficients (mol⁻¹ cm⁻¹) of [60]PCBM and Higher Fullerene PCBMs

	400 nm	650 nm
[60]PCBM	4,900	<1,000
[70]PCBM	19,000	2,000
[84]PCBM	28,000	4,000

*All values taken from Reference 7 of this article.

Materials for Organic Photovoltaics

Name	Synonym	Structure	Assay	Prod. No.
[6,6]-Phenyl C ₆₁ butyric acid methyl ester	[60]PCBM		>99% >99.5% >99.9%	684430-1G 684449-100MG 684449-500MG 684457-100MG
[6,6]-Pentadeuterophenyl C ₆₁ butyric acid methyl ester	d ₅ -PCBM		99.5%	684503-100MG
[6,6]-Phenyl-C ₆₁ butyric acid butyl ester	PCBB		>97%	685321-100MG
[6,6]-Phenyl-C ₆₁ butyric acid octyl ester	PCB-C ₈		99%	684481-100MG
[60]ThPCBM	[60]ThCBM		99%	688215-100MG
(6,6)-Phenyl C ₇₁ butyric acid methyl ester	[70]PCBM		99%	684465-100MG
(6,6)-Phenyl C ₈₅ butyric acid methyl ester	[84]PCBM		99%	684473-100MG
Poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylenevinylene]	MDMO-PPV			546461-1G
Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene]	MEH-PPV		Mn~40,000-70,000	541443-1G
			Mn~70,000-100,000	541435-1G
			Mn~150,000-250,000	536512-1G
Poly(3-hexylthiophene-2,5-diyl)	P3HT		regioregular	445703-1G
			regiorandom	510823-1G
			regioregular, electronic grade, >99.995%	669067-300MG 669067-1G

Poly(3-alkylthiophenes) are available with many other linear, branched, and cyclic alkyl side-chains. Please visit us at sigma-aldrich.com/organicelectronics for the complete listing of polythiophene products.

Achieving High Efficiency In Organic Light-Emitting Devices



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Introduction: Heterostructure OLEDs

Electroluminescence of organic molecules has been a well-known phenomenon for more than 50 years.^{1,2} However, it wasn't until the late 1980's that it became promising for practical use. Successful application of organic luminescence in light-emitting devices required device structures that overcame the problems associated with the high resistivity of organic materials, and achieved a well-balanced charge injection from the electrodes into organics. These two problems were solved by Tang and van Slyke³ with the thin film heterostructure concept for the organic LEDs (OLEDs). **Figure 1** shows a schematic of a double heterostructure OLED consisting of three organic layers sandwiched between the electrodes. The organic layers adjacent to the cathode and anode are the electron transport layer (ETL), and the hole transport layer (HTL), respectively.

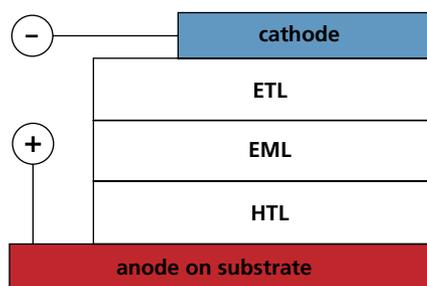


Figure 1. Schematic of a double heterostructure OLED consisting of a hole transport layer (HTL), electron transport layer (ETL), emissive layer (EML), and the electrodes.

During OLED operation, holes and electrons injected from the opposite electrodes are transported to the emissive layer (EML) where they recombine to form excitons. Film thicknesses of 500 Å or less lower drive voltages to the 5–10 V level, and separate hole and electron conducting layers provide efficient charge injection and carrier recombination. This leads to exciton formation, and ultimately emission as the exciton decays to the ground state. Shortly after the introduction of thin film heterostructure based OLEDs it was demonstrated that two-component emissive layers with emitter molecules doped into an appropriate host matrix increase the device efficiency by improving the level of charge recombination and exciton confinement in the emissive layer. This also eliminates self quenching of the emitting dopants.⁴

Increasing Efficiency of OLEDs Using Phosphorescence

The hole and electron in OLEDs are odd electron species with an equal distribution of $m_s = \pm \frac{1}{2}$. Thus, when the hole and electron recombine to form the exciton, a statistical mixture of singlet and triplet excitons are generated.^{5,6} This leads to a population of excitons that is 25% singlet and 75% triplet and has a profound effect on OLED efficiency. Most of the emitting dopants developed for OLEDs prior to the late 1990's emit from fluorescent states, which only utilize the singlet fraction of formed excitons.⁷ This limits the internal quantum efficiency of fluorescence based devices to 25%, corresponding to an external efficiency (front face) of only about 5%. In the late 1990's a new family of emissive dopants was introduced that gave marked increases in OLED efficiency. The key to this enhanced efficiency was the recognition that the triplet exciton fraction is more important than the singlet. Efficient harvesting of triplet excitons requires a phosphorescent dopant, which will trap both singlet and triplet excitons. An added requirement for the phosphorescent dopant is that it has a radiative lifetime comparable to the RC time constant of the OLED, which is typically in the microsecond time scale. The best way to achieve both high phosphorescence efficiency and a radiative lifetime on the order of microseconds is to incorporate a heavy metal atom into the dopant, whose spin orbit coupling will efficiently promote intersystem crossing between singlet and triplet states. The most commonly used metal for this

purpose is Ir, however, efficient phosphorescent dopants have been also prepared with other heavy metals as well, including Pt, Ru, Re, Au and Os.

Figure 2 shows structures and the CIE color coordinates of a number of Ir-based organometallic dopants. OLEDs have been prepared with the four circled dopants; their CIE coordinates are labeled with colored arrows. Since the introduction of Ir based phosphors in OLEDs in 1999,⁸ close to 200 different Ir complexes have been incorporated into OLEDs, most giving external efficiencies of 8% or greater.⁹ Several groups have reported that use of Ir based materials in optimized devices can give external efficiencies > 20%, corresponding to internal efficiencies of close to 100%.¹⁰⁻¹²

The emission energy for organometallic phosphors is closely related to the structure of organic ligands, making it possible to design a series of efficient phosphorescent emitters that covers most of the visible spectrum.^{13,14} The metal center of the complex can also be used to fine tune its emission energy. The emission from a transition metal complex originates from its lowest energy triplet excited state. Spectroscopic analysis shows that this state is predominantly localized on the cyclometalating ligands, mixed with singlet metal-to-ligand charge transfer (¹MLCT) character. Modification of ancillary ("non-emissive") ligands affects the energy of the metal orbitals and thus the amount of ¹MLCT character in the excited state. Varying the ratio of ligand centered to ¹MLCT character directly affects the energy of the mixed excited state.¹³ Thus, with modification of the ancillary ligand in (F₂ppy)₂Ir(L[^]X) complexes (L[^]X=ancillary ligand) it is possible to shift the emission energy of the complex from 458 to 512 nm. One of the deep blue complexes of this series [(F₂ppy)₂Ir(pz₂Bpz₂)] has been used to fabricate OLEDs which give external efficiencies > 11%.¹⁵

WOLEDs: Application of OLEDs in Illumination

An important potential application for LEDs is in illumination. The requirements for devices that serve as illumination sources are somewhat different than for the monochromatic OLEDs described above. OLEDs targeted for RGB displays have to give

electroluminescent spectra with a relatively narrow lineshape centered on the peak wavelength. On the other hand, an illumination source is meant to approximate the blackbody solar spectrum and needs to have a broad lineshape with roughly equal intensity across the entire visible spectrum. Therefore, in order to attain complete coverage across the visible spectrum, an OLED used for illumination purposes typically employs multiple emitters that are either co-deposited into a single emissive layer or distributed into different layers or regions of the device. A number of the different device architectures have been reported to achieve efficient white electroluminescence.

Most white organic LEDs (WOLEDs) utilize luminescence from several different colored emitters such that the combined output covers the visible spectrum uniformly. While WOLEDs with less than three distinct emitters have been reported, the most common approach in WOLEDs is to use three, *i.e.* blue, green and red. One of the simplest device architectures involves mixing blue, green and red dopants into a single emissive layer, such that the sum of the three emission spectra covers the visible spectrum.¹⁶⁻¹⁸ The use of phosphorescent emitters in a triple doped emissive layer can then lead to highly efficient devices. However, using three dopants in a single layer is problematic because energy readily transfers from the higher energy blue dopant to the green dopant and from the green dopant to the red dopant. Therefore, careful adjustment of the concentration of each dopant is required to achieve a well-balanced emission color, with doping levels in the ratio blue > green >> red. In order to get well-balanced white emission, the doping level of the red dopant typically needs to be well below 1%.

One solution to the inter-dopant energy transfer problem is to segregate the dyes into different layers. Efficient WOLEDs have been prepared using this stacked concept with either fluorescent¹⁸⁻²⁰ or phosphorescent emitters.²¹ More simplified structures have also been described that use dual component fluorescent blue and orange emitters doped into separate layers.^{19,22} While stacking the emitters in separate layers eliminates these energy transfer problems, the device architecture can become significantly more complicated due

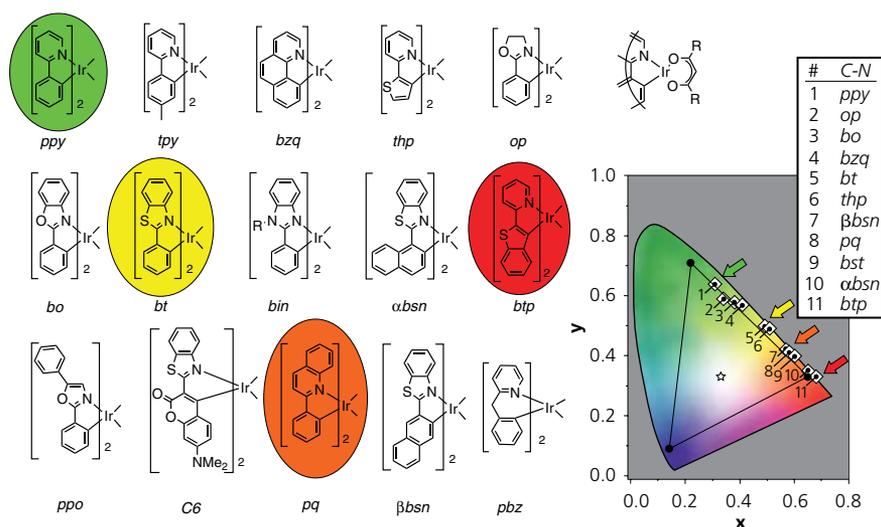


Figure 2. Chemical structures, CIE (Commission Internationale de L'Eclairage) chromaticity coordinates of OLEDs, and phosphorescence spectra of iridium cyclometalated complexes. The CIE coordinates for OLEDs with the ppy₂Ir(acac), bt₂Ir(acac), pq₂Ir(acac), and btp₂Ir(acac) phosphorescent dopants (the circled structures on the left) are marked with colored arrows. The CIE coordinates of the phosphorescence spectra of the rest of the C[^]N₂Ir(acac) complexes are also shown in square boxes on the CIE diagram. The NTSC standard coordinates for the red, green, and blue subpixels of a CRT are at the corners of the black triangle.

to difficulties in achieving balanced carrier recombination and exciton localization within each of the emitting layers.

The use of planar platinum based dopants makes it possible to prepare a broadband emitting (white) OLED with only a single dopant, contrary to approaches described above, which utilized two or three different emitters. **Figure 3** shows how the white color is achieved by combining the emission from the monomer (blue) and the aggregate (yellow-to-red) of the same organometallic platinum complex, giving an emission spectrum that covers the full range of visible wavelengths. The ratio of the monomer-to aggregate emission is controlled by both the doping concentration and the steric bulk of the dopant.²³ Increasing the steric bulk on the dopant impedes the aggregate formation, whereas increasing the dopant concentration favors it. Minimizing the number of dopants significantly reduces the complexity of the device. It has recently been shown that devices based on the monomer-aggregate approach to broadband emission can be used to achieve external efficiencies of 15–20%.^{24,25}

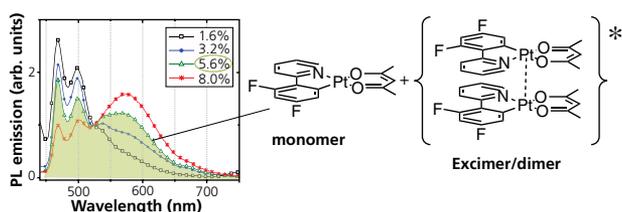


Figure 3. Photoluminescence spectra of F_2 -ppyPt(acac) doped films showing the spectral lineshape dependence on the doping level. The spectra consist of aggregate and monomer emission components. At doping concentration of 5.6%, the F_2 -ppyPt(acac) monomer-to aggregate ratio in the film is balanced to produce white light. Chemical structures of F_2 -ppyPt(acac) and its dimer are shown on the right.

White light is composed of roughly 25% blue, with the balance covering the energies between green and red. It also happens that the excitons formed on recombination of the holes and electrons in the OLED are formed in a ratio of 25% singlets to 75% triplets. The similarity in blue fraction of white light and the singlet fraction suggests an alternative approach to achieving high efficiency white emission: couple the singlet excitons to a blue fluorescent dopant and the triplets to phosphors covering the green and red portions of the spectrum. Such an implementation of combined fluorescent and phosphorescent emission has proven to have a number of advantages. Introduction of the stable fluorescent blue is expected to alleviate a well-known problem of limited operational life times of blue components of WOLEDs. The shape of the quantum efficiency-current density plots of the phosphorescent three-component WOLED, typically shows a steep roll-off of the efficiency curve at higher current densities soon after the efficiency achieves its maximum.²⁶ Triplet-triplet annihilation responsible for the unwanted efficiency decrease at high currents is decreased in the combined fluorescent/phosphorescent device, since the triplets are at lower concentration in the middle of the emissive layer than near the ETL or HTL interface where they are formed.

A significant advance has recently been reported for phosphorescent based WOLEDs. Nakayama, *et al.*, have prepared a WOLED in which blue, green and red phosphors are used to generate a broad spectrum white OLED.²⁷ Their device gave an efficiency of 64 lm/W at a brightness of 1000 cd/m². This efficiency exceeds compact fluorescent sources and is close

to that of fluorescent tube sources (ca. 75–90 lm/W). Moreover this device gave a device lifetime of greater than 10,000 hours at this brightness. These values are more than a factor of two higher than the previous records for OLEDs and clearly show that OLEDs have a bright future in lighting.

Conclusion

OLEDs have promise to make a marked impact in full color displays and lighting applications. Both of these families of devices require high efficiency and long lifetime, as well as low-cost fabrication, a wide-gamut for sets of devices and high color saturation. OLEDs have demonstrated all of these properties; however, large area fabrication remains a significant challenge, making manufacturing costs quite high. Another technological challenge is the device lifetimes for deep blue devices. There are a large number of stable red and green phosphorescent emitters, giving device lifetimes approaching 10⁶ hours. In contrast, the operational stability of the blue phosphor based OLEDs are typically markedly shorter, with the best values between 15K and 20K hours. The source of the enhanced instability of these blue devices is still an open question. While many fluorescent and phosphorescent OLEDs have been commercialized in small area mobile displays, there is still ample room for scientific investigation to better understand the parameters controlling and limiting organic electroluminescence.

References:

- (1) Pope, M.; Kallmann, H. P.; Magnante, P. J. *J. Chem. Phys.* **1963**, *38*, 2042.
- (2) Bernanose, A.; Comte, M.; Vouaux, P. *J. Chim. Phys.* **1953**, *50*, 64.
- (3) Tang, C. W.; VanSlyke, S. A. *Appl. Phys. Lett.* **1987**, *51*, 913.
- (4) Tang, C. W.; VanSlyke, S. A.; Chen, C. H. *J. Appl. Phys.* **1989**, *65*, 3610.
- (5) Segal, M.; Baldo, M. A.; Holmes, R. J.; Forrest, S. R.; Soos, Z. G. *Physical Review B: Condensed Matter and Materials Physics* **2003**, *68*, 075211/1.
- (6) Baldo, M. A.; O'Brien, D. F.; Thompson, M. E.; Forrest, S. R. *Physical Review B: Condensed Matter and Materials Physics* **1999**, *60*, 14422.
- (7) Shoustikov, A. A.; You, Y.; Thompson, M. E. *IEEE Journal of Selected Topics in Quantum Electronics* **1998**, *4*, 3.
- (8) Baldo, M. A.; Lamansky, S.; Burrows, P. E.; Thompson, M. E.; Forrest, S. R. *Appl. Phys. Lett.* **1999**, *75*, 4.
- (9) *Comprehensive Organometallic Chemistry III*; Crabtree, R. H.; Mingos, D. M., Eds.; Elsevier: Oxford, UK, 2007; Vol. 12, pp 101–194.
- (10) Tsuboyama, A.; Iwawaki, H.; Furugori, M.; Mukaide, T.; Kamatani, J.; Igawa, S.; Moriyama, T.; Miura, S.; Takiguchi, T.; Okada, S.; Hoshino, M.; Ueno, K. *J. Am. Chem. Soc.* **2003**, *125*, 12971.
- (11) Watanabe, S.; Agata, Y.; Tanaka, D.; Kido, J. *Journal of Photopolymer Science and Technology* **2005**, *18*, 83.
- (12) Meerheim, R.; Walzer, K.; Pfeiffer, M.; Leo, K. *Appl. Phys. Lett.* **2006**, *89*, 061111/1.
- (13) Li, J.; Djurovich, P. I.; Alleyne, B. D.; Yousufuddin, M.; Ho, N. N.; Thomas, J. C.; Peters, J. C.; Bau, R.; Thompson, M. E. *Inorg. Chem.* **2005**, *44*, 1713.
- (14) Brooks, J.; Babayan, Y.; Lamansky, S.; Djurovich, P. I.; Tsyba, I.; Bau, R.; Thompson, M. E. *Inorg. Chem.* **2002**, *41*, 3055.
- (15) Holmes, R. J.; D'Andrade, B. W.; Forrest, S. R.; Ren, X.; Li, J.; Thompson, M. E. *Appl. Phys. Lett.* **2003**, *83*, 3818.
- (16) Kawamura, Y.; Yanagida, S.; Forrest, S. R. *J. Appl. Phys.* **2002**, *92*, 87.
- (17) Tasch, S.; List, E. J. W.; Ekstrom, O.; Graupner, W.; Leising, G.; Schlichting, P.; Rohr, U.; Geerts, Y.; Scherf, U.; Mullen, K. *Appl. Phys. Lett.* **1997**, *71*, 2883.
- (18) Kido, J.; Shionoya, H.; Nagai, K. *Appl. Phys. Lett.* **1995**, *67*, 2281.
- (19) Jiang, X. Y.; Zhang, Z. L.; Zhao, W. M.; Zhu, W. Q.; Zhang, B. X.; Xu, S. H. *Journal Of Physics D-Applied Physics* **2000**, *33*, 473.
- (20) Ko, C. W.; Tao, Y. T. *Appl. Phys. Lett.* **2001**, *79*, 4234.
- (21) D'Andrade, B. W.; Thompson, M. E.; Forrest, S. R. *Advanced Materials* **2002**, *14*, 147.
- (22) Yang, J. P.; Jin, Y. D.; Heremans, P. L.; Hoefnagels, R.; Dieltiens, P.; Blockhuys, F.; Geise, H. J.; Van der Auweraer, M.; Borghs, G. *Chem. Phys. Lett.* **2000**, *325*, 251.
- (23) Adamovich, V.; Brooks, J.; Tamayo, A.; Alexander, A. M.; Djurovich, P. I.; D'Andrade, B. W.; Adachi, C.; Forrest, S. R. *New J. Chem.* **2002**, *26*, 1171.
- (24) Cocchi, M.; Kalinowski, J.; Virgili, D.; Fattori, V.; Develay, S.; Williams, J. A. G. *Appl. Phys. Lett.* **2007**, *90*, 163508/1.
- (25) Williams, E. L.; Haavisto, K.; Li, J.; Jabbour, G. E. *Advanced Materials (Weinheim, Germany)* **2007**, *19*, 197.
- (26) Sun, Y.; Giebnc, N. C.; Kanno, H.; Ma, B.; Thompson, M. E.; Forrest, S. R. *Nature* **2006**, *440*, 908.
- (27) Nakayama, T.; Hiyama, K.; Furukawa, K.; Ohtani, H. *Society for Information Display (SID) Symposium Digest* **2007**, *38*, 1018.

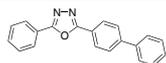
OLED Materials

Sigma-Aldrich offers a wide selection of OLED materials. A portion of our offer is presented here by common usage in OLED research. Please visit us at sigma-aldrich.com/organelectronics for the complete list and the latest products.

Electron Transport

2-(4-Biphenyl)-5-phenyl-1,3,4-oxadiazole, 99%

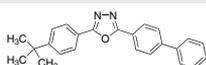
PBD
[852-38-0]



257850-5G	5 g
257850-25G	25 g

2-(4-tert-Butylphenyl)-5-(4-biphenyl)-1,3,4-oxadiazole, 99%

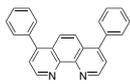
Butyl-PBD
[15082-28-7]



B8378-5G	5 g
B8378-100G	100 g

Bathophenanthroline, 97%

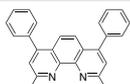
Bphen
[1662-01-7]



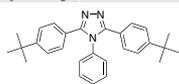
133159-500MG	500 mg
133159-1G	1 g

Bathocuproine, 96%

BCP
[4733-39-5]



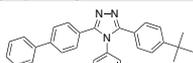
140910-500MG	500 mg
140910-1G	1 g

Tris-(4-carbazoyl-9-yl-phenyl)-amine

685682-1G	1 g
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Tris-(4-carbazoyl-9-yl-phenyl)-amine

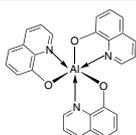
TAZ



685720-1G	1 g
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8-Hydroxyquinoline aluminum salt, 99.995%

Alq3
 λ_{abs} : 259 nm
 λ_{em} : 512 nm (lit.)
[2085-33-8]

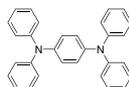


444561-1G	1 g
444561-5G	5 g

Hole Transport

1,4-Bis(diphenylamino)benzene, 97%

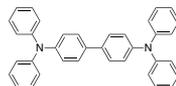
[14118-16-2]



663271-1G	1 g
663271-10G	10 g

Tetra-N-phenylbenzidine, 97%

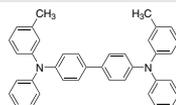
TPB
[15546-43-7]



658812-5G	5 g
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N,N'-Bis(3-methylphenyl)-N,N'-diphenylbenzidine

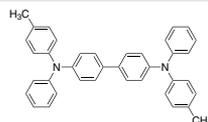
TPD
[65181-78-4]



443263-1G	1 g
443263-5G	5 g

N,N'-Diphenyl-N,N'-di-p-tolylbenzene-1,4-diamine

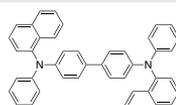
[138171-14-9]



663263-1G	1 g
663263-5G	5 g

N,N'-Di-[(1-naphthyl)-N,N'-diphenyl]-1,1'-biphenyl)-4,4'-diamine, sublimed, 99%

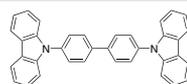
NPD
[123847-85-8]



556696-500MG	500 mg
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4,4'-Bis(N-carbazoyl)-1,1'-biphenyl, 97%

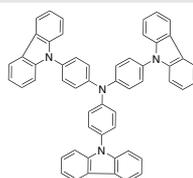
CBP, DCBP
[58328-31-7]



660124-1G	1 g
660124-5G	5 g

Tris-(4-carbazoyl-9-yl-phenyl)-amine, 97%

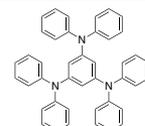
TCTA
[13909-27-87]



688053-500MG	500 mg
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1,3,5-Tris(diphenylamino)-benzene, 97%

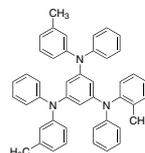
TDAB
[126717-23-5]



663247-5G	5 g
663247-10G	10 g

1,3,5-Tris[(3-methylphenyl)-phenylamino]benzene, 97%

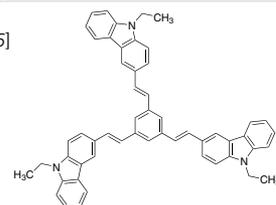
[138143-23-4]



663239-1G	1 g
663239-10G	10 g

1,3,5-Tris(2-(9-ethylcabazyl)-3)ethylene)benzene

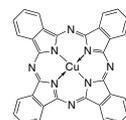
TECEB
[848311-04-6]



661732-500MG	500 mg
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Copper(II) phthalocyanine, sublimed, 99%

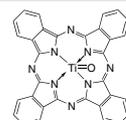
CuPc
[147-14-8]
 λ_{abs} : 678 nm (CHCl₃)
 λ_{em} : 404 nm (film, lit.)



546674-1G	1 g
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Titanyl phthalocyanine, dye content 95%

[26201-32-1]
 λ_{abs} : 692 nm (chlorobenzene)
 λ_{em} : 392 nm (film, lit.)

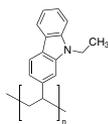


404551-250MG	250 mg
404551-1G	1 g

Polymer Hole Transporter/Host

Poly(*N*-ethyl-2-vinylcarbazole)

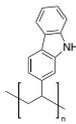
λ_{abs} : 239 nm (CHCl₃)
[41008-78-0]



649325-500MG 500 mg

Poly(2-vinylcarbazole), $M_w \sim 6,400$

[55447-28-4]



649287-500MG 500 mg

Poly(9-vinylcarbazole), $M_n = 25,000 - 50,000$

PVK
[25067-59-8]



368350-5G 5 g

$M_w \sim 1,100,000$

182605-10G 10 g

182605-25G 25 g

Poly(1-vinylnaphthalene), $M_w \sim 30,000$

[29793-40-6]



541451-1G 1 g

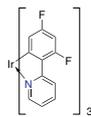
$M_n \sim 100,000$

191965-1G 1 g

Emitters/Dopants

Tris[2-(4,6-difluorophenyl)pyridinato-C2,N]iridium(III)

Ir(Fppy)₃, blue
 λ_{abs} : 347 nm
 λ_{em} : 471 nm (lit.)



682594-250MG 250 mg

Perylene, sublimed, 99.5%

blue
 λ_{abs} : 436 nm
 λ_{em} : 447 nm,
471 nm (lit.)
[198-55-0]



394475-1G 1 g

394475-5G 5 g

See p. 8 for more perylene derivatives under "n-Type Semiconductors."

Tris[2-phenylpyridinato-C2,N]-iridium(III)

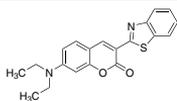
Ir(ppy)₃, green
 λ_{abs} : 282 nm
 λ_{em} : 510 nm (lit.)
[94928-86-6]



688096-250MG 250 mg

Coumarin 6, 99%

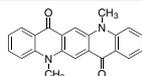
green
 λ_{abs} : 457 nm
 λ_{em} : 505 nm (EtOH)
[38215-36-0]



546283-100MG 100 mg

5,12-Dihydro-5,12-dimethylquino[2,3-b]acridine-7,14-dione

DMQA, green
 λ_{abs} : 295 nm
 λ_{em} : 523 nm
[19205-19-7]

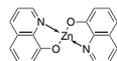


557587-100MG 100 mg

557587-500MG 500 mg

8-Hydroxyquinoline zinc salt, 99%

Znq, yellow
 λ_{abs} : 251 nm
 λ_{em} : 478 nm (CHCl₃)



471755-5G 5 g

471755-25G 25 g

Tris[1-phenylisoquinolino-C2,N]iridium(III)

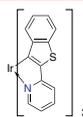
Ir(piq)₃, red
 λ_{abs} : 324 nm
 λ_{em} : 615 nm (lit.)
[435293-93-9]



688118-250MG 250 mg

Tris[2-(benzo[b]thiophen-2-yl)pyridinato-C3,N]iridium(III)

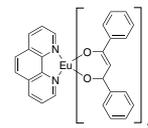
Ir(btpp)₃, red
 λ_{abs} : 324 nm
 λ_{em} : 590 nm (lit.)
[405289-74-9]



680877-250MG 250 mg

Tris(dibenzoylmethane) mono(1,10-phenanthroline)europium(III)

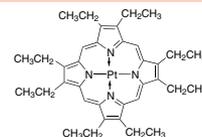
Eu(dbm)₃(phen), red
 λ_{abs} : 355 nm
 λ_{em} : 615 nm (lit.)
[17904-83-5]



538965-250MG 250 mg

Platinum octaethylporphyrin, dye content 98%

PtOEP, red
 λ_{abs} : 381 nm
 λ_{em} : 650 nm (lit.)
[31248-39-2]



673625-100MG 100 mg

5,6,11,12-Tetraphenylnaphthacene, sublimed

Rubrene, red
 λ_{abs} : 299 nm
 λ_{em} : 553 nm
[517-51-1]

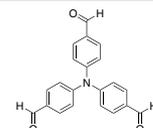


551112-100MG 100 mg

551112-500MG 500 mg

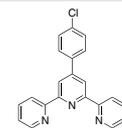
Synthetic Intermediates

Tris(4-formylphenyl)amine, 97%



679658-5G 5 g

4'-(4-Chlorophenyl)-2,2':6',2''-terpyridine, 97%



687073-1G 1 g

687073-5G 5 g

Light-Emitting Polymers



Prof. Qibing Pei

Department of Materials Science and Engineering, California NanoSystems Institute, and Henry Samuli School of Engineering and Applied Science, UCLA

Introduction

Conjugated polymers with long range π -electron delocalization behave as processable organic “metals” in their doped state and as semiconducting materials in their neutral undoped state.¹⁻³ Many undoped polymers exhibit strong photoluminescence (PL) in the visible and near infrared range. Switching between doped and undoped states induces changes in a number of Light Emitting Polymer (LEP) properties, such as polymer volume, absorption color, and reversible PL quenching. These controlled changes make LEPs promising for applications: an induced variation in absorption color may be exploited for electrochromic displays while a change in volume may be utilized for electroactive artificial polymer muscles.⁴⁻⁵ The combination of semiconductivity and intense PL results in LEP electroluminescence and their use in polymer light emitting diodes (PLEDs). The high sensitivity of PL quenching to doping or charge transfer can be used to detect biological and explosive species. Therefore, the LEPs represent an important category of low-temperature processable materials useful for many scientific and technological explorations.

PLEDs are currently under development for applications in flat panel displays and lighting with strong commercialization potential that depends on understanding and improvement of properties of the LEPs. For example, although a PLED has a relatively simple thin-film device structure as illustrated in **Figure 1**, a high-performance PLED requires the LEP layer to meet several stringent requirements: (1) color purity, which is determined by the polymer bandgap and film morphology; (2) matching of ionization potentials and electron affinities between LEP and the different electrode materials; (3) high PL quantum efficiency; (4) chemical and thermal stability; and (5) processability which involves solubility, solution viscosity, and solvent-substrate compatibility. These properties can be adjusted by changing the chemical structure of the conjugated polymer chains, side groups, incorporation of heteroatoms, molecular weight, structural regularity, and/or copolymerization. This article reviews the main categories of LEPs tailored for different applications. Note that LEPs include both polymers containing fully conjugated main chain and those with conjugated segments in the main chain or side groups. Most conjugated oligomers exhibit similar processability and luminescent properties as their polymeric counterparts.

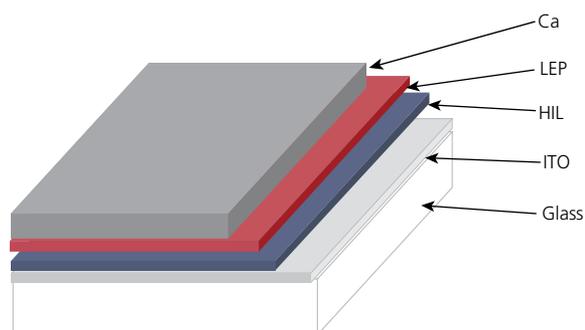


Figure 1. Schematic illustration of a polymer light emitting diode (PLED). HIL=hole injection layer, usually a spin-cast film of an inherently conductive polymer (PEDOT or polyaniline). See page 15.

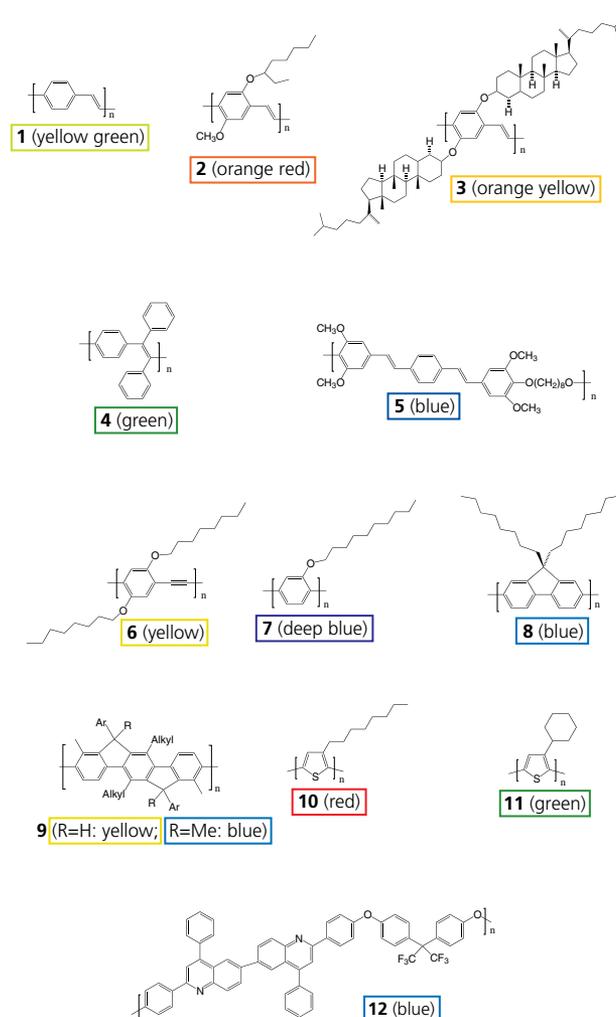
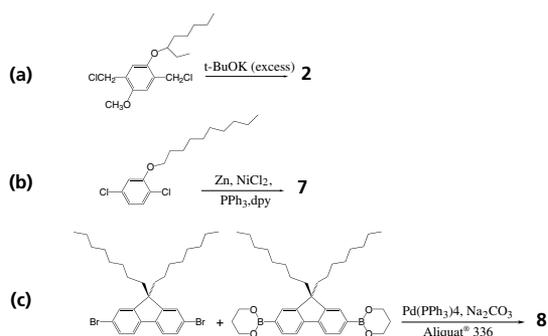


Figure 2. Representative classes of light-emitting polymers referenced in the following paragraphs.

Poly(1,4-phenylene vinylene) (PPV)

References to polymer structures depicted in **Figure 2** are shown in boldface. PPV (**1**) and its soluble derivatives are among the most widely studied LEPS. PPV is generally prepared via a precursor, poly(xylylidene tetrahydrothiophenium chloride) (**540765**), which is soluble in water and methanol. PPV was used to make the earliest conjugated polymer light emitting diode (LED), but the relatively low PL quantum efficiency and high-temperature conversion of the precursor to PPV prompted the synthesis of many new PPV derivatives that are soluble in common organic solvents. MEH-PPV (**2**, **541443**) can be conveniently synthesized from the corresponding monomer 1,4-bis(chloromethyl)-2-methoxy-5-(2'-ethylhexyloxy)benzene (**536250**) (**Scheme 1a**).⁶ The dialkoxy side groups also modify the polymer's bandgap, so that the emission color bathochromically shifts to orange from the yellow-green of the unsubstituted PPV. MEH-PPV was used in the fabrication of first high efficiency polymer LEDs. The emission color is slightly shifted further toward red when the 2'-ethylhexyloxy side group is replaced by 3',7'-dimethyloctyloxy group (MDMO-PPV **546461**). In BCHA-PPV(**3**) where the side groups are bulky 2,5-bis(cholestanoxyl), the color is shifted in the opposite direction, to orange-yellow. Many other side groups have also been used to modify the emission color.^{7,8,9} Side groups can also be introduced to the vinyl moieties of PPV. For instance, poly[(1,4-phenylene-1,2-diphenylvinylene)] (**4**) is a green emitter with high PL efficiency and stability.



Scheme 1: Synthetic routes to polymers (**2**), (**7**), and (**8**).

Gilch polymerization was used to prepare MEH-PPVs in high yield and high molecular weight. In the Gilch reaction of 1,4-bis(chloromethyl)-2,5-bis(3',7'-dimethyloctyloxy)benzene (**546488**), 1.5–2.0% of tolane-bisbenzyl moieties were found to be the only defects on the PPV mainchain.¹⁰ In the polymerization of 1,4-bis(chloromethyl)-2-methoxy-5-(3-decyloxyphenyl)benzene, the *p*-quinodimethane intermediate is fairly polar. The subsequent free-radical polymerization is almost exclusively a head-to-tail coupling that yields a substituted PPV containing 0.5% of the tolane-bisbenzyl defects. Such low defects are important for achieving high performance polymer LEDs. Substituted PPV with relatively low molecular weights can also be synthesized by condensation polymerization routes (Wittig, Heck, Knoevenagel).¹¹ In the Knoevenagel polymers, a cyano group is introduced to each vinylene moiety of dialkoxy-PPV. The resulting polymers show an intra molecular “push–pull” effect of π -electron clouds that effectively reduces the bandgap and shifts the emission color into deep red region.

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The emission color and the PL quantum efficiency of substituted PPV can be finessed via copolymers of PPV containing different side groups. For instance, varying the ratio of the comonomers in poly[(2-dimethyloctylsilyl-1,4-phenylene vinylene)-co-(MEH-PPV)], can systematically tune the emission color from green of the silyl-PPV to orange in MEH-PPV. To obtain emission colors in the green to blue range, one may adopt copolymers consisting of short segments of PPV strung together with non-conjugated moieties such as alkylenedioxy, oligo(ethylene oxide), and dimethylsilane.¹² Copolymer (**5**) is an efficient blue emitter. These copolymers, however, generally exhibit poor charge carrier conductivity. Poly(2,5-dialkoxy-1,4-phenyleneethynylene) (PPE) are dehydro analogs of dialkoxy-PPV. The emission peak of the PPE (**6**) (**636991**) is narrower and blue shifted compared to corresponding PPVs.¹³

Poly(1,4-phenylene) (PPP)

Blue LEPS can be made from poly(1,4-phenylene) (PPP) and its various derivatives. Soluble PPPs can be synthesized from the corresponding dichloro, dibromo or diborate monomers via Grignard, Ni⁰-catalyzed Yamamoto, or Suzuki reactions.^{14,15} The molecular weights of the resulting polymers, however are rather low, often less than 10,000. High molecular weight soluble PPPs containing electron-withdrawing groups such as benzoyl, can be obtained via the Ni⁰-catalyzed Yamamoto coupling of the corresponding dichloro-monomers (**Scheme 1b**). All of the substituted PPP emit deep blue light with a significant portion of the emission in the UV region. Poly(2-decyloxy-1,4-phenylene) (**7**) exhibits both high PL and EL quantum yields. The emission peaks at about 410 nm.

Polyfluorenes (PFO)

Polyfluorene, in which every pair of phenyl rings are locked in plane by the C-9, has a slightly smaller bandgap than PPP. Most of its PL is within the blue region of the visible spectrum.^{16,17} In poly(9,9-dioctylfluorene) (**8**) (**571652**), the solubilizing alkyl groups are located on the C-9, far away from the C-2 and C-7 positions and interfere little with the polymerization of the corresponding monomers that links the fluorene units through C-2 and C-7. Polymers with Mw > 100,000 and PL quantum yield > 70% have been obtained by both the Ni⁰-catalyzed Yamamoto coupling and the Pd⁰-catalyzed Suzuki coupling polymerization.¹⁷ With the use of a surfactant (for example, Aliquat[®] 336, **205613**) to increase the mixing of solvents in the Suzuki polymerization (**Scheme 1c**), the molecular weights can be further increased up to 1,000,000.¹⁸ Alternating PF copolymers can be synthesized by the Suzuki route. Introduction of triphenylamine comonomers enhances the hole-transporting ability of the polyfluorenes, whereas thiophene and 1,3,4-benzothiadiazole comonomers reduce the polyfluorene's bandgap and shift the emission color toward green or even red.¹⁹ Soluble derivatives of polyfluorenes and PPVs are currently commercialized for LED display and illumination products.

Further locking of the phenyl rings into its coplanar structure is obtained in ladder-type PPPs. The enhanced conjugation along the polymer backbone and excimer formation due to inter-chain interaction entails large side groups for solubility.²⁰ The ladder polymer (**9**, R=H) exhibits intense blue luminescence in dilute solution. The PL of the solid thin film shifts to yellow with only 10% quantum yield due to excimer formation. When R is replaced with a methyl group, the excimer formation is suppressed, and the resulting solid thin film exhibits intense blue luminescence, similar to the polymer in dilute solution.

Poly(thiophenes)

Poly(3-alkylthiophene)s have been extensively studied for their thermo- and solvatochromism, as well as for applications in field effect transistors. Regiorandom poly(3-octylthiophene) (**10**) (**510831**) shows relatively weak red PL in dilute solution. The emission is largely quenched in concentrated solutions and solid thin films. Bulky side groups such as cyclohexyl (**11**) (**557625**) twist the coplanarity of the polythiophene main chain and shift the emission color to green.²¹ Poly(3-methyl-4-cyclohexylthiophene) emits blue light. On the other hand, regioregular poly(3-alkylthiophene) (see products on page 7) is shown to have coplanar polymer main chains that can orderly pack into crystalline nanometer-size domains with high hole mobility. They are being studied as p-type semiconductors for thin film transistors and solar cells. Thiophene, 3-alkylthiophene, and 3-alkoxythiophene are frequently used as comonomers to reduce the bandgap of PPP, PF, and PPV.

Nitrogen-Containing Polymers

Heterocyclic rings containing imino-N are electron-acceptors when conjugated with hydrocarbon-based π -systems. Poly(2,5-pyridinevinylene) emits red light in dilute solutions, but PL quantum efficiency is relatively low due to strong dipole interaction that promotes aggregate formation. Protonation or alkylation of the N-atom causes a complicated change of emission color and efficiency.²² Quinoline is a useful building unit for PPP-type copolymers with high electron affinity. Polyquinoline (**12**) is an efficient blue emitter. 1,3,4-Oxadiazole is another heterocyclic aromatic ring often copolymerized with phenyl rings to increase electron affinity.²³ 1,3,4-Oxadiazole containing polymers and copolymers with large bandgap are often used as electron-transporting materials, while those with smaller bandgap and visible light emission are also used in PLEDs. On the other hand, tertiary amine and derivatives are used as hole transporting polymers. Poly(9-vinylcarbazole) (PVK) (**182605**) is a good photoconductive material. It is a popular wide-bandgap host for other emissive materials such as perylene and phosphorescent dopants.

Water-Soluble LEPS

Ionic groups such as quaternary ammonium and sulfonate can be attached to conjugated polymers via a flexible tether to render solubility in water or methanol. The sulfonato-substituted polythiophene is self-dopable in water and does not show appreciable luminescence upon doping. The sulfonated PPV (**659894**), PPP, and PF exhibit intense PL in dilute water solution^{24,25} with emission color similar to analogous polymers without the sulfonato groups. These water-soluble luminescent polymers have been studied for biosensing due to the high sensitivity quenching of the PL by electron-acceptors like methyl viologen (**856177**).

In conclusion, LEPS are characterized by (1) a high absorption coefficient, as high as $10^5/\text{cm}$, (2) a high PL efficiency, since a quantum efficiency greater than 50% is frequently obtained for blue and green emissive polymers in solid state thin films, and (3) a large Stokes' shift and thus show little self absorption of its PL emission. Polymer synthesis provides a convenient tool to tune these properties: **Figure 3** illustrates a series of LEPS covering the entire visible spectrum. The LEPS enable a wide range of important applications including sensors, flexible LED displays and lighting devices,

optical pump lasers, and potentially polymer diode lasers. It is important to note that susceptibility of the LEPS to environmental oxygen, moisture, and UV may present certain limitations and may inhibit the future commercialization of some of the products.

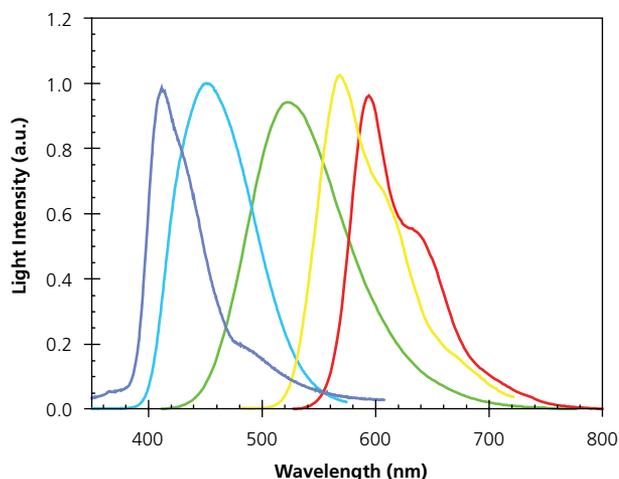


Figure 3. Film electroluminescence spectra of representative LEPS. Peak position from left to right: (**7**), (**12**), (**4**), (**3**) (**2**).

References:

- (1) *Handbook of Conducting Polymers*, 2nd ed.; Skotheim, T.A.; Elsenbaumer, R. L.; Reynolds, J. R., Eds. Marcel Dekker: New York, **1998**.
- (2) Akcelrud, L. *Prog. Polym. Sci.* **2003**, *28*, 875.
- (3) McQuade, D.T.; Pullen, A. E.; Swager, T. M. *Chem. Rev.* **2000**, *100*, 2537.
- (4) Argun, A.; Aubert, P. H.; Thompson, B. C.; Schwendeman, I.; Gaupp, C. L.; Hwang, J.; Pinto, N. J.; Tanner, D. B.; MacDiarmid, A. G.; Reynolds, J. R. *Chem. Mater.* **2004**, *16*, 4401.
- (5) Pei, Q.; Inganas, O. *Adv. Mater.* **1992**, *4*, 277.
- (6) Wudl, F.; Srdanov, G. *United States Patent* 5,189,136, **1993**.
- (7) Kim, S. T.; Hwang, D. H.; Li, X. C.; Grüner, J.; Friend, R. H.; Holmes, A. B.; Shim, H. K. *Adv Mater.* **1996**, *8*, 979.
- (8) Spreitzer, H.; Becker, H.; Kluge, E.; Kreuder, W.; Schenk, H.; Demandt, R.; Schoo, H. *Adv. Mater.* **1998**, *10*, 1340–1343.
- (9) Johansson, D. M.; Srdanov, G.; Yu, G.; Theander, M.; Inganäs, O.; Andersson, M. *Macromolecules* **2000**, *33*, 2525.
- (10) Becker, H.; Spreitzer, H.; Ibrom, K.; Kreuder, W. *Macromolecules* **1999**, *32*, 4925.
- (11) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem. Int. Ed.* **1998**, *37*, 402.
- (12) Hu, B.; Karasz, F. J. *Appl. Phys.* **2003**, *93*, 1995.
- (13) Montali, A.; Smith, P.; Weder, C. *Synth. Met.* **1998**, *97*, 123.
- (14) Rehahn, M.; Schlüter, A.-D.; Wegner, G. *Makromol. Chem.* **1990**, *191*, 1991.
- (15) Yang, Y.; Pei, Q.; Heeger, A. J. *J. Appl. Phys.* **1996**, *79*, 934.
- (16) Fukuda, M.; Sawada, K.; Yoshino, K. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 2465.
- (17) Pei, Q.; Yang, Y. *J. Am. Chem. Soc.* **1996**, *118*, 7416.
- (18) Inbasekaran, M.; Woo, E.; Wu, W. S.; Bernius, M.; Wujkowski, L. *Synth. Met.* **2000**, *111*, 397.
- (19) Bernius, M. T.; Inbasekaran, M.; Woo, E.; Wu, W.; Wujkowski, L. *J. Mater. Sci.: Mater. Electron.* **2000**, *11*, 111.
- (20) Scherf, U. *J. Mater. Chem.* **1999**, *9*, 1853.
- (21) Andersson, M. R.; Berggren, M.; Inganäs, O.; Gustafsson, G.; Gustafsson-Carlberg, J. C.; Selse, D.; Hjertberg, T.; Wennerström, O. *Macromolecules* **1995**, *28*, 7525.
- (22) Wang, Y. Z.; Epstein, A. J. *Acc. Chem. Res.* **1999**, *32*, 217.
- (23) Pei, Q.; Yang, Y. *Chem. Mater.* **1995**, *7*, 1568.
- (24) Huang, F.; Wu, H. B.; Wang, D.; Yang, W.; Cao, Y. *Chem. Mater.* **2004**, *16*, 708–716.
- (25) Chen, L.; McBranch, D. W.; Wang, H.; Helgeson, R.; Wudl, F.; Whitten, D. *Proc. Natl. Acad. Sci. U.S.A.* **1999**, *96*, 12287.

Light-Emitting Polymer Products

The list below represents a selection of our LEP products. For the complete list, including PPV-PFO co-polymers, PFE polymers, and polyacetylenes, visit us at sigma-aldrich.com/LEP.

Polyphenylene Vinylene (PPV) Polymers and Co-Polymers

Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene]	
MEH-PPV	
λ_{emr} nm: 554 (toluene)	
Mn~51,000	
541443-1G	1 g
Mn~86,000	
541435-1G	1 g
Mn~125,000	
536512-1G	1 g
Poly[2-(2',5'-bis(2"-ethylhexyloxy)-phenyl)-1,4-phenylenevinylene]	
BEHP-PPV	
λ_{emr} nm: 489, 524 (film, lit.) 476 (toluene)	
546615-1G	1 g
Poly(2,5-bis(1,4,7,10-tetraoxaundecyl)-1,4-phenylenevinylene)	
BTEM-PPV	
λ_{emr} nm: 433 (CHCl ₃)	
644218-1G	1 g
Poly[2,5-bis(3',7'-dimethyloctyloxy)-1,4-phenylenevinylene]	
λ_{emr} nm: 548 (toluene)	
546518-1G	1 g
Poly[2,5-bis(octyloxy)-1,4-phenylenevinylene]	
λ_{emr} nm: 548 (CHCl ₃)	
555037-1G	1 g

Poly(2,5-dihexyloxy-1,4-phenylenevinylene)	
λ_{emr} nm: 547 (CHCl ₃)	
560804-1G	1 g
Poly(2,5-dioctyl-1,4-phenylenevinylene)	
λ_{emr} nm: 490 (CHCl ₃)	
653438-1G	1 g
Poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylenevinylene]	
MDMO-PPV	
λ_{emr} nm: 550 (toluene)	
546461-1G	1 g
Poly[[2-[2',5'-bis(2"-ethylhexyloxy)phenyl]-1,4-phenylenevinylene]-co-[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene]]	
BEHP-co-MEH-PPV	
λ_{emr} nm: 551 (film, lit.) 526 (CHCl ₃)	
570265-1G	1 g
Poly[(m-phenylenevinylene)-alt-(2-methoxy-5-(2-ethylhexyloxy)-p-phenylenevinylene)]	
λ_{emr} nm: 451 (CHCl ₃)	
594318-1G	1 g

Poly[(p-phenylenevinylene)-alt-(2-methoxy-5-(2-ethylhexyloxy)-p-phenylenevinylene)]	
λ_{emr} nm: 517 (CHCl ₃)	
594199-1G	1 g
Poly[(o-phenylenevinylene)-alt-(2-methoxy-5-(2-ethylhexyloxy)-p-phenylenevinylene)]	
λ_{emr} nm: 471 (CHCl ₃)	
594083-1G	1 g
Poly[(m-phenylenevinylene)-alt-(2,5-dihexyloxy-p-phenylenevinylene)]	
λ_{emr} nm: 451 (CHCl ₃)	
575410-1G	1 g
Poly[tris(2,5-bis(hexyloxy)-1,4-phenylenevinylene)-alt-(1,3-phenylenevinylene)]	
PTDPV	
λ_{emr} nm: 518 (CHCl ₃)	
664936-500MG	500 mg

Cyano-Polyphenylene Vinylene (CN-PPV) Polymers

Poly(2,5-di(3,7-dimethyloctyloxy)cyanoterephthalylidene)	
646571-250MG	250 mg

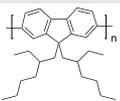
Poly(5-(3,7-dimethyloctyloxy)-2-methoxy-cyanoterephthalylidene)	
646628-250MG	250 mg
Poly(5-(2-ethylhexyloxy)-2-methoxy-cyanoterephthalylidene)	
646644-250MG	250 mg

Poly(2,5-di(hexyloxy)-cyanoterephthalylidene)	
646652-250MG	250 mg
Poly(2,5-di(octyloxy)-cyanoterephthalylidene)	
646660-250MG	250 mg

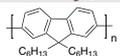
For questions, product data, or new product suggestions, please contact the Materials Science team at matsci@sial.com.

Polyfluorene (PFO) Polymers and Selected Monomers

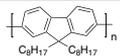
Poly[9,9-bis(2-ethylhexyl)-9H-fluorene-2,7-diyl]

 λ_{emr} nm:
409 (CHCl₃)

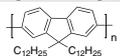
571032-1G 1 g

Poly(9,9-di-*n*-hexylfluorenyl-2,7-diyl) λ_{emr} nm:
414 (CHCl₃)

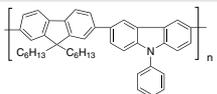
571040-1G 1 g

Poly(9,9-di-*n*-octylfluorenyl-2,7-diyl) λ_{emr} nm:
417 (CHCl₃)

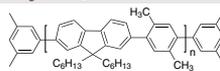
571652-500MG 500 mg

Poly(9,9-di-*n*-dodecylfluorenyl-2,7-diyl)

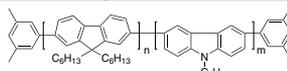
571660-500MG 500 mg

Poly(9,9-*N*-dihexyl-2,7-fluorene-*alt*-9-phenyl-3,6-carbazole) λ_{emr} nm:
398 (CHCl₃)

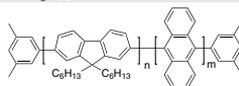
678791-250MG 250 mg

Poly(9,9-*N*-dihexyl-2,7-fluorene-*alt*-2,5-dimethyl-1,4-phenylene)

685690-500MG 500 mg

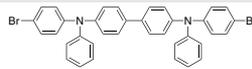
Poly[(9,9-dihexylfluorene-2,7-diyl)-*alt*-(9-ethylcarbazol-2,7-diyl)]

685704-500MG 500 mg

Poly[(9,9-Dihexylfluorene-2,7-diyl)-*alt*-(anthracen-9,10-diyl)]

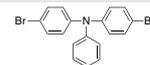
685712-500MG 500 mg

4,4'-Bis[(4-bromophenyl)phenylamino]biphenyl, 97%



656674-1G 1 g

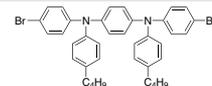
4,4'-Dibromotriphenylamine, 96%



679917-1G 1 g

679917-5G 5 g

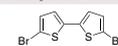
N1,N4-bis(4-bromophenyl)-N1,N4-bis(4-butylphenyl)benzene-1,4-diamine



688037-1G 1 g

688037-5G 5 g

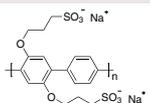
5,5'-Dibromo-2,2'-bithiophene, 99%



515493-1G 1 g

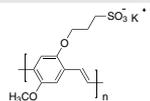
515493-5G 5 g

Water-Soluble LEPS

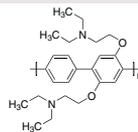
Poly(2,5-bis(3-sulfonatopropoxy)-1,4-phenylene, disodium salt-*alt*-1,4-phenylene)(-)PPP
 λ_{emr} nm:
424 (H₂O)

659223-500MG 500 mg

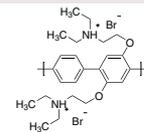
Poly[5-methoxy-2-(3-sulfopropoxy)-1,4-phenylenevinylene] potassium salt solution

MPS-PPV
 λ_{emr} nm:
525 (H₂O)

659894-10ML 10 mL

Poly[[2,5-bis(2-(*N,N*-diethylamino)ethoxy)-1,4-phenylene]-*alt*-1,4-phenylene] λ_{emr} nm:
401 (CHCl₃)

678066-300MG 300 mg

Poly[(2,5-bis(2-(*N,N*-diethylammonium bromide)ethoxy)-1,4-phenylene)-*alt*-1,4-phenylene] λ_{emr} nm:
421 (DMSO)

678074-300MG 300 mg

Monomers for LEPS

Sigma-Aldrich offers monomers for the synthesis of PPV, CN-PPV, and PFO Polymers. For a complete list visit us at sigma-aldrich.com/organicelectronics.

OLED Substrates and Electrode Materials

Indium Tin Oxide (ITO) Coated Substrates

Prod. No.	*Product description	Surface Resistivity, Ω/\square
636932	ITO coated PET slide	8–12
636924	ITO coated PET slide	60–100
639311	ITO coated PET sheet	35
668559	ITO coated PET sheet	45
639303	ITO coated PET sheet	60
639281	ITO coated PET sheet	100
578274	ITO coated glass slide	8–12
636916	ITO coated glass slide	15–25
636908	ITO coated glass slide	30–60
576352	ITO coated glass sheet	70–100
576360	ITO coated aluminosilicate glass slide	5–15

*PET = poly(ethylene terephthalate); slide = 25 x 75 x 1.1 mm; sheet = 1ft x 1ft x 5mil

Electrode Materials

Prod. No.	Product Description	Purity
669431	Lithium fluoride, precipitated	99.995%
255645	Cesium carbonate	99.995%
203815	Molybdenum(VI) oxide	99.990%
441872	Calcium, distilled	99.995%
433705	Aluminum, evaporation slug	99.999%
373249	Silver, evaporation slug	99.99%

Numerous other electronic grade oxides and metals are available from Sigma-Aldrich. For a complete list visit sigma-aldrich.com/electronicgrade.

Additions and Corrections to *Material Matters*™ Vol. 2 No. 2 "Hydrogen Storage Materials"

Recent Developments on Hydrogen Release from Ammonia Borane

A. Karkamkar, C. Aardahl, T. Autrey
Pacific Northwest National Laboratory

The pioneering work from the Manners group on catalytic release of hydrogen from dimethylamine borane was inadvertently left out of our review. Their work should have superseded reference 17 in the review. (17)(a) Jaska, C. A., Temple, K., Lough, A. J., Manners, I. *Chem. Comm.* **2001**, 962. (b) Jaska, C. A., Temple, K., Lough, A. J., Manners, I. *J. Am. Chem. Soc.* **2003**, 125, 9424.

For questions, product data, or new product suggestions,
please contact the Materials Science team at matsci@sial.com.

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