N-TYPE MATERIALS AND ORGANIC ELECTRONIC DEVICES

FIELD OF THE INVENTION

[0001] The present invention relates to organic compounds, n-type acceptor material derived from such compounds and devices comprising such n-type acceptor material.

BACKGROUND OF THE INVENTION

[0002] Organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), and organic solar cells (also referred to as organic photovoltaics or OPVs) based on organic molecules have been extensively studied. Such devices are becoming increasingly popular due to their low-cost processing, relatively simple packaging, and compatibility with flexible substrates.

[0003] More specifically, OPVs come with the promise of efficient conversion of sunlight into direct usable electrical energy at a much lower cost than the traditional silicon based solar cells.

[0004] It is known that for efficient energy conversion in OPVs, a mixture of at least two (sometimes more) organic materials are needed: at least one material that can act as an electron donor (p-type) and at least one material that can act as electron acceptor (n-type).

[0005] Materials research in OPVs since the mid-1990s has focused primarily on the development of donor materials. As a result, there are many more organic donor materials commercially available than organic acceptor materials. For example, the most widely investigated organic semiconductors are donor materials based on aromatic amines and thiophene materials (Katz et al., *Acc. Chem. Res.* **2001**, *34*, 359; Chan and Ng, *Prog. Polym. Sci.* **1998**, *23*, 1167; Y. F. Li, Y.P. Zhou, *Adv. Mater.* **2008**, *20*, 2952; and Thelakkat, *Macromol. Mater. Eng.* **2002**, *287*, 442).

[0006] In contrast, research in electron acceptors has substantially lagged behind. Work in this area has primarily focussed on perylene and fullerene materials, which in general are relatively difficult to work with in terms of synthesis of the materials. (Greenham, et al., *Nature* **1993**, *365*, 628; Kulkarni et al., *Chem. Mater.* **2004**, *16*, 4556; and Hughes and Bryce, *J. Mater. Chem.* **2005**, *15*, 94). The chemistry of these

compounds is relatively well known, with little room for new developments. Furthermore, production of these materials tends to be very expensive, especially in the case of fullerene based materials. Perylenes are typically insoluble, meaning that often only vacuum deposition of these compounds is possible. Since the mid-1990s, fullerene compounds have been optimized for use in solution processable organic solar cells, providing power conversion efficiencies in the range of 2-5% when combined with selected commercial donor materials. Despite this, fullerenes tend to have low absorption coefficients in the visible range, are difficult to synthesize, and have low open circuit voltage in blend devices.

[0007] Accordingly, there is a need for production of alternative n-type organic materials useful for production of efficient electronic devices, including OPVs.

SUMMARY ~~OF THE INVENTION~~

[0008] The disclosure~~invention~~ relates to organic compounds that can be used as acceptor materials in organic devices, including organic photovoltaic devices.

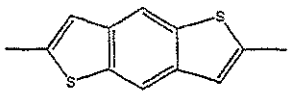
[0009] The compounds of the disclosure~~invention~~ incorporate alternating blocks of electron accepting groups and electron donating groups, and are terminated at each end with a block of electron accepting groups.

[0010] The compounds of the disclosure~~invention~~ may exhibit strong absorption in the visible region and thus may serve as n-type materials that allow for tuning of light absorption range and HOMO/LUMO energy levels, depending on the particular electron accepting groups and electron donating groups incorporated into the compounds.

[0011] The compounds thus may be useful in organic solar cells, also known as organic photovoltaic devices, and may allow for production of organic photovoltaic devices at lower cost than traditional silicon-based solar cells, even when using a flexible substrate.

[0012] Thus, according to one embodiment~~aspect~~ of the disclosure~~invention~~, there is provided a compound of formula I:

$$\left(A_n—D_p\right)_r—A_n \qquad \text{I}$$



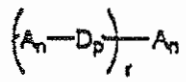
D21

wherein s is an integer from 1 to 5; and each R is independently H, straight or branched alkyl, straight or branched alkenyl, straight or branched alkynyl, straight or branched heteroalkyl provided that the heteroatom is not bonded to N or Si, alkaryl, alkheteroaryl, heteroalkaryl, heteroalkheteroaryl, aralkyl, arheteroalkyl, heteroaralkyl, or heteroarheteroalkyl.

[0015] In certain embodiments, each A may independently be optionally substituted by one or more halo, fluoroalkyl, perfluoroalkyl, carboxyl, cyano, ammonio, nitro, thionyl, sulfonyl, amido linked to the backbone through the oxygen, pyridinium, phosphonium, pyridyl, thiazolyl, oxadiazolyl, triazolyl, alkoxyl, alkylthio, amino, hydroxyl, amido connected to the backbone through the nitrogen, carboxyl connected to the backbone through the oxygen, phenyl, naphthyl, thienyl, furyl, pyrrolyl, carbazolyl, alkyl, alkenyl or alkynyl or any combination thereof, provided that when substituted the electronic character of each A is electron accepting.

[0016] As well, each D may independently be optionally substituted with one or more alkoxyl, alkylthio, amino, hydroxyl, amido connected to the backbone through the nitrogen, carboxyl connected to the backbone through the oxygen, phenyl, naphthyl, thienyl, furyl, pyrrolyl, carbazolyl, alkyl, alkenyl, alkynyl, halo, fluoroalkyl, perfluoroalkyl, carboxyl, cyano, ammonio, nitro, thionyl, sulfonyl, amido linked to the backbone through the oxygen, pyridinium, phosphonium, pyridyl, thiazolyl, oxadiazolyl or triazolyl or any combination thereof, provided that when substituted the electronic character of each D is electron donating.

[0016a] In a first aspect, there is provided a compound of formula I:



I

wherein

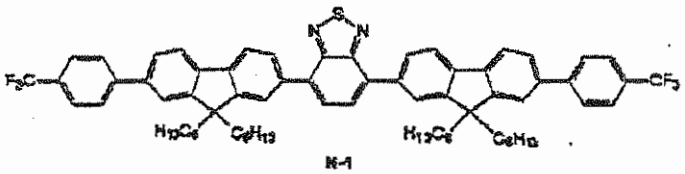
each A is an independently selected conjugated electron withdrawing aromatic or heteroaromatic group having from 5 to 50 backbone atoms, each A optionally substituted with one or more electron withdrawing substituents or electron donating substituents, provided that even when substituted the electronic character of each A is electron withdrawing and provided that A is not fluorenonyl;

each D is an independently selected ethenylene group, ethynylene group or a conjugated electron donating aromatic or heteroaromatic group having from 5 to 50 backbone atoms; each D being optionally substituted with one or more electron donating substituents or electron withdrawing substituents provided that even when substituted the electronic character of each D is electron donating;

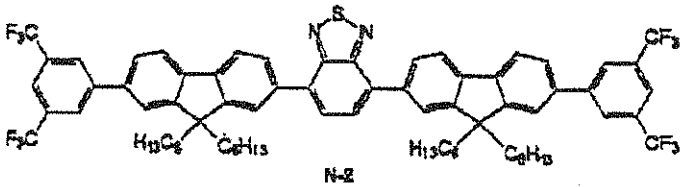
r is an integer having a value of 2 or greater; and

each n is independently an integer from 1 to 20 and each p is independently an integer from 1 to 10,

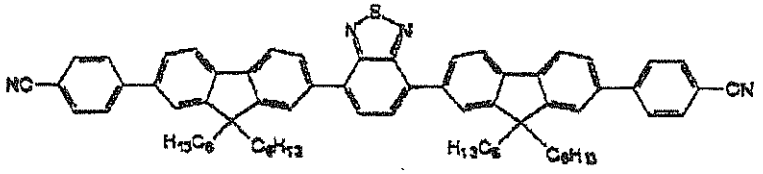
the compound selected from optionally substituted N-1, N-2, N-3, N-4, N-5, N-6, N-7, N-8, N-9, N-10 or N-11:



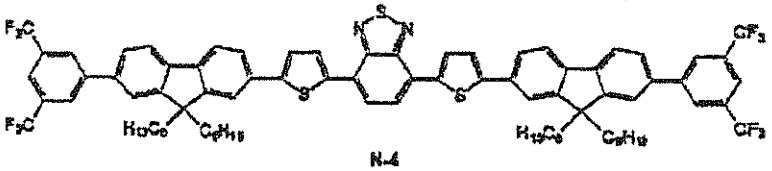
N-1



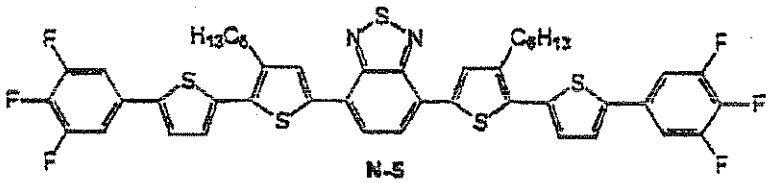
N-2



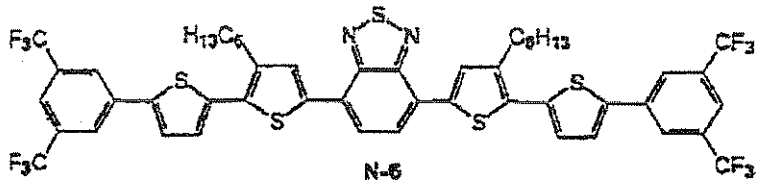
N-3



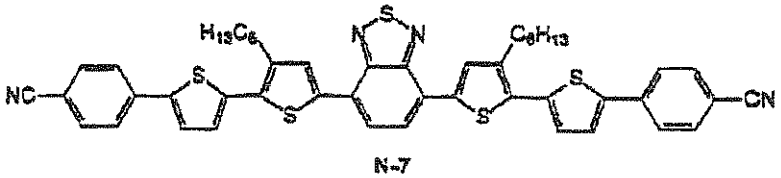
N-4



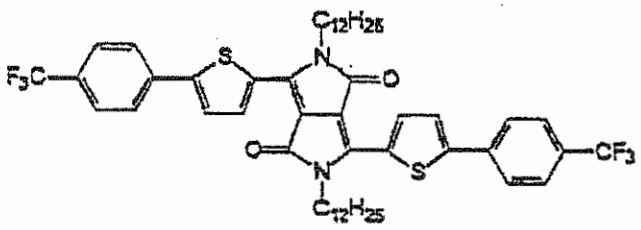
N-5



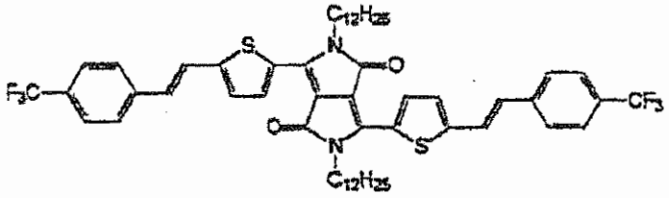
N-6



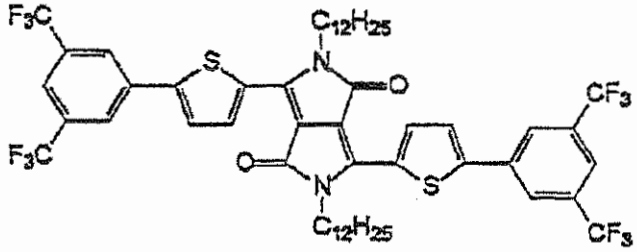
N-7



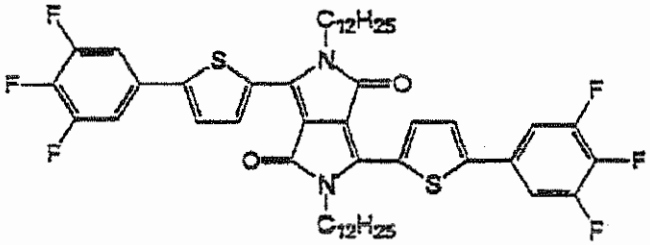
N-8



N-9



N-10

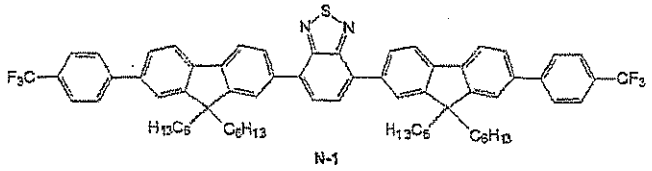


N-11

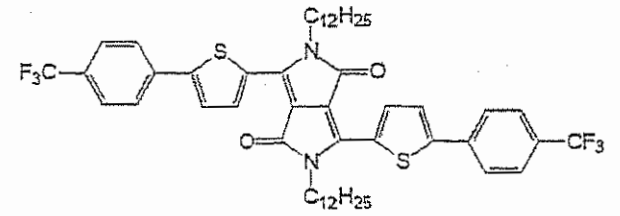
wherein each A is independently optionally substituted by one or more halo, fluoroalkyl, perfluoroalkyl, carboxyl, cyano, ammonio, nitro, thionyl, sulfonyl, amido linked to the backbone through the oxygen, pyridinium, phosphonium, pyridyl, thiazolyl, oxadiazolyl, triazolyl, alkoxyl, alkylthio, amino, hydroxyl, amido connected to the backbone through the nitrogen, carboxyl connected to the backbone through the oxygen, phenyl, naphthyl, thienyl, furyl, pyrrolyl, carbazolyl, alkyl, alkenyl or alkynyl

or any combination thereof, provided that when substituted the electronic character of each A is electron accepting;and wherein each D is independently optionally substituted with one or more alkoxyl, alkylthio, amino, hydroxyl, amido connected to the backbone through the nitrogen, carboxyl connected to the backbone through the oxygen, phenyl, naphthyl, thienyl, furyl, pyrrolyl, carbazolyl, alkyl, alkenyl, alkynyl, halo, fluoroalkyl, perfluoroalkyl, carboxyl, cyano, ammonio, nitro, thionyl, sulfonyl, amido linked to the backbone through the oxygen, pyridinium, phosphonium, pyridyl, thiazolyl, oxadiazolyl or triazolyl or any combination thereof, provided that when substituted the electronic character of each D is electron donating.

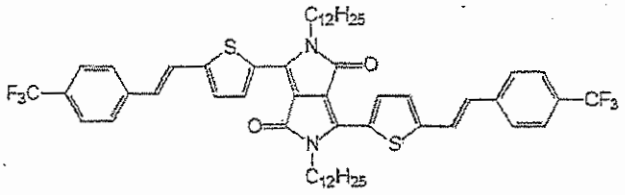
[0017] In particular embodiments, compounds of the disclosure~~invention~~ include each of N-1, N-2, N-3, N-4, N-5, N-6, N-7, N-8, N-9, N-10 and N-11:



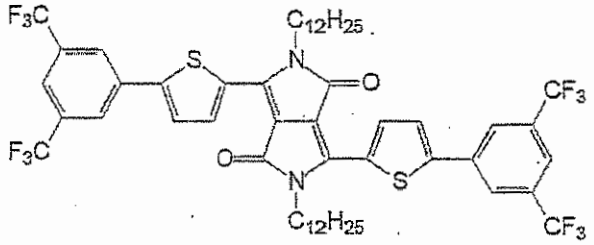
N-1



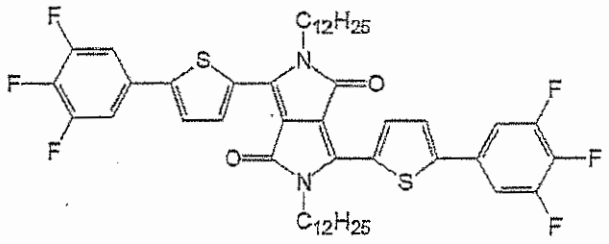
N-8



N-9



N-10



N-11

[0018] According to a secondanother aspect of the invention, there is provided a thin film comprising a compound as described herein.

[0019] The thin film may further comprise an electron donor material, which may be regioregular poly(3-hexylthiophene-2,5-diyl) (P3HT), regioregular poly(3-ocylthiophene-

2,5-diyl) (P3OT), regioregular poly(quarterthiphene) (PQT), a-poly(phenylene ethynylene)-poly(phenylene vinylene) (A-PPE-PPV), poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV), poly[2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV), poly(9,9-dihexyl-fluoren-2,7-diyl-alt-bithiophen-2,5'-diyl), poly(N-alkyl-carbazo-2,7-diyl-alt-4,7-dithienyl-2,1,3-benzothiadiazo-2,5"-diyl), poly[2,6-(4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT), poly(9,9-dioctyl-silafluoren-2,7-diyl-alt-4,7-dithienyl-2,1,3-benzothiadiazo-2,5"-diyl), or poly[2,6-(4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophenesilole)-alt-4,7-(2,1,3-benzothiadiazole)] .

[0020] In particular embodiments, the donor material comprises P3HT.

[0021] According to a third~~In another~~ aspect ~~of the present invention~~, there is provided a device comprising an anode, a cathode and an electron acceptor material comprising a compound as described herein, the electron acceptor material disposed between the anode and the cathode.

[0022] The electron acceptor material may be included in a photoactive layer. The photoactive layer may further comprise an electron donor material, including as described above.

[0023] The device may also further comprise a smoothing layer disposed between the photoactive layer and the anode, or between the photoactive layer and the cathode.

[0024] Other aspects and features of the present disclosure~~invention~~ will become apparent to those of ordinary skill in the art upon review of the following description of specific embodiments of the disclosure~~invention~~ in conjunction with the accompanying figures.

BRIEF DESCRIPTION OF THE DRAWINGS

[0025] In the figures, which illustrate, by way of example only, embodiments of the present invention,

[0026] **Figure 1** is a UV absorption spectra from 300 nm to 700 nm for compounds N-4 to N-7 in toluene;

[0027] **Figure 2** is a UV absorption spectra from 300 nm to 750 nm for compounds