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(54) Title: ENERGY STORAGE DEVICE

(57) Abstract: An electrochemical cell comprising a first electrode comprising a first polymer comprising the formula (I) or (Ia) as defined herein.



ENERGY STORAGE DEVICE

FIELD OF INVENTION

The invention relates to a water-based electrochemical device, such as an energy storage
5 device, comprising electrodes comprising solution-processable n-type and p-type
conjugated polymers.

BACKGROUND

Batteries currently represent the preferred solution for powering portable electronics and
10 electric vehicles and are considered a promising solution for home and grid energy
storage. These devices have the ability to store electrochemical energy via a combined
electronic and ionic charging of two electrodes connected by an electrolyte which can
transport the ionic but not the electronic charge. Metal oxides and carbon-based
materials are the most commonly used electrodes in high performance batteries.
15 However, materials used for battery technologies such as lithium ion cells raise concerns
in terms of toxicity and cost, limiting their full deployment at a larger scale. Additionally,
the organic liquid electrolytes used as ion conductors in most of these batteries represent
a significant safety problem due to their flammability.

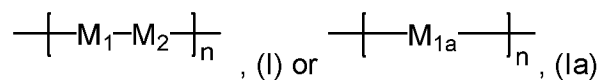
20 Electrodes made from polymers represents an attractive alternative route towards safe
and inexpensive battery devices. Conjugated polymers are a class of polymers which
allow injection and transport of electrical charges through extended pi-orbitals and
delocalization of electronic charges, and thus act as molecular semiconductors. In
addition to electrical conduction, modification to the side chains of the polymer backbone
25 can enable thin films of these materials to have good ion transport properties making them
potential candidates for use as battery electrodes.

Particularly interesting is the possibility of using some of these materials to function in
water environments rather than organic electrolytes and previous studies of electrodes
30 investigated in neutral water have been presented. The electronic transport properties of
conjugated polymers and their tunable redox behavior allow a broad range of capabilities
to be engineered including high specific capacities or high power densities. However,
further improvements in performance and versatility are needed before conjugated
polymers become a viable player in the battery market. Batteries using all-polymer
35 electrodes with comparable performance to carbon, alkaline metal and metal oxide based
cells have yet to be reported.

SUMMARY OF INVENTION

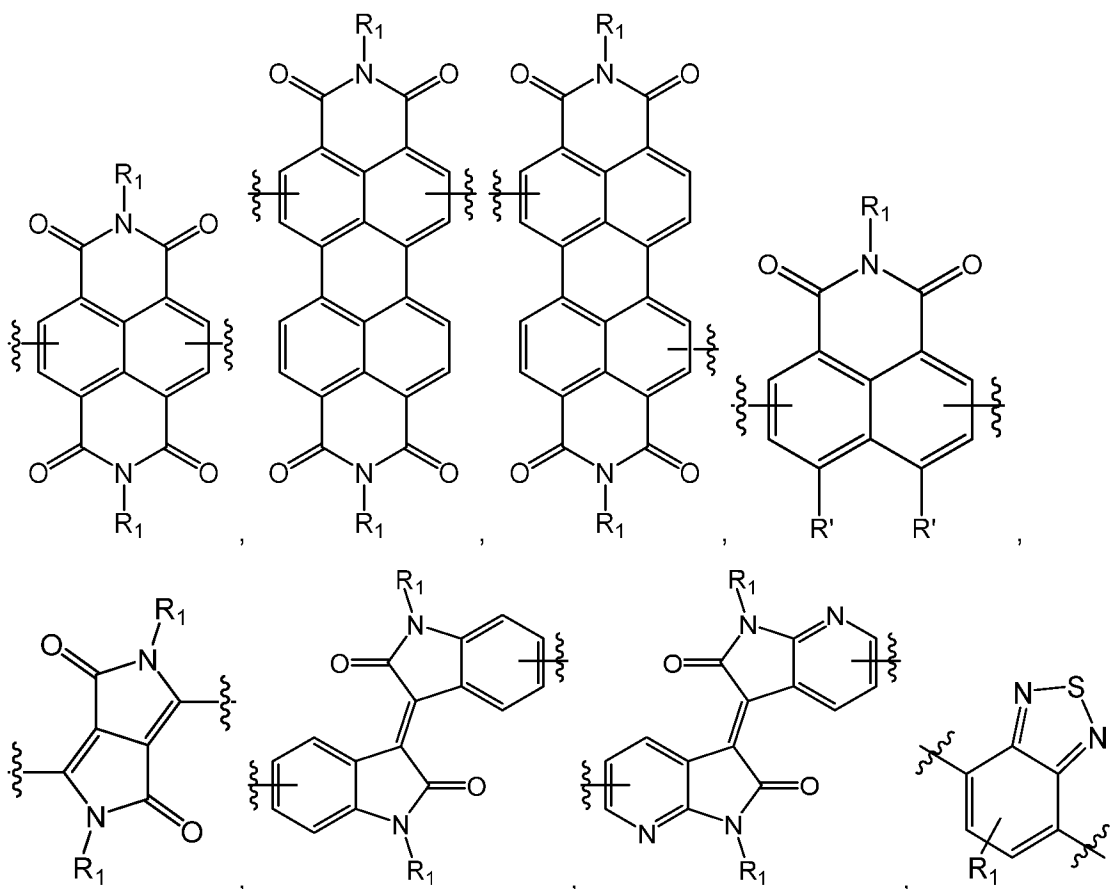
The invention provides a strategy which allows for the preparation of a water-based electrochemical device, for example an electrochemical energy storage device,
 5 comprising solution-processable n-type and p-type conjugated polymers as the electrodes. Accordingly, in a first aspect, the invention provides an electrochemical cell comprising:

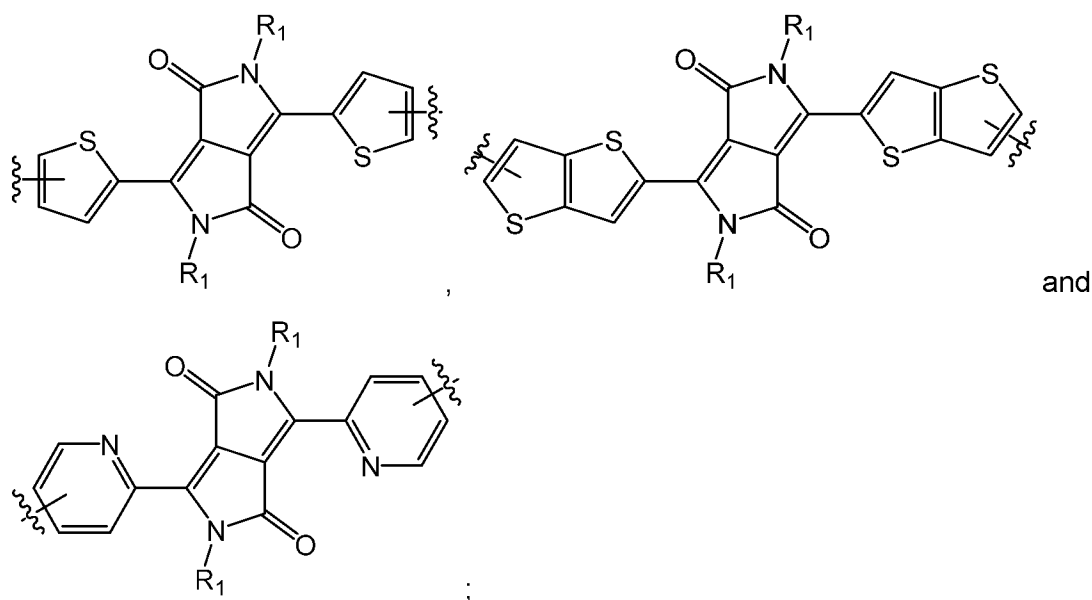
a first electrode comprising a first polymer comprising the formula (I) or (Ia):



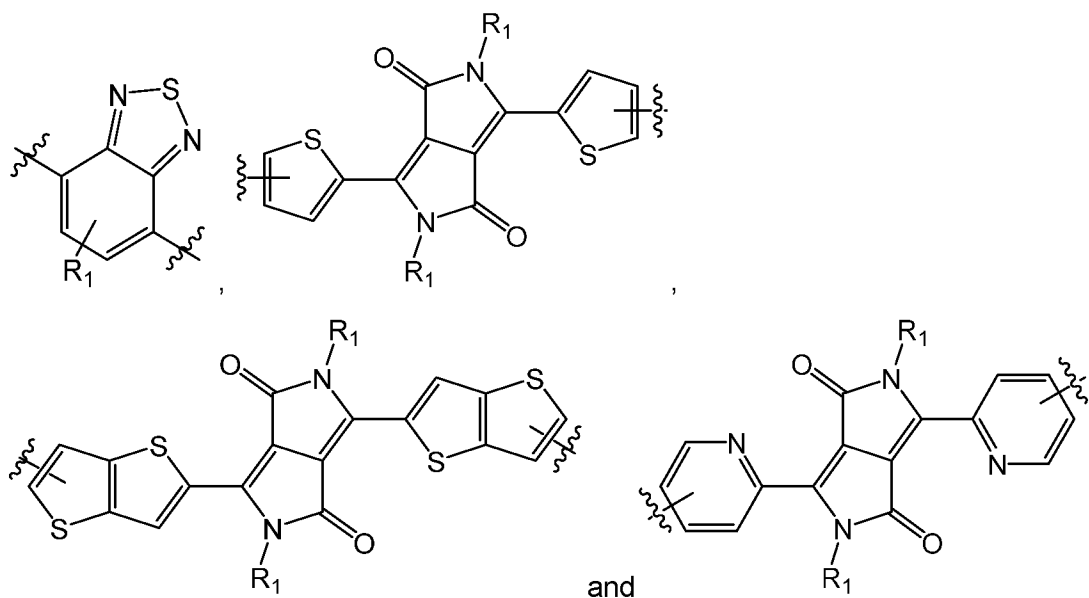
10 wherein:

each M_1 is independently selected from:





each M_{1a} is independently selected from:



wherein R₁, at each occurrence, is independently a moiety comprising at least one -alkylene-O- unit or a moiety comprising at least two functional groups of which at least one has a positive and one has a negative electrical charge;

R', at each occurrence, is independently selected from H, an electron-withdrawing group, a C₁₋₄₀alkyl group optionally substituted with 1-5 electron-withdrawing groups, a moiety comprising at least one (preferably at least two) -alkylene-O- units or a moiety comprising at least two functional groups of which at least one has a positive and one has a negative electrical charge;

each M₂ is independently a repeat unit comprising one or more heteroaryl groups
15 optionally substituted with one or more groups selected from a moiety comprising at least

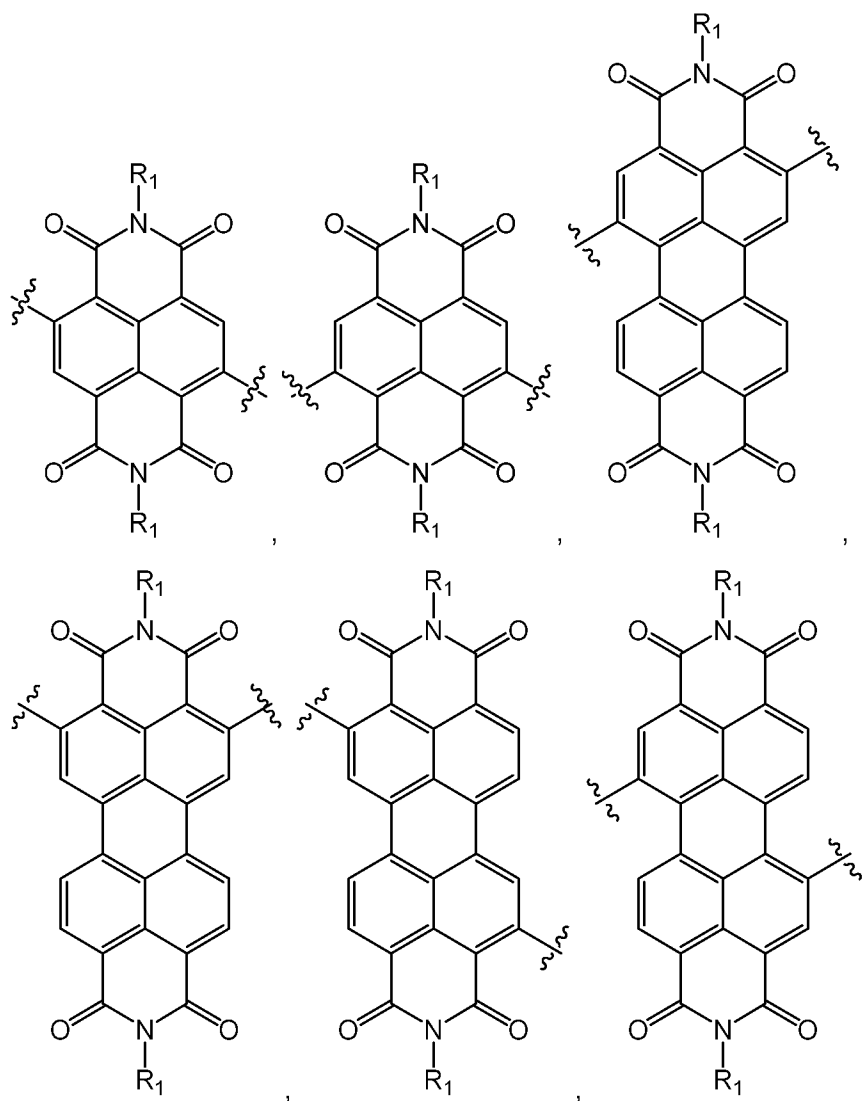
one -alkylene-O- unit and a moiety comprising at least two functional groups of which at least one has a positive and one has a negative electrical charge; and

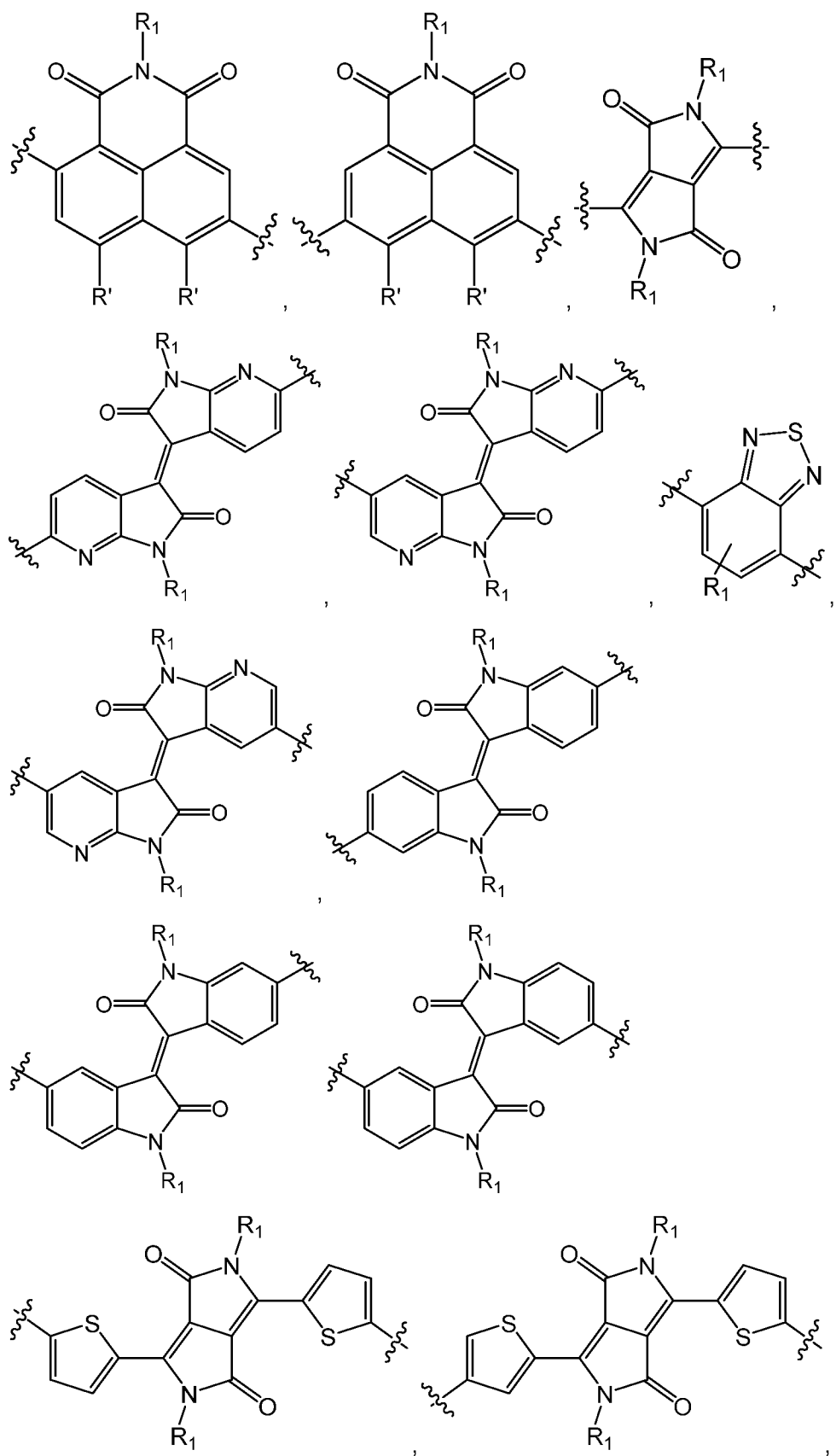
n is an integer of at least 2, optionally between 2 and 5,000; and

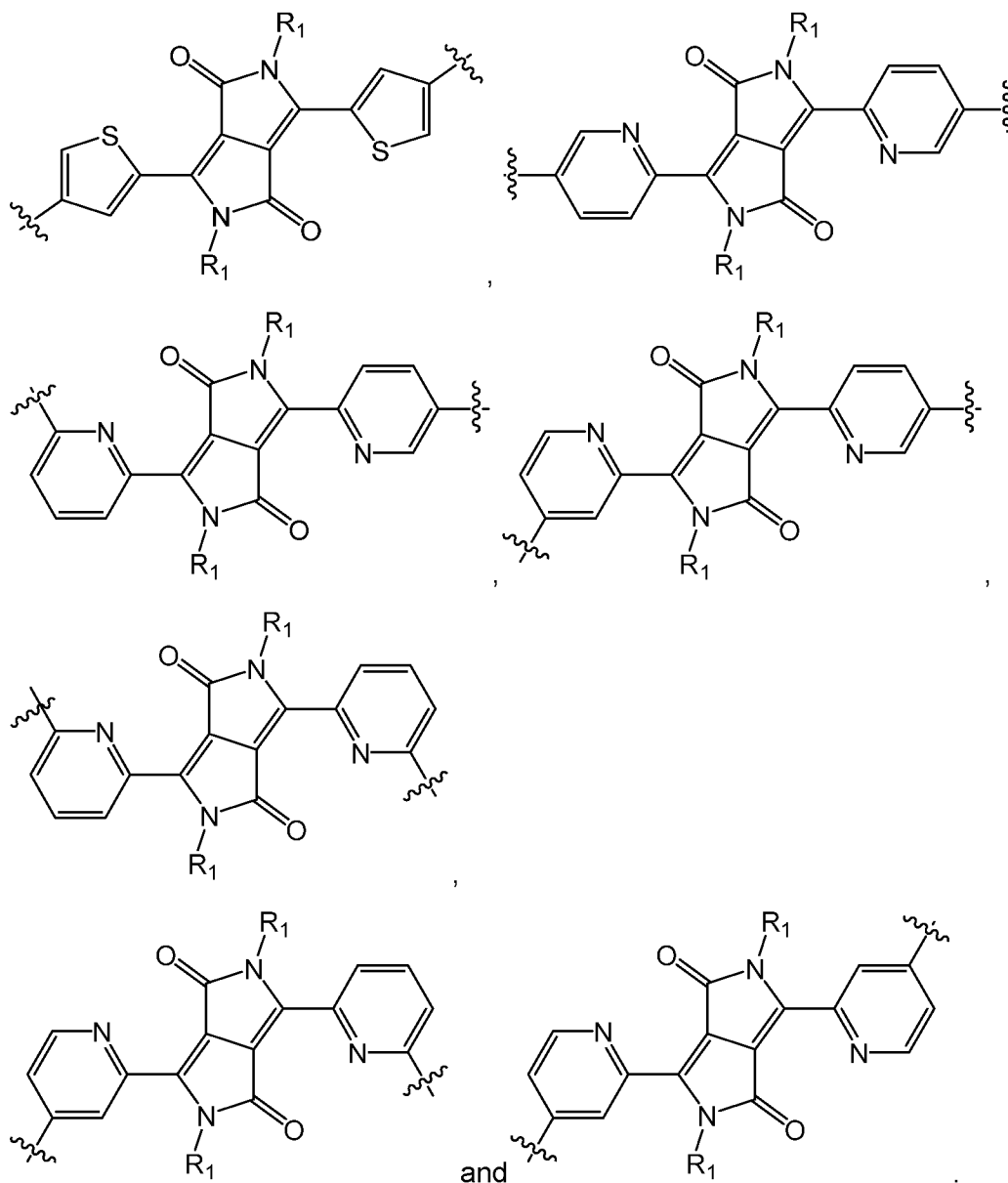
- a second electrode comprising a second polymer comprising one or more repeat units comprising one or more heteroaryl groups substituted with one or more moieties comprising at least one -alkylene-O- unit.

Preferably, the first polymer comprises the formula (I).

- 10 Each M_1 may independently be selected from:



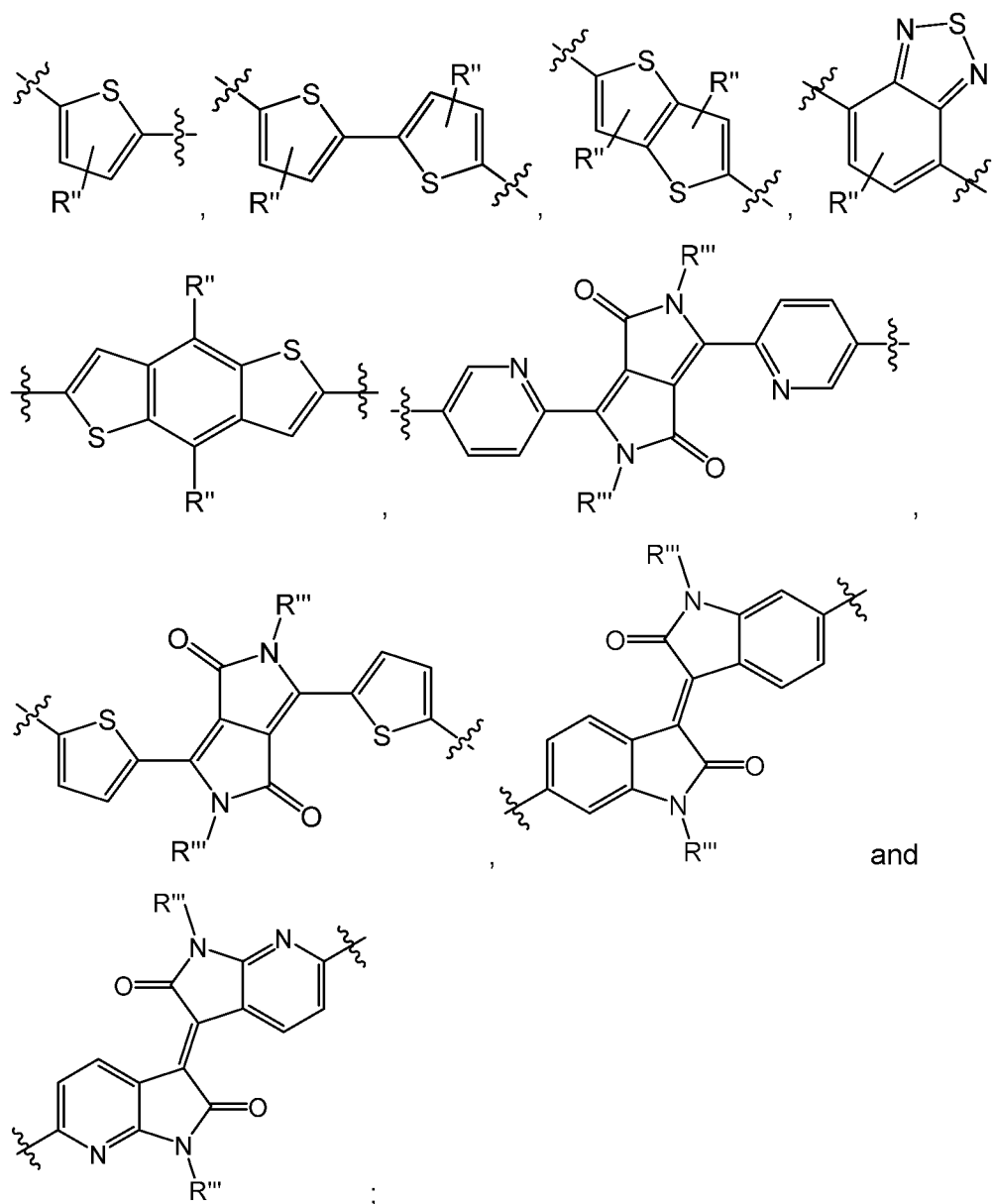




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Each M_2 may independently be a repeat unit comprising one or more heteroaryl groups wherein the heteroaryl group is selected from thiophene, 2,5-dihydropyrrolo[3,4-c]pyrrol-1,4-dione (diketopyrrolopyrrole, DPP) and (3E)-3-(2-oxo-1H-indol-3-ylidene)-1H-indol-2-(isoindigo), and [3,3'-bipyrrolo[2,3-b]pyridinylidene]-2,2'(1H,1'H)-dione (pyridine isoindigo),

10 preferably thiophene, bithiophene, thieno[3,2-b]thiophene, 3,6-alkoxy-thieno[3,2-b]thiophene, 3,3'-alkoxybithiophene 2,5-dihydropyrrolo[3,4-c]pyrrol-1,4-dione (diketopyrrolopyrrole, DPP), (3E)-3-(2-oxo-1H-indol-3-ylidene)-1H-indol-2-one (isoindigo) and [3,3'-bipyrrolo[2,3-b]pyridinylidene]-2,2'(1H,1'H)-dione (pyridine isoindigo). Each M_2 may independently be selected from:

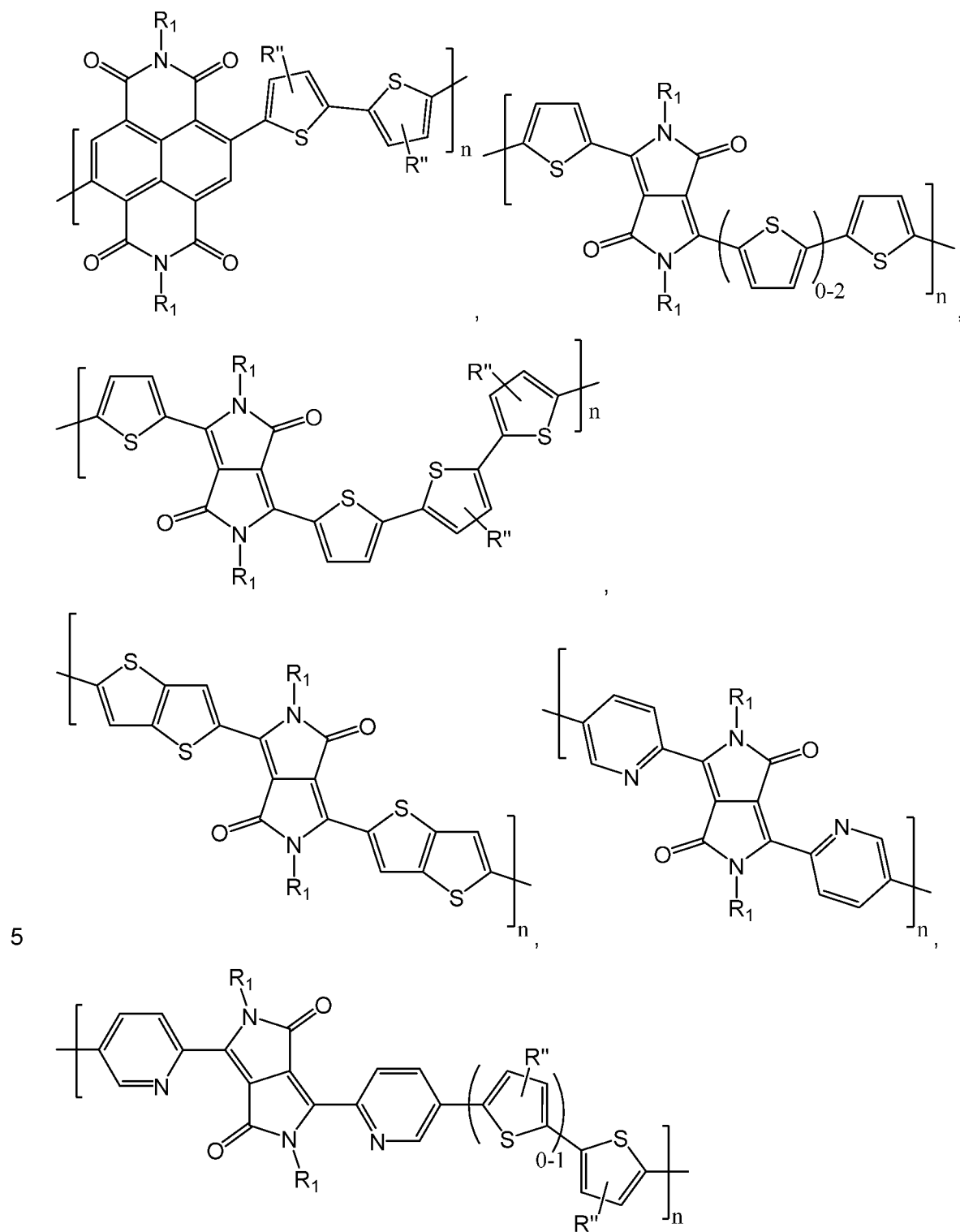


5 wherein:

R'' , at each occurrence, is independently selected from H, $-O-C_{1-6}$ alkyl, $-COOH$, $-C(O)O-C_{1-6}$ alkyl, a (poly)alkylene glycol chain having 1-30 alkylene glycol units, a C_{3-6} alkyl group substituted with one or more (poly)alkylene glycol chains having 1-30 alkylene glycol units, C_{1-6} alkyl substituted with a crown ether or a moiety comprising at least two functional groups of which at least one has a positive and one has a negative electrical charge; and

R''' , at each occurrence, is independently selected from a (poly)alkylene glycol chain having 1-30 alkylene glycol units, a C_{3-6} alkyl group substituted with one or more (poly)alkylene glycol chains having 1-30 alkylene glycol units, and C_{1-6} alkyl substituted with a crown ether or a moiety comprising at least two functional groups of which at least one has a positive and one has a negative electrical charge.

The first polymer may be selected from:



In each M_1 group, each R_1 may be the same or different, preferably the same.

10 Each R_1 may independently be selected from (i), (ii) or (iii):

(i) A moiety comprising at least one -alkylene-O- unit of formula -A-[-alkylene-O-]_n-X, wherein n' is 1-30; A is absent, an alkyl linker (preferably a C₁₋₆alkyl or C₁₋₃alkyl linker) or O; and X is hydrogen, alkyl, -alkyl-SO₃H, -alkyl-COOH or haloalkyl. Preferably, a group of formula -A-[-ethylene-O-]_n-X, wherein n' is 1-30 (preferably 1-20, 1-10 or 1-5); A is absent or O; and X is C₁₋₆alkyl, -alkyl-SO₃H, -alkyl-COOH or haloalkyl, preferably C₁₋₆alkyl (preferably methyl).

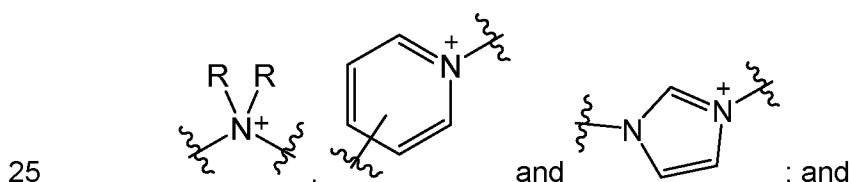
(ii) A moiety comprising at least two functional groups of which at least one has a positive and one has a negative electrical charge of formula -W-X-Y-Z, wherein:

W and Y are each independently a linker moiety selected from alkylene, arylene, heteroarylene or a moiety comprising at least one -alkylene-O- unit (optionally a moiety of formula -[-alkylene-O-]_n-, wherein n' is 1-30), or a combination thereof;

one of X and Z is a positively charged moiety and the other is a negatively charged moiety, optionally wherein a positively charged moiety is a moiety comprising a cationic nitrogen group (e.g., quaternized ammonium, protonated amine, azomethine, amidine, guanidien or a cationic nitrogen containing heteroaryl, such as pyridinium or imidazolium), or a sulfonium or phosphonium cation, and a negatively charged moiety is a moiety comprising a phosphate, sulfonate, carboxylate, phosphonate, phosphinante, sulfate, alkoxydicyanobenzenolate, boronate, phenolate, sulfonamide or sulfonimide anion. Preferably, a group of formula -W-X-Y-Z, wherein:

W and Y are each independently a linker moiety selected from C₁₋₃₀alkylene (preferably C₁₋₂₀alkylene or C₁₋₁₀alkylene), phenylene, pyridylene or a moiety of formula -[-ethylene-O-]_n-, wherein n' is 1-30, or a combination thereof;

X is a positively charged moiety selected from quaternized ammonium, protonated amine, pyridinium and imidazolium, for example:



Z is a negatively charged moiety selected from a phosphate anion, a phosphonate anion, a sulfonate anion and a carboxylate anion, for example -P(=O)(O⁻)OH, -OP(=O)(O⁻)-O-, -SO₃⁻ and -COO⁻.

(iii) A moiety comprising at least two functional groups of which at least one has a positive and one has a negative electrical charge of formula -W'-X'(Z')-Y', wherein:

W' is a linker moiety selected from alkylene, arylene, heteroarylene or a moiety comprising at least one -alkylene-O- unit (optionally a moiety of formula -[-alkylene-O-]_n-, wherein n' is 1-30), or a combination thereof;

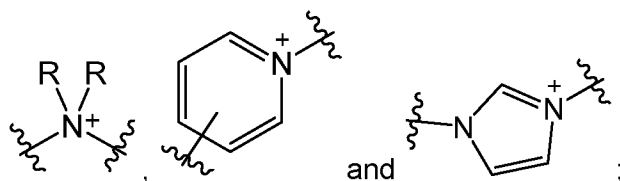
Y' is absent, H or a linker moiety selected from alkylene, arylene, heteroarylene or a moiety comprising at least one -alkylene-O- unit (optionally a moiety of formula -[alkylene-O-]_{n'}-, wherein n' is 1-30), or a combination thereof;

X' is a positively charged moiety or a negatively charged moiety and Z' is a mobile counter ion, optionally wherein a positively charged moiety is a moiety comprising a cationic nitrogen group (e.g., quaternary ammonium, protonated amine, azomethine, amidine, guanidene or a cationic nitrogen containing heteroaryl, such as pyridinium or imidazolium), or a sulfonium or phosphonium cation, and a negatively charged moiety is a moiety comprising a phosphate, sulfonate, carboxylate, phosphonate, phosphinante, sulfate, alkoxydicyanobenzenolate, boronate, phenolate, sulfonamide or sulfonimide anion. Preferably, a group of formula -W'-X'(Z')-Y', wherein:

W' is a linker moiety selected from C₁₋₃₀alkylene (preferably C₁₋₂₀alkylene or C₁₋₁₀alkylene), phenylene, pyridylene or a moiety of formula -[ethylene-O-]_{n'}-, wherein n' is 1-30, or a combination thereof;

Y' is absent, H or a linker moiety selected from C₁₋₃₀alkylene (preferably C₁₋₂₀alkylene or C₁₋₁₀alkylene), phenylene, pyridylene or a moiety of formula -[ethylene-O-]_{n'}-, wherein n' is 1-30), or a combination thereof;

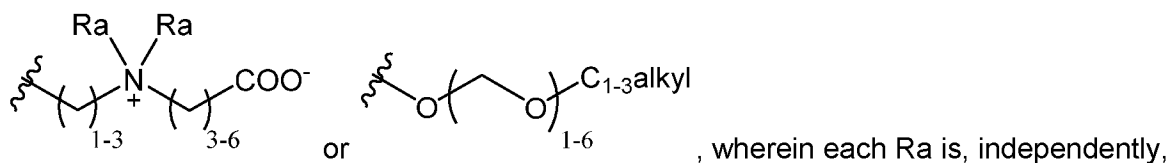
X' is a positively charged moiety or a negatively charged moiety, wherein a positively charged moiety is a moiety selected from quaternized ammonium, protonated amine, pyridinium and imidazolium, for example:



and a negatively charged moiety is a moiety selected from a phosphonate anion, a phosphate anion, a sulfonate anion and a carboxylate anion, for example -P(=O)(O⁻)OH, -OP(=O)(O⁻)-O-, -SO₃⁻ and -COO⁻; and

Z' is a mobile counter ion selected from H⁺, M⁺ or a halide anion, wherein M⁺ is a metal cation (optionally an alkali metal cation, e.g. Na⁺ or K⁺).

Preferably, each R₁ is independently a group of structure:



H or C₁₋₆alkyl.

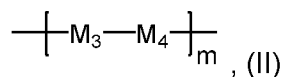
R', at each occurrence, may be independently selected from H, a halogen, -CN, C₁₋₁₀haloalkyl, moiety comprising at least one -alkylene-O- unit and a moiety comprising at least two functional groups of which at least one has a positive and one has a negative electrical charge. A moiety comprising at least one -alkylene-O- unit and/or a moiety comprising at least two functional groups of which at least one has a positive and one has a negative electrical charge may be as defined in relation to R₁ above.

In each M₂, each R'' and/or R''' may be the same or different, preferably the same.

Each R'' may independently be selected from H, a C₁₋₄₀alkoxy group, a (poly)alkylene glycol chain having 1-30 alkylene glycol units, and a C₃₋₆alkyl group substituted with one or more (poly)alkylene glycol chains having 1-30 alkylene glycol units or a moiety comprising at least two functional groups of which at least one has a positive and one has a negative electrical charge, preferably H, a (poly)alkylene glycol chain having 1-30 alkylene glycol units or a moiety comprising at least two functional groups of which at least one has a positive and one has a negative electrical charge. Preferably each R'' may independently be selected from H or a moiety of formula -O-[-alkylene-O-]_m-X, wherein m' is 1-30 and X is hydrogen, alkyl, -alkyl-SO₃H, -alkyl-COOH or haloalkyl, optionally wherein alkylene is ethylene. Preferably, a group of formula -O-[-ethylene-O-]_m-X, wherein m' is 1-30 (preferably 1-20, 1-10 or 1-5); and X is H, C₁₋₆alkyl, -alkyl-SO₃H, -alkyl-COOH or haloalkyl, preferably C₁₋₆alkyl (preferably methyl).

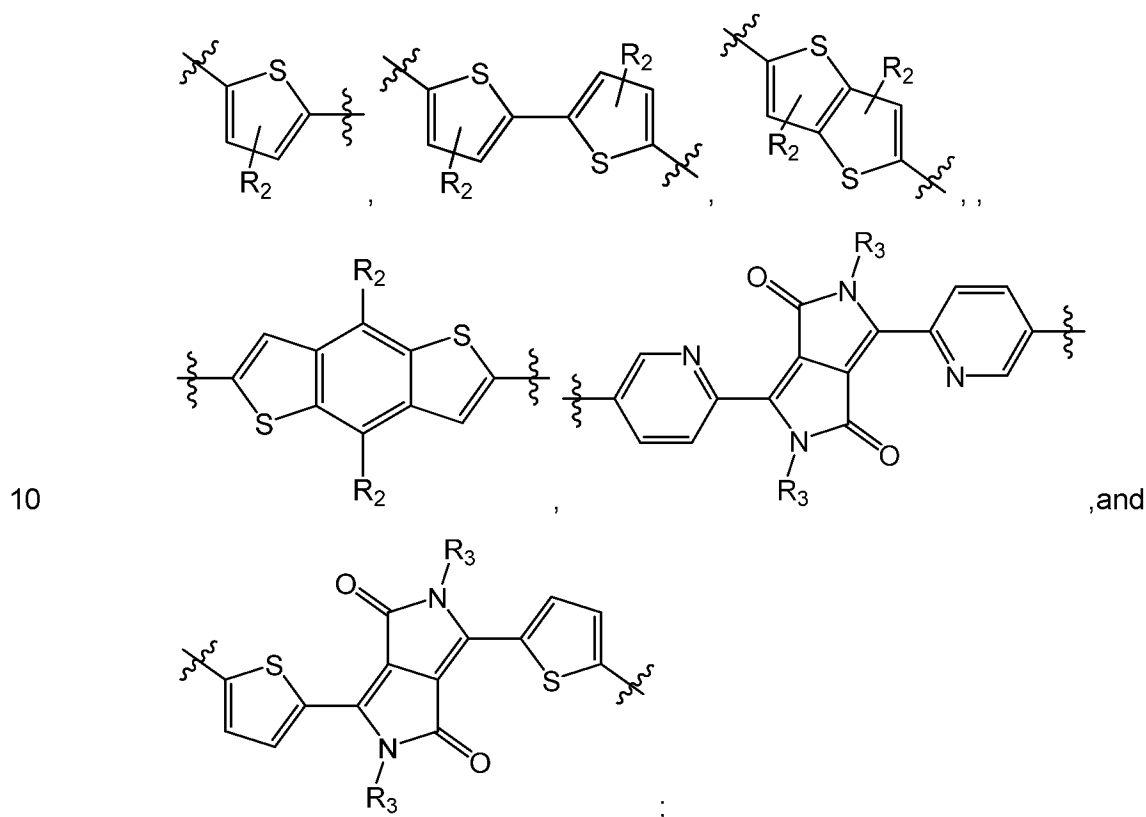
Each R''' may independently be selected from a (poly)alkylene glycol chain having 1-30 alkylene glycol units, and a C₃₋₆alkyl group substituted with one or more (poly)alkylene glycol chains having 1-30 alkylene glycol units or a moiety comprising at least two functional groups of which at least one has a positive and one has a negative electrical charge, preferably a (poly)alkylene glycol chain having 1-30 alkylene glycol units or a moiety comprising at least two functional groups of which at least one has a positive and one has a negative electrical charge. Preferably each R''' may independently be a moiety of formula -B-[-alkylene-O-]_m-X, wherein m' is 1-30; B is absent or a C₁₋₆alkyl or C₁₋₃alkyl linker; and X is hydrogen, alkyl, -alkyl-SO₃H, -alkyl-COOH or haloalkyl, optionally wherein alkylene is ethylene. Preferably, a group of formula -[-ethylene-O-]_m-X, wherein m' is 1-30 (preferably 1-20, 1-10 or 1-5); and X is H, C₁₋₆alkyl, -alkyl-SO₃H, -alkyl-COOH or haloalkyl, preferably C₁₋₆alkyl (preferably methyl).

The second polymer may be a conjugated homo or co-polymer comprising the formula (II):



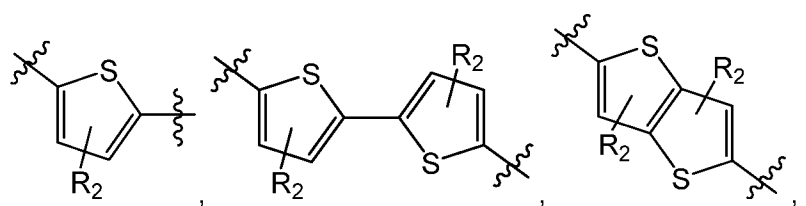
wherein, M_3 is a repeat unit comprising one or more heteroaryl groups, optionally substituted with one or more moieties comprising at least one -alkylene-O- units, and M_4 is absent or a repeat unit comprising a heteroaryl group, optionally substituted with one or more moieties comprising at least one -alkylene-O- units. Preferably moieties comprising at least one -alkylene-O- units are linked to the heteroaryl group by an O atom.

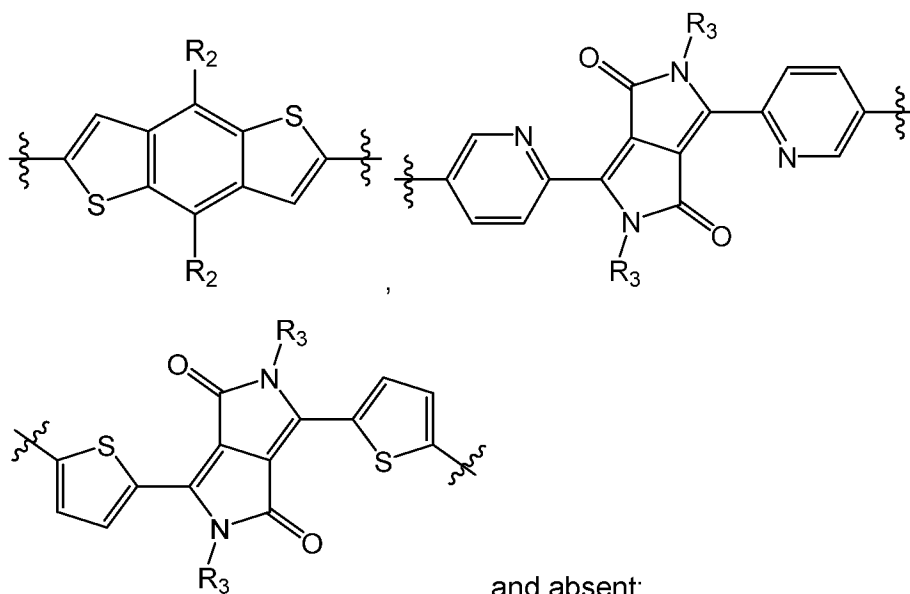
Each M_3 group may be selected from:



wherein R_2 and R_3 are each independently a moiety comprising at least one -alkylene-O- unit.

15 Each M_4 group may be selected from:





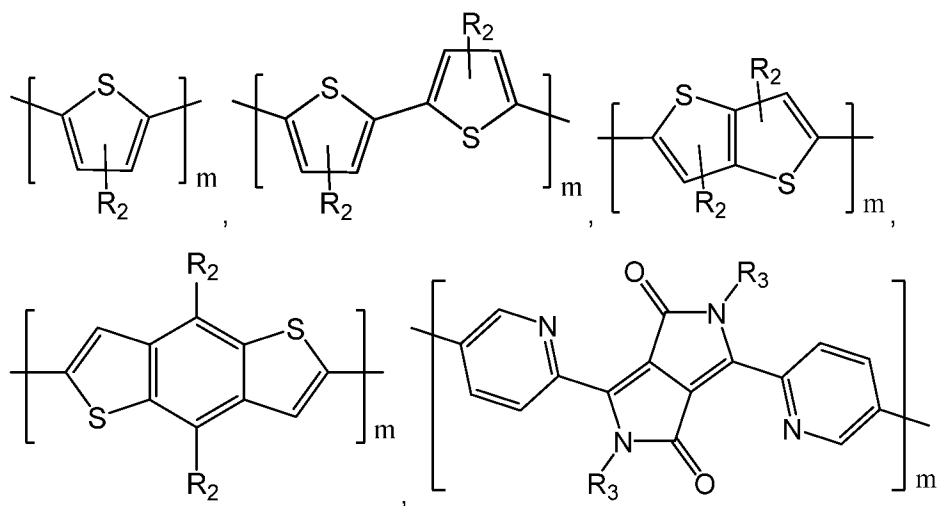
wherein R_2 and R_3 are each independently a moiety comprising at least one -alkylene-O- unit. Preferably, M_3 is absent.

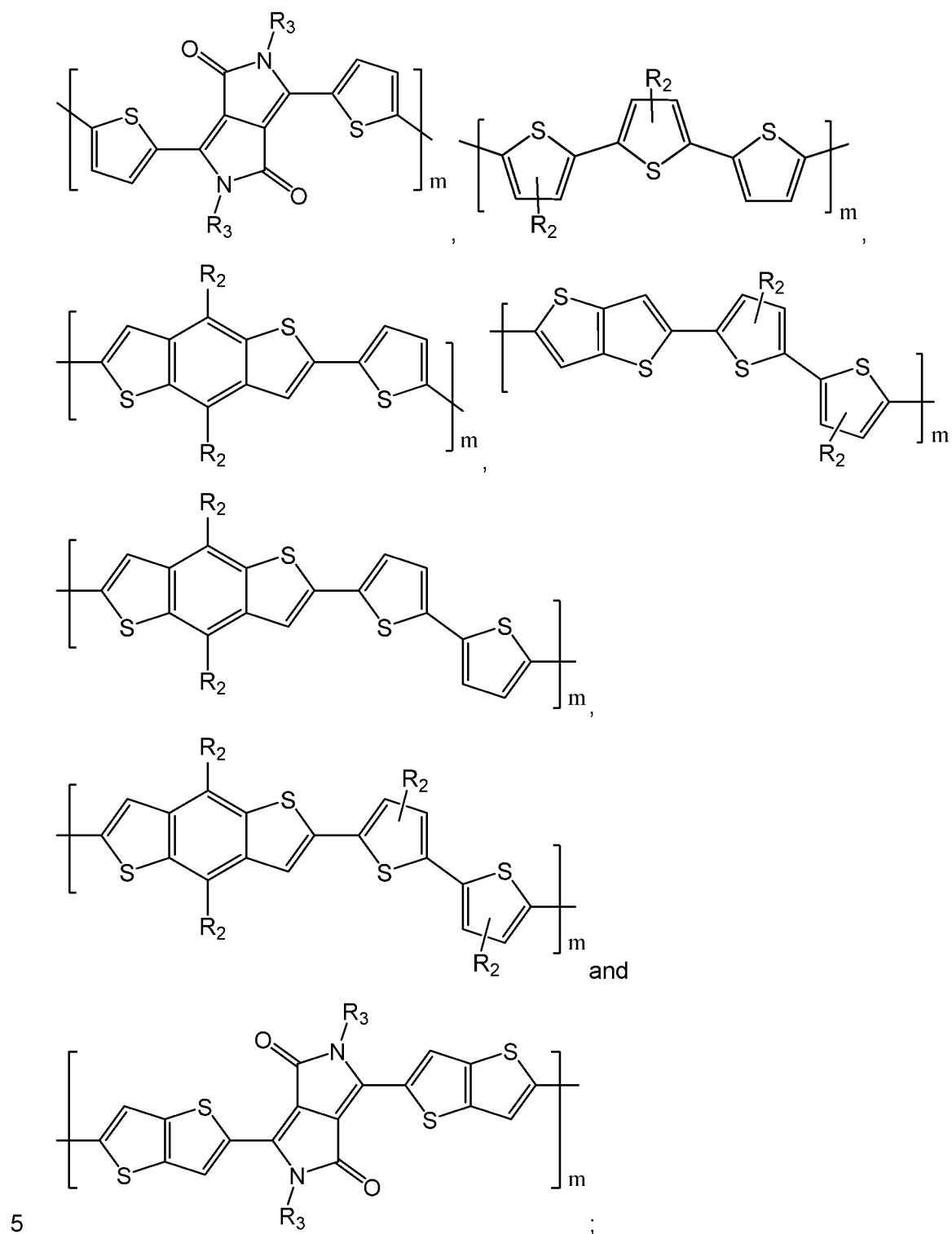
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The second polymer may comprise a repeat unit comprising one or more heteroaryl groups selected from thiophene, 2,5-dihydropyrrolo[3,4-c]pyrrol-1,4-dione (diketopyrrolopyrrole, DPP) and (3E)-3-(2-oxo-1H-indol-3-ylidene)-1H-indol-2-(isoindigo), and [3,3'-bipyrrolo[2,3-b]pyridinylidene]-2,2'(1H,1'H)-dione (pyridine isoindigo), preferably

10 thiophene, bithiophene, thieno[3,2-b]thiophene, 3,6-alkoxy- thieno[3,2-b]thiophene, 3,3'-alkoxybithiophene 2,5-dihydropyrrolo[3,4-c]pyrrol-1,4-dione (diketopyrrolopyrrole, DPP), (3E)-3-(2-oxo-1H-indol-3-ylidene)-1H-indol-2-one (isoindigo) and [3,3'-bipyrrolo[2,3-b]pyridinylidene]-2,2'(1H,1'H)-dione (pyridine isoindigo).

15 The second polymer may be selected from:





m is an integer of at least 2, optionally between 2 and 5,000.

Each R_2 may independently be a moiety comprising at least one -alkylene-O- unit linked via an O atom, for example a (poly)alkylene glycol chain having 1-30 alkylene glycol units.

10 Preferably each R_2 is independently a moiety of formula -O-[-alkylene-O-] m' -X, wherein m' is 1-30 and X is hydrogen, alkyl, -alkyl-SO₃H, -alkyl-COOH or haloalkyl, optionally wherein alkylene is ethylene. Preferably, a group of formula -O-[-ethylene-O-] m' -X,

wherein m' is 1-30 (preferably 1-20, 1-10 or 1-5); and X is H, C_{1-6} alkyl, -alkyl-SO₃H, -alkyl-COOH or haloalkyl, preferably C_{1-6} alkyl (preferably methyl).

Each R_3 may independently be a moiety comprising at least one -alkylene-O- unit linked
 5 via a C atom, for example a (poly)alkylene glycol chain having 1-30 alkylene glycol units. Preferably R_3 is independently a moiety of formula -B-[-alkylene-O-] m' -X, wherein m' is 1-30; B is absent or a C_{1-6} alkyl or C_{1-3} alkyl linker; and X is hydrogen, alkyl, -alkyl-SO₃H, -alkyl-COOH or haloalkyl, optionally wherein alkylene is ethylene. Preferably, a group of
 10 formula -[-ethylene-O-] m' -X, wherein m' is 1-30 (preferably 1-20, 1-10 or 1-5); and X is H, C_{1-6} alkyl, -alkyl-SO₃H, -alkyl-COOH or haloalkyl, preferably C_{1-6} alkyl (preferably methyl).

The first and/or second polymer may have a number average molecular weight of about 1 to about 500 kD, optionally about 1 to about 400 kD, optionally about 1 to about 300 kD, optionally about 1 to about 200 kD, optionally about 1 to about 100 kD, optionally about 5
 15 to about 50 kD.

The first electrode may comprise a substrate with the first polymer deposited thereon. The second electrode may comprise a substrate with the second polymer deposited thereon. The substrate is an electrically conductive material, for example fluorine-doped
 20 tin oxide (FTO), indium tin oxide (ITO) or gold. The first and/or second polymer may be provided in the form of a bulk material or a film, optionally a film deposited on a surface of the substrate.

The electrochemical cell may be an energy storage device, optionally a battery, capacitor
 25 or a supercapacitor, or an electrochromic energy storage device.

The electrochemical cell may further comprise an electrolyte in contact with the electrodes. The electrolyte is preferably an aqueous electrolyte.

30 The first electrode may be the anode and the second electrode may be the cathode. Alternatively, the first electrode may be the cathode and the second electrode may be the anode.

In a second embodiment, the invention provides a process for producing a device as
 35 described herein, comprising

providing a first substrate and a second substrate;

dispersing a first polymer as described herein in a liquid medium to form a first composition;

depositing the first composition on a surface of the first substrate to form a first electrode;

5 dispersing a second polymer as described herein in a liquid medium to form a second composition; and

depositing the second composition on a surface of the second substrate to form a second electrode;

10 optionally further comprising immersing both the first and second electrodes in an electrolyte (for example, an aqueous electrolyte).

The liquid medium may preferably be water or an organic solvent (for example, chloroform, chlorobenzene, dichloromethane, or dimethylformamide). The first and/or second compositions may be deposited on the substrates by, for example, drop casting, blade coating or spin coating. Advantageously, no additional activation steps or treatment steps may be required after deposition of the first and/or second compositions. For example, no annealing step may be required.

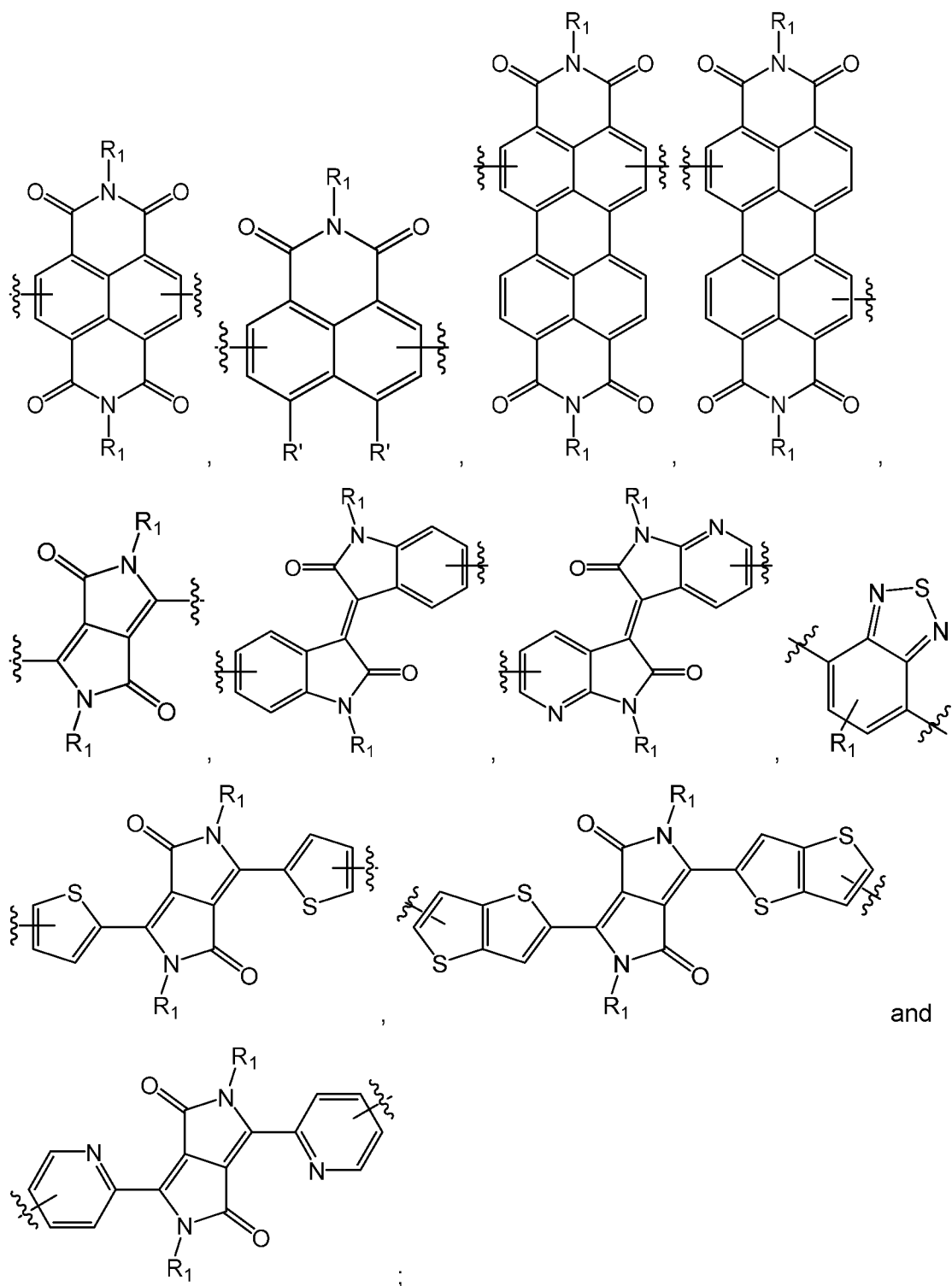
20 The process may further comprise the step of drying the first and/or second composition after deposition and optionally rinsing the dried first and/or second composition with, for example, water.

In a third aspect, the invention provides an n-type conjugated polymer comprising the formula (I):



wherein:

each M_1 is independently selected from:



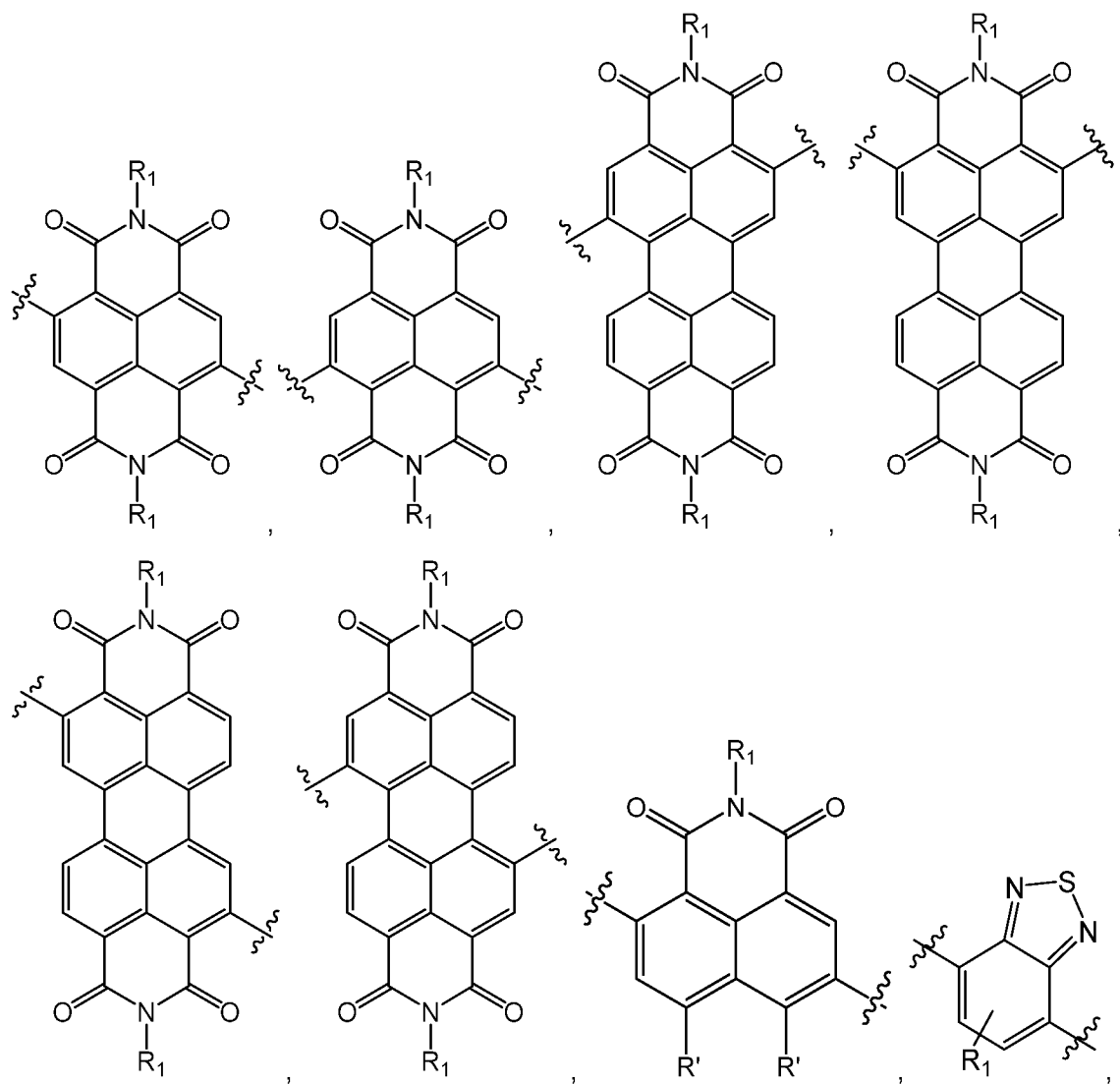
5 R' , at each occurrence, is independently selected from H, an electron-withdrawing group, a C_{1-40} alkyl group optionally substituted with 1-5 electron-withdrawing groups, a moiety comprising at least one (preferably at least two) -alkylene-O- units or a moiety comprising at least two functional groups of which at least one has a positive and one has a negative electrical charge; and

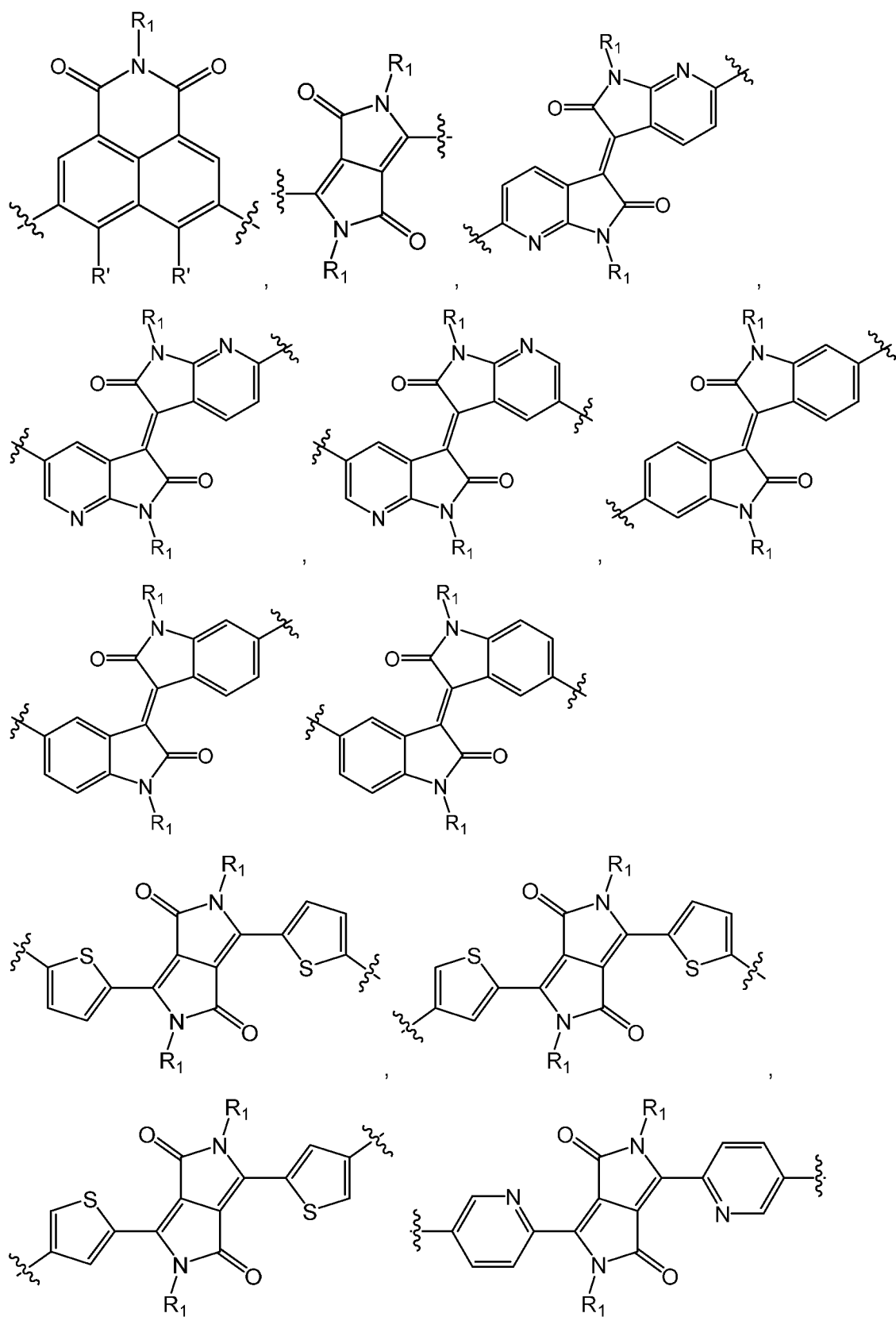
10 wherein R_1 , at each occurrence, is independently a moiety comprising at least one -alkylene-O- unit and each M_2 is independently a repeat unit comprising one or more

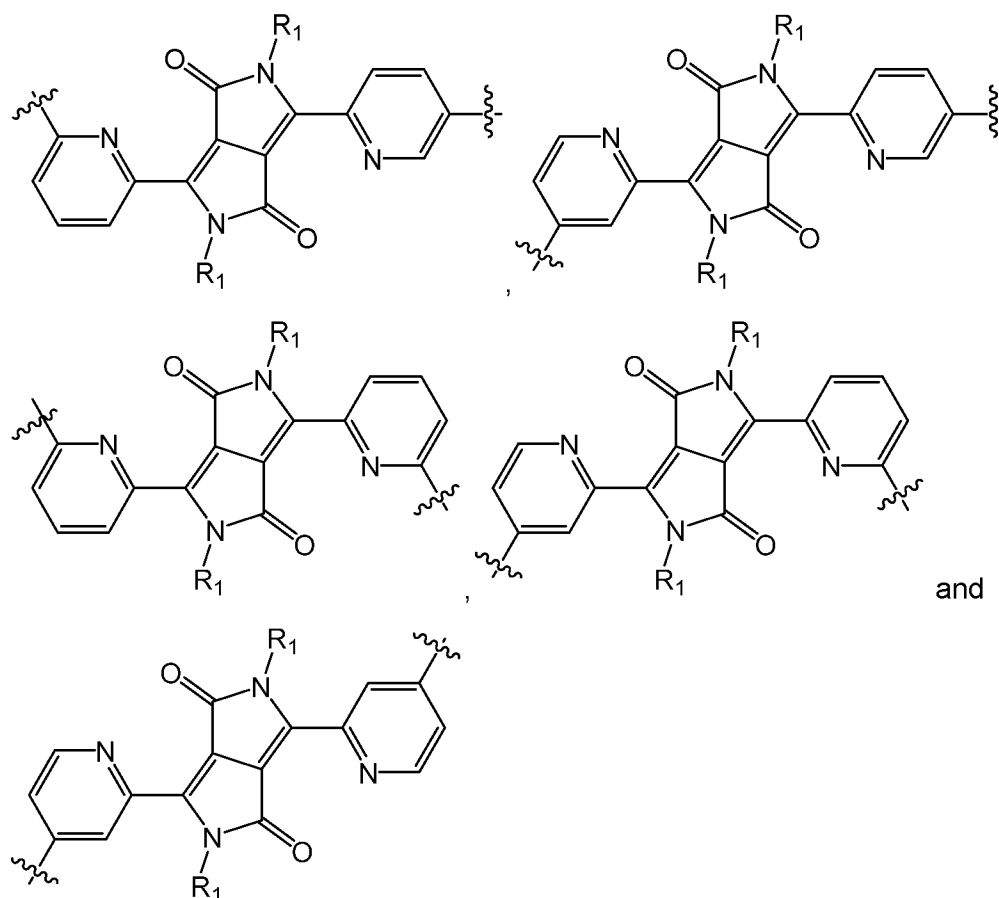
heteroaryl groups substituted with one or more groups selected from a moiety comprising at least one -alkylene-O- unit and a moiety comprising at least two functional groups of which at least one has a positive and one has a negative electrical charge; or

- wherein R_1 , at each occurrence, is independently a moiety comprising at least two functional groups of which at least one has a positive and one has a negative electrical charge and each M_2 is independently a repeat unit comprising one or more heteroaryl groups optionally substituted with one or more groups selected from a moiety comprising at least one -alkylene-O- unit and a moiety comprising at least two functional groups of which at least one has a positive and one has a negative electrical charge; and
- n is an integer of at least 2, optionally between 2 and 5,000.

Each M_1 may independently be selected from:

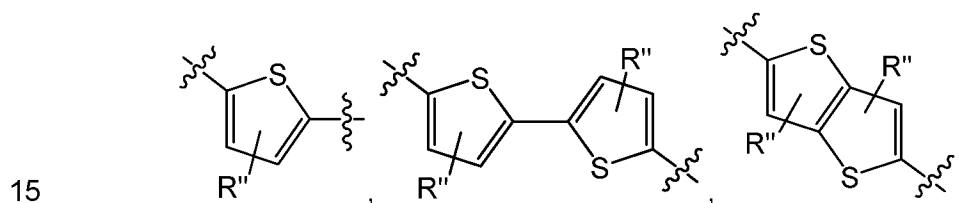


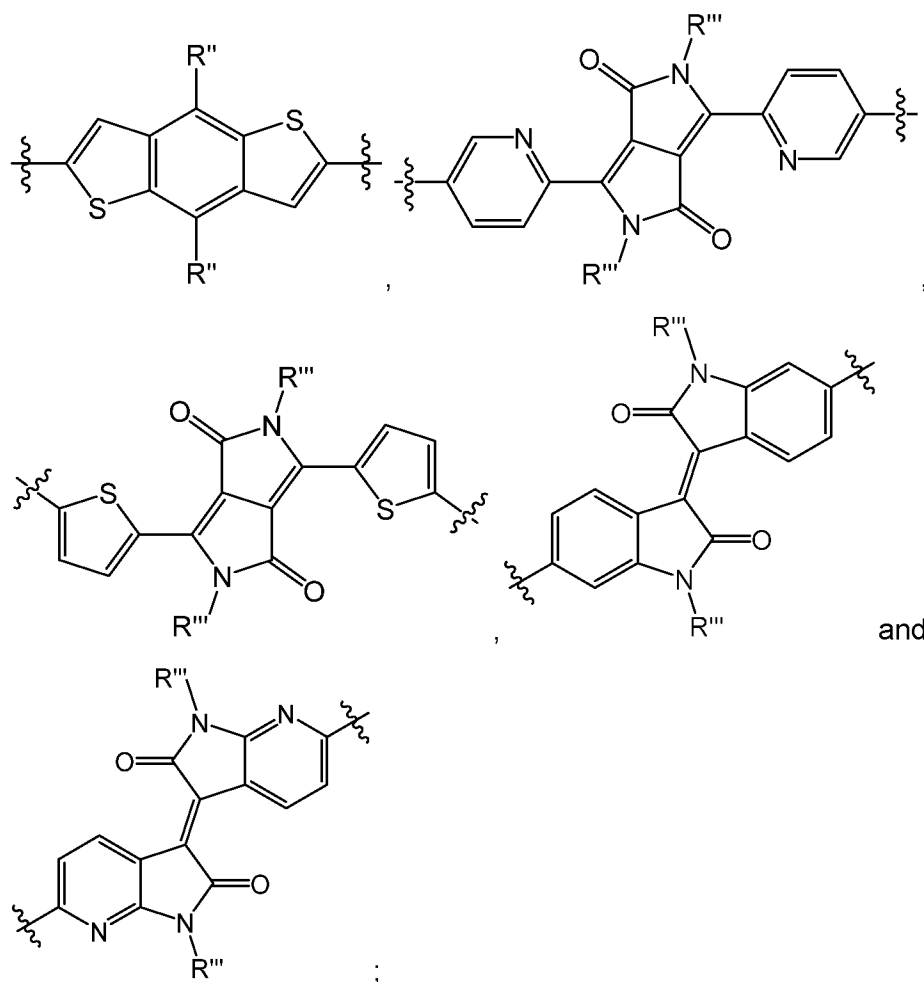




- 5 Each M₂ may independently be a repeat unit comprising one or more heteroaryl groups wherein the heteroaryl group is selected from thiophene, 2,5-dihydropyrrolo[3,4-c]pyrrol-1,4-dione (diketopyrrolopyrrole, DPP) and (3E)-3-(2-oxo-1H-indol-3-ylidene)-1H-indol-2-one (isoindigo), and [3,3'-bipyrrolo[2,3-b]pyridinylidene]-2,2'(1H,1'H)-dione (pyridine isoindigo), preferably thiophene, bithiophene, 3,6-alkoxy-thieno[3,2-b]thiophene, thieno[3,2-
- 10 b]thiophene, 3,3'-alkoxybithiophene 2,5-dihydropyrrolo[3,4-c]pyrrol-1,4-dione (diketopyrrolopyrrole, DPP), (3E)-3-(2-oxo-1H-indol-3-ylidene)-1H-indol-2-one (isoindigo) and [3,3'-bipyrrolo[2,3-b]pyridinylidene]-2,2'(1H,1'H)-dione (pyridine isoindigo).

Each M₂ may independently be selected from:



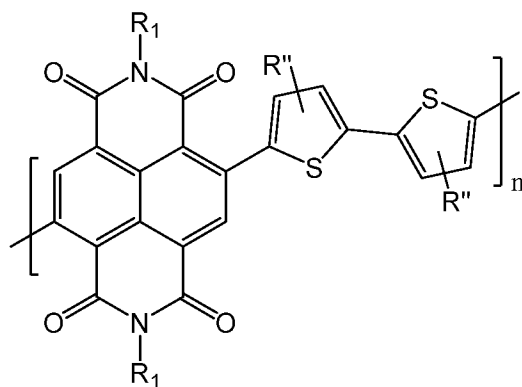


wherein:

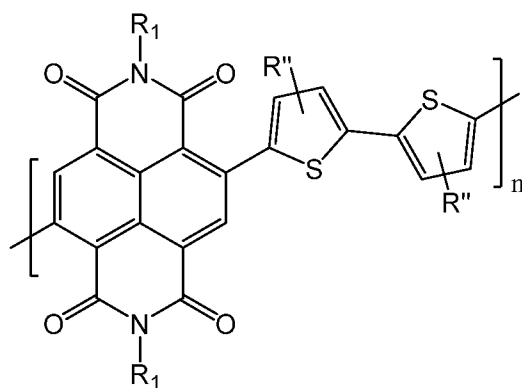
- 5 R'' , at each occurrence, is independently selected from H, $-O-C_{1-6}$ alkyl, $-COOH$, $-C(O)O-C_{1-6}$ alkyl, a (poly)alkylene glycol chain having 1-30 alkylene glycol units, a C_{3-6} alkyl group substituted with one or more (poly)alkylene glycol chains having 1-30 alkylene glycol units, C_{1-6} alkyl substituted with a crown ether or a moiety comprising at least two functional groups of which at least one has a positive and one has a negative electrical
- 10 charge; and

- R''' , at each occurrence, is independently selected from a (poly)alkylene glycol chain having 1-30 alkylene glycol units, a C_{3-6} alkyl group substituted with one or more (poly)alkylene glycol chains having 1-30 alkylene glycol units, and C_{1-6} alkyl substituted with a crown ether or a moiety comprising at least two functional groups of which at least
- 15 one has a positive and one has a negative electrical charge.

The polymer may be selected from:



wherein R_1 is a moiety comprising at least two functional groups of which at least one has a positive and one has a negative electrical charge; and R_2 is H or a moiety comprising at least one -alkylene-O- unit or a moiety comprising at least two functional groups of which at least one has a positive and one has a negative electrical charge; or



wherein R_1 is a moiety comprising at least one -alkylene-O- units; and R_2 is a moiety comprising at least one -alkylene-O- unit or a moiety comprising at least two functional groups of which at least one has a positive and one has a negative electrical charge.

In each M_1 group each R_1 may be the same or different, preferably the same.

R_1 may be as defined for R_1 in relation to the first aspect of the invention. Each R_1 may independently be selected from:

- (i) a group of formula $-A-[-alkylene-O-]_{n'}-X$, wherein n' is 1-30; A is absent, an alkyl linker or O; and X is hydrogen, alkyl, -alkyl-SO₃H, -alkyl-COOH or haloalkyl; and
- (ii) a group of formula $-W-X-Y-Z$, wherein W and Y are each independently a linker moiety selected from alkylene, arylene, heteroarylene or a moiety comprising at least one -alkylene-O- unit (optionally a moiety of formula $-[-alkylene-O-]_{n'}-$, wherein n' is 1-30); one of X and Z is a positively charged moiety and the other is a negatively charged moiety, optionally wherein a positively

charged moiety is a moiety comprising a cationic nitrogen group (e.g., quaternary ammonium, protonated amine, azomethine, amidine, guanidiene or a cationic nitrogen containing heteroaryl, such as pyridinium or imidazolium), or a sulfonium or phosphonium cation, and a negatively charged moiety is a moiety comprising a phosphate, sulfonate, carboxylate, phosphonate, phosphinante, sulfate, alkoxydicyanobenzenolate, boronate, phenolate, sulfonamide or sulfonimide anion; and

(iii) a group of formula $-W'-X'(Z')-Y'$, wherein W' is a linker moiety selected from alkylene, arylene, heteroarylene or a moiety comprising at least one $-alkylene-O-$ unit (optionally a moiety of formula $-[alkylene-O-]_{n'}$, wherein n' is 1-30); Y' is absent, H or a linker moiety selected from alkylene, arylene, heteroarylene or a moiety comprising at least one $-alkylene-O-$ unit (optionally a moiety of formula $-[alkylene-O-]_{n'}$, wherein n' is 1-30); X' is a positively charged moiety or a negatively charged moiety and Z' is a mobile counter ion, optionally wherein a positively charged moiety is a moiety comprising a cationic nitrogen group (e.g., quaternary ammonium, protonated amine, azomethine, amidine, guanidiene or a cationic nitrogen containing heteroaryl, such as pyridinium or imidazolium), or a sulfonium or phosphonium cation, and a negatively charged moiety is a moiety comprising a phosphate, sulfonate, carboxylate, phosphonate, phosphinante, sulfate, alkoxydicyanobenzenolate, boronate, phenolate, sulfonamide or sulfonimide anion.

Each R_1 may independently be selected from:

((i) a group of formula $-A-[ethylene-O-]_{n'}-X$, wherein n' is 1-30; A is absent or O; and X is methyl, $-alkyl-SO_3H$, $-alkyl-COOH$ or haloalkyl;

((ii) a group of formula $-W-X-Y-Z$, wherein W and Y are each independently a linker moiety selected from C_{1-30} alkylene, phenylene, pyridylene or a moiety of formula $-[ethylene-O-]_{n'}$, wherein n' is 1-30; X is a positively charged moiety selected from quaternized ammonium, protonated amine, pyridinium and imidazolium, and Z is a negatively charged moiety selected from a phosphate anion, a sulfonate anion and a carboxylate anion; and

((iii) a group of formula $-W'-X'(Z')-Y'$, wherein W' is a linker moiety selected from C_{1-30} alkylene, phenylene, pyridylene or a moiety of formula $-[ethylene-O-]_{n'}$, wherein n' is 1-30; Y' is absent, H or a linker moiety selected from C_{1-30} alkylene, phenylene, pyridylene or a moiety of formula $-[ethylene-O-]_{n'}$, wherein n' is 1-30); X' is a positively charged moiety or a negatively charged moiety, wherein a positively charged moiety is a moiety selected from quaternized ammonium, protonated amine, pyridinium and imidazolium, and a negatively charged moiety is

a moiety selected from a phosphonate anion, a phosphate anion, a sulfonate anion and a carboxylate anion; and Z' is a mobile counter ion selected from H⁺, M⁺ or a halide anion, wherein M⁺ is a metal cation (optionally an alkali metal cation).

5 R' may be as defined for R' in relation to the first aspect of the invention. R', at each occurrence, may be independently selected from H, a halogen, -CN, C₁₋₁₀haloalkyl, a moiety comprising at least one O-alkylene unit and a moiety comprising at least two functional groups of which at least one has a positive and one has a negative electrical charge.

10

R'' may be as defined for R'' in relation to the first aspect of the invention. Each R'' may independently be selected from H, a C₁₋₄₀alkoxy group, a (poly)alkylene glycol chain having 1-30 alkylene glycol units, and a C₃₋₆alkyl group substituted with one or more (poly)alkylene glycol chains having 1-30 alkylene glycol units or a moiety comprising at least two functional groups of which at least one has a positive and one has a negative electrical charge, preferably H, a (poly)alkylene glycol chain having 1-30 alkylene glycol units or a moiety comprising at least two functional groups of which at least one has a positive and one has a negative electrical charge. Preferably each R'' may independently be selected from H or a moiety of formula -O-[-alkylene-O-]_{m'}-X, wherein m' is 1-30 and X is hydrogen, alkyl, -alkyl-SO₃H, -alkyl-COOH or haloalkyl, optionally wherein alkylene is ethylene.

R''' may be as defined for R''' in relation to the first aspect of the invention. Each R''' may independently be selected from a (poly)alkylene glycol chain having 1-30 alkylene glycol units, and a C₃₋₆alkyl group substituted with one or more (poly)alkylene glycol chains having 1-30 alkylene glycol units or a moiety comprising at least two functional groups of which at least one has a positive and one has a negative electrical charge, preferably a (poly)alkylene glycol chain having 1-30 alkylene glycol units or a moiety comprising at least two functional groups of which at least one has a positive and one has a negative electrical charge. Preferably each R''' may independently be a moiety of formula -[-alkylene-O-]_{m'}-X, wherein m' is 1-30 and X is hydrogen, alkyl, -alkyl-SO₃H, -alkyl-COOH or haloalkyl, optionally wherein alkylene is ethylene.

The polymer may have a number average molecular weight of about 1 to about 500 kD, optionally about 5 to about 50 kD. The polymer may be provided in the form of a bulk material or a film, optionally a film.

In a fourth aspect, the invention provides the use of the polymer according to the third aspect of the invention in an optical or electronic device, in non-linear optics or as an antifouling coating, preferably in an optical or electronic device. The device may be an electrochemical energy storage device (optionally a battery, capacitor or supercapacitor),
 5 an electrochromic energy storage device, a photovoltaic cell (optionally an organic solar cell), an organic transistor (optionally an organic electrochemical transistor or an organic field effect transistor), a light emitting diode, a photodetector or a photocatalytic device, optionally wherein the device is an electrochemical energy storage device. The polymer may form an electrode or an active layer in the device, optionally an electrode. Preferably,
 10 the device is battery comprising an electrode comprising the polymer.

In a fifth aspect, the invention provides an electrochemical device comprising the polymer according to the third aspect of the invention.

15 Embodiments described herein in relation to the first aspect of the invention apply *mutatis mutandis* to the second to fifth aspects of the invention

BRIEF DESCRIPTION OF FIGURES

Figure 1 shows the spectroelectrochemistry of p(gT2) polymer on FTO in 0.1M NaCl:DIW electrolyte: (a) first 3 cyclic voltammetry scans performed on the sample using scan rate
 20 of 50 mV s⁻¹; (b) UV vis absorbance spectra for the charging of the polymer film during the first cyclic voltammetry scan as a function of potential applied to the sample vs Ag/AgCl.

Figure 2 shows the spectroelectrochemistry of p(g7NDI-gT2) and p(ZI-NDI-gT2) polymers
 25 on FTO in 0.1M NaCl:DIW electrolyte: (a) and (b) show the first cyclic voltammetry scans performed on (a) p(g7NDI-gT2) and on (b) p(ZI-NDI-gT2) polymers at a scan rate of 50 mV s⁻¹; (c) and (d) show the UV vis absorbance spectra of the polymer films during the cyclic voltammetry measurement as a function of potential applied to the sample vs Ag/AgCl. (c) refers to the 5th scan, (d) refers to the 1st scan.

30

Figure 3 shows charge density and coulombic efficiency for two (a) p(gT2) and (b) p(ZI-NDI-gT2) films with different thicknesses extracted from galvanostatic charging
 discharging measurements displayed as a function of C-rate.

35 **Figure 4** shows a polymer battery with structure FTO / p(gT2) (87 nm)/ 0.1M NaCl:DIW / p(ZI-NDI-gT2) (70 nm) / FTO. Voltage is applied/measured at the cathode (p(gT2) electrode) with respect to the anode (p(ZI-NDI-gT2) electrode). (a) cyclic voltammetry

measurements performed at 100 mV s^{-1} ; (b) evolution in optical absorbance for the two films in series corresponding to the charging of the cell; (c) normalized specific capacity of the battery and coulombic efficiency measured as a function of cycle number; and (d) schematics of the working mechanism of a polymer battery including the reactions at the cathode and at the anode.

Figure 5 shows the dynamic performance of the polymer battery: (a) specific capacity and coulombic efficiency as a function of C-rate (inset shows the galvanostatic charge-discharge curves at different C-rates); and (b) cyclic voltammetry measurements performed at different scan rate.

DETAILED DESCRIPTION

The present invention provides a strategy for the design of polymers where separately optimized structures for the backbone and side chains of conjugated polymers are combined to achieve efficient mixed electronic-ionic conduction. Such polymers may be used as, for example, electrodes in electrochemical energy storage devices (e.g., a battery or supercapacitor).

Firstly, we consider conjugated polymers with a large electron affinity, herein referred to as n-type, or low ionization potential, herein referred to as p-type, or to address specifications for both anode and cathode materials with redox potentials which fit well with the allowed electrochemical window for water.

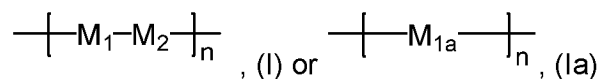
Secondly, we design the side chains of the polymers using alkylene glycol-based structures for the p-type and alkylene glycol or zwitterion structures for the n-type polymer. These side chains were attached with the intention of favouring conduction of sodium and chloride ions and to enable the use of neutral pH, sodium chloride water based electrolyte.

Provided herein are variations of these n-type polymer structures that can be used as, for example, the electrodes of polymer batteries and illustrate the potential to further improve the specific capacity of these materials through side chain engineering. For example, charging and discharging of $\sim 100 \text{ nm}$ thick polymer films occurs efficiently on the second timescale. This material design strategy enables efficient ion transport within the polymer films for fast charging/discharging, results in p-type and n-type polymers with redox activity which takes advantage of nearly the full available electrochemical window of water, and results in highly reversible electrochemical charging which is extended to the whole polymer film.

Also provided herein is a battery comprising the combination of p and n-type conjugated polymers used as the cathode and the anode of a water based electrochemical storage cell that can be operated under a nearly unipolar potential window of 1.4 V at >1000 C-rate (i.e. using current values which charge/discharge the battery in 1/1000 hours). The device is a demonstration of a solution-processable polymer battery working under neutral pH water conditions and showing rate capabilities comparable to supercapacitors.

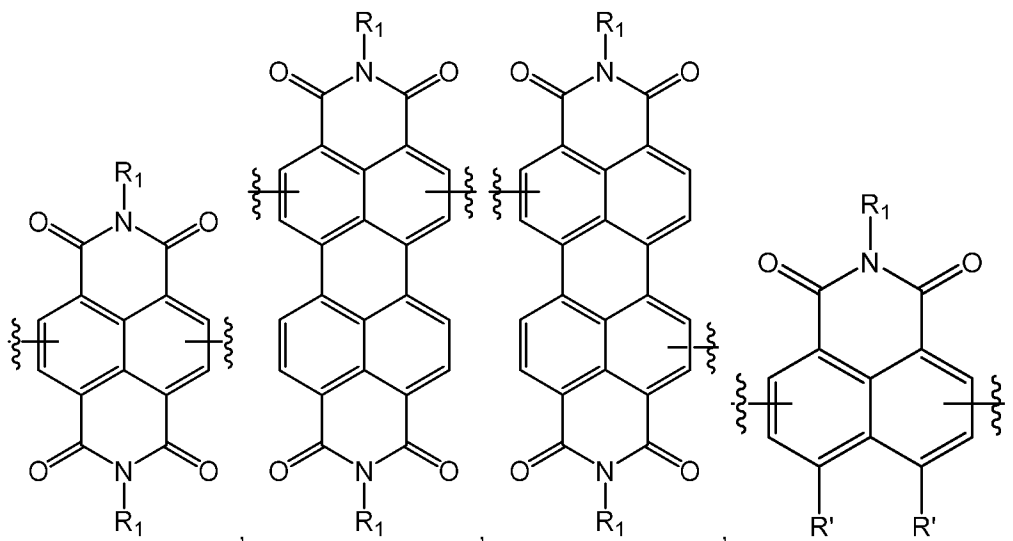
In a first aspect, the invention provides an electrochemical cell comprising:

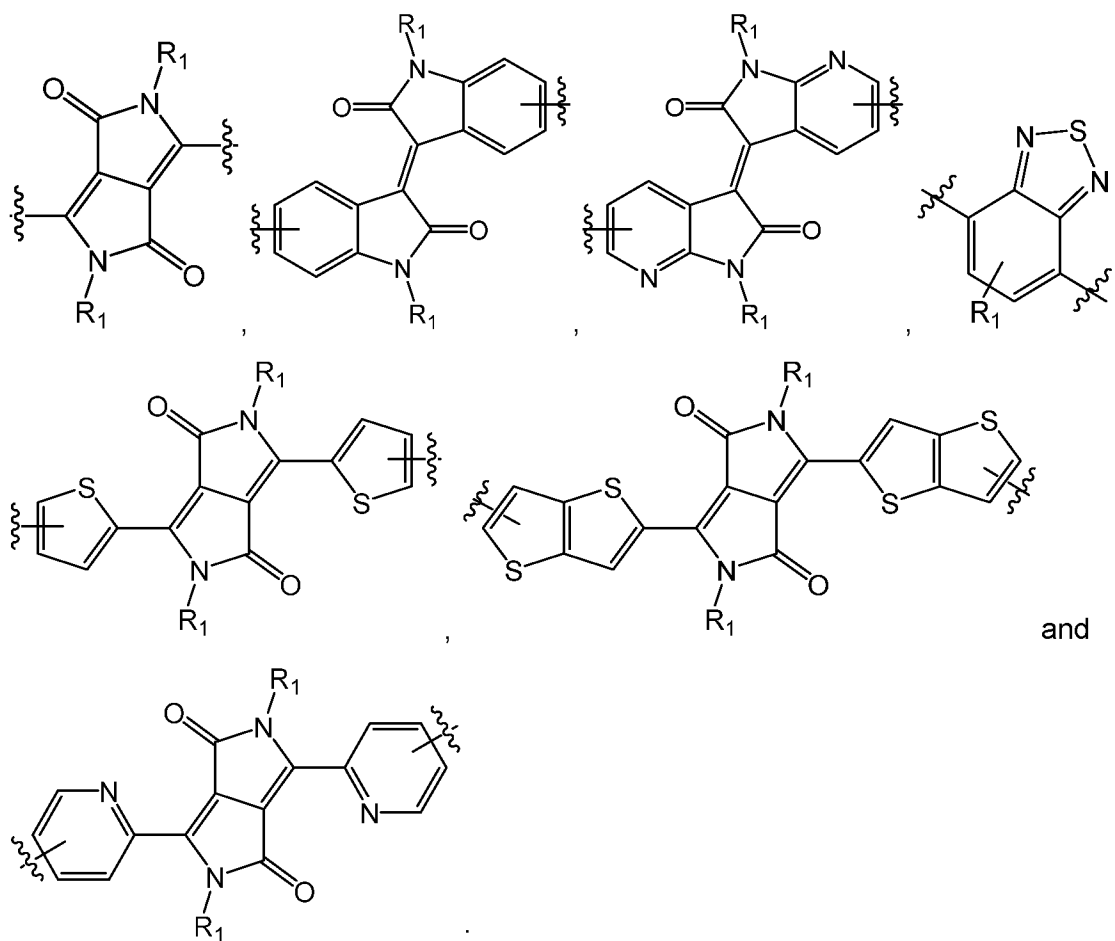
a first electrode comprising a first polymer comprising the formula (I) or (Ia):



wherein:

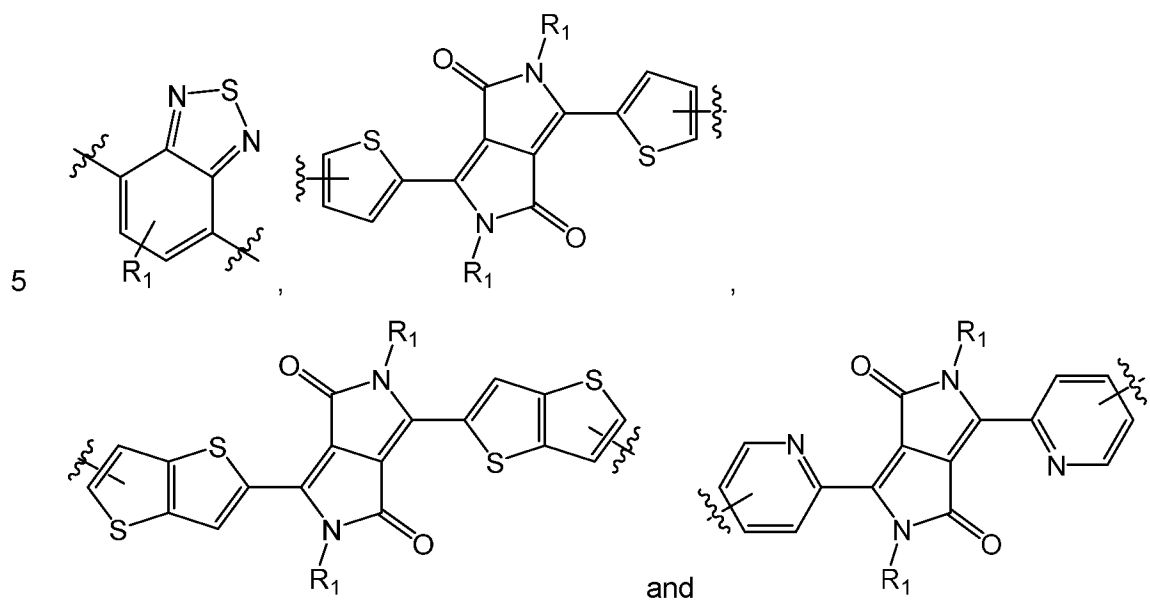
each M_1 is independently selected from:





and

each M_{1a} is independently selected from:



wherein R_1 , at each occurrence, is independently a moiety comprising at least one -alkylene-O- unit or a moiety comprising at least two functional groups of which at least one has a positive and one has a negative electrical charge;

R' , at each occurrence, is independently selected from H, an electron-withdrawing group, a C_{1-40} alkyl group optionally substituted with 1-5 electron-withdrawing groups, a

moiety comprising at least two -alkylene-O- units or a moiety comprising at least two functional groups of which at least one has a positive and one has a negative electrical charge;

each M_2 is independently a repeat unit comprising one or more heteroaryl groups
 5 optionally substituted with one or more groups selected from a moiety comprising at least one -alkylene-O- unit and a moiety comprising at least two functional groups of which at least one has a positive and one has a negative electrical charge; and

n is an integer of at least 2, optionally between 2 and 5,000; and

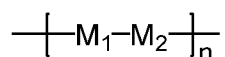
a second electrode comprising a second polymer comprising one or more repeat
 10 units comprising one or more heteroaryl groups substituted with one or more moieties comprising at least one -alkylene-O- unit.

The first polymer is a co-polymer formed from two groups of monomers: M_1 , which may preferably be an electron acceptor moiety, and M_2 , which may preferably be an electron
 15 donor moiety, the structure of which maintains the conjugation of the polymer. A polymer that comprises a combination of donor and acceptor moieties may provide a material with a large electron affinity. This helps to enable electrochemical reduction (or redox) reactions on the n-type polymers at a low potential/voltages. Usually a donor-acceptor polymer has a small band gap. In addition, the polymerisations of such donor-acceptor
 20 polymers work with high yields and form high molecular weights

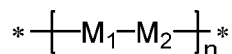
The first polymer may comprise one or more different M_1 and/or M_2 monomers. As used herein, the term monomer may be used interchangeably with the term repeat unit. For example, the first polymer may have formula (II): $(M_1'-M_2')_x(M_1''-M_2'')_y$, where both x and y
 25 are integers whose sum totals at least 2, preferably between 2 and 5,000, inclusive. It will be appreciated that formula (II) does not require the $M_1'-M_2'$ and the $M_1''-M_2''$ repeating units to be present in two distinct "blocks" in each of the sections defined by " x " and " y ", but instead the $M_1'-M_2'$ and $M_1''-M_2''$ repeating units may be statistically distributed along the polymer backbone, or may be arranged so that the $M_1'-M_2'$ and $M_1''-M_2''$ repeating
 30 units are not in two distinct blocks. Thus, the polymer may be referred to as a random copolymer.

The copolymers may be formed as random copolymers by, for example, Stille or Suzuki polymerisation, by mixing one or more different M_1 monomers and one or more different
 35 M_2 monomers under suitable conditions. Alternatively, the polymers may be formed by polymerisation of prepared M_1-M_2 units.

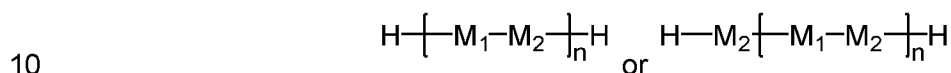
The first polymer is a conjugated co-polymer comprising the formula:



The first polymer may consist essentially of a structure of the formula:



- 5 with termination of the polymer at the position marked *. A skilled person will appreciate that termination may be with any suitable moiety such that a stable polymer is formed. For example, termination may be with either of the monomers M_1 or M_2 . The polymer may be terminated with H or a heteroaryl group, such that a stable polymer is formed. For example, the first polymer may consist essentially of:

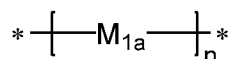


Preferably, the polymer is terminated with heteroaryl endcap groups (preferably thiophene groups).

Alternatively, the first polymer may be a homopolymer comprising the formula:

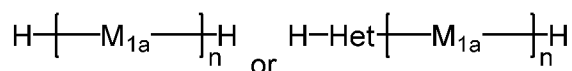


The first polymer may consist essentially of a structure of the formula:



with termination of the polymer at the position marked *. A skilled person will appreciate that termination may be with any suitable moiety such that a stable polymer is formed.

- 20 For example, termination may be with monomer M_{1a} or another suitable group, such as H or a heteroaryl, such that a stable polymer is formed. For example, the first polymer may consist essentially of:



- 25 Preferably, the polymer is terminated with heteroaryl endcap groups (preferably thiophene groups).

- The first, and/or second, polymer of the invention may have a number average molecular weight (M_n) of about 1 to about 500 kD, optionally about 1 to about 100 kDa, optionally about 5 to about 50 kD, optionally about 10 to about 35 kD. The polymer may have a
- 30 weight average molecular weight (M_w) of about 20 to about 100 kD.

The M_n and M_w of the polymer may be measured using Gel Permeation Chromatography (GPC). For example, the GPC may be measured using an Agilent Technologies 1260

infinity system operating in DMF with 5 mM NH_4BF_4 with 2 PLgel 5 μm mixed-C columns (300 $\times$ 7.5mm), a PLgel 5 mm guard column (50 $\times$ 7.5mm) at 50 °C with a refractive index detector as well as a variable wavelength detector. The instrument was calibrated with linear narrow poly(methyl methacrylate) standards in the range of 0.6 to 47kDa.

5

The attachment of polar side chains on such n-type polymers enables reversible ion penetration which is important for highly reversible redox reactions in aqueous electrolytes. Accordingly, the backbone of the n-type polymer is provided with side chain groups, R_1 on the M_1 monomers. Side chain groups may also be provided on the M_2 monomers, R'' and R''' . Each R_1 may independently be H or a moiety comprising at least one -alkylene-O- unit or a moiety comprising at least two functional groups of which at least one has a positive and one has a negative electrical charge.

Suitable side chains are, for example, ethylene glycol or zwitterion side chains which may be reduced (i.e., charged with electrons), when the polymer is a thin film coated on top of a substrate (e.g. Au, FTO, ITO), in aqueous MX salt electrolytes or organic solvents (e.g. DMF, DMSO, THF or acetonitrile) at voltages between +0.5 V and -1.5 V vs Ag/AgCl. M is M^+ , e.g., alkali metal cations, organic cations, or M^{2+} , e.g., alkaline earth metal ions; and X is a halide, organic anion, sulfates or carboxylates. For example, the first polymer may have an electron affinity of 3 eV to 5 eV. Electro affinity may be calculated by measuring the ionisation potential (IP) and subtracting the band gap energy (determined from the UV spectrum). IP may be measured by photoelectron spectroscopy in air (PESA) using, for example, a Riken AC-2 Photoelectron Spectrometer which measures the Work Function of the sample surface. A PESA measurement may be carried out as follows: UV photons emitted from a deuterium lamp are monochromated by a grating spectrometer and focused on a sample. Then, photoelectrons emitted from the sample are counted by an open counter, the energy of the emitted electrons can be related to the ionisation potential. See, for example, D. Yamashita et al., J. of Surface Analysis, 2008, 14 (4), 433-436, the entire contents of which are herein incorporated by reference.

30

The use of a moiety comprising at least one -alkylene-O- unit as a side chain may also help increase the solubility of the polymer in organic solvents and enable the use of solution processing techniques for the deposition of the materials.

A moiety comprising at least one -alkylene-O- unit is preferably a (poly)alkylene glycol chain having 1-30 alkylene glycol units, a C_{3-6} alkyl group substituted with one or more (poly)alkylene glycol chains having 1-30 alkylene glycol units, and C_{1-6} alkyl substituted

with a crown ether. Preferably, a moiety comprising at least one -alkylene-O- unit is a moiety of formula -Q-[-alkylene-O-]_p-X (wherein p is 1-30, Q is O or absent, and X is hydrogen, alkyl, -alkyl-SO₃H, -alkyl-COOH or haloalkyl, preferably alkyl (e.g., methyl). In the context of a moiety comprising at least one -alkylene-O- unit, alkylene is preferably

5 methylene, ethylene or propylene, preferably ethylene.

Preferably a moiety comprising at least one -alkylene-O- unit is a moiety of formula -Q-[-ethylene-O-]_p-C₁₋₆alkyl, preferably wherein p is 1-10, preferably 1-5, preferably 3 and preferably wherein C₁₋₆alkyl is C₁₋₃alkyl, preferably methyl.

10

As used herein a moiety comprising at least two functional groups of which at least one has a positive and one has a negative electrical charge may also be referred to as a zwitterion. The use of a zwitterion side chain may decrease the interaction of the side chain and positive ions penetrating the film during electrochemical doping. In addition, the

15 advantage of a zwitterion side chain may be that ions of opposite charge are included within the chemical structure of the same side chain. As a result these ions are not able to migrate away from the active layer during operation which could affect the stability during charging of the polymers as well as avoiding the possible exchange of the mobile ions.

20

Suitable moieties comprising at least two functional groups of which at least one has a positive and one has a negative electrical charge (zwitterion groups) that may be used as side chains in the polymers described herein are described in Laschewsky A. *et al.*, Polymers, 2014, 6, 1544-1601, the entire contents of which are herein incorporated by

25 reference.

Moieties comprising at least two functional groups of which at least one has a positive and one has a negative electrical charge comprise at least one positively charged functional group. Exemplary positively charged functional groups include groups comprising a

30 cationic nitrogen moiety. For example, a quaternized ammonium (a group of structure R'₄N⁺), a protonated amine (R₃N⁺H), an azomethine (R₂C=NR'), an amidine (RC(=NR)NR₂), a guanidiene (R₂NC(=NR)NR₂). A positively charged functional group may also comprise a cationic nitrogen containing heteroaryl, such as pyridinium or imidazolium), sulfonium (R₃S⁺) or phosphonium (R₄P⁺). Moieties comprising at least two

35 functional groups of which at least one has a positive and one has a negative electrical charge comprise at least one negatively charged functional group. Exemplary negatively charged functional groups include groups comprising a phosphate (ROP(O⁻)(=O)OR),

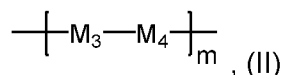
- sulfonate ($\text{RS(=O)}_2\text{O}^-$), carboxylate (COO^-), phosphonate ($\text{RP(O}^-\text{)(=O)OR}$), phosphinante ($\text{RP(O}^-\text{)(=O)R}$), sulfate (SO_3^-), alkoxydicyanoethenolate ($\text{ROC(O}^-\text{)=C(CN)}_2$), boronate ($\text{RB(O}^-\text{)OR}$), phenolate ($\text{C}_6\text{H}_5\text{O}^-$), sulphonamide ($\text{RS(=O)}_2\text{N}^-\text{R}$) or sulfonimide ($\text{RS(=O)}_2\text{N}^-\text{C(=O)R}$). Each R is independently hydrogen, alkyl, alkenyl, alkynyl, cycloalkyl, heterocycloalkyl, aryl or heteroaryl. Each R' is independently alkyl, alkenyl, alkynyl, cycloalkyl, heterocycloalkyl, aryl or heteroaryl. As would be appreciated by a skilled person, any R or R' group may be the point of attachment of the positively or negatively charged functional group to the rest of the side chain moiety.
- Such positively or negatively charged functional groups may be present within the moiety (i.e., linked by covalent bond(s) to the rest of the moiety) or as a mobile counter charge (i.e., a counter ion) associated with other of the positively or negatively charged group in the moiety. Exemplary moieties comprising at least two functional groups of which at least one has a positive and one has a negative electrical charge and wherein one of the positively or negatively charged groups is present as a mobile counter charge include moieties comprising a cationic nitrogen moiety and a halide anion (e.g., F^- or Cl^-) as the counter ion, or a phosphate ($\text{ROP(O}^-\text{)(=O)OR}$), sulfonate ($\text{RS(=O)}_2\text{O}^-$), carboxylate (COO^-), or phosphonate ($\text{RP(O}^-\text{)(=O)OR}$) with a mobile counter ion selected from H^+ or M^+ , wherein M^+ is a metal cation (optionally an alkali metal cation such as Na^+ or K^+).
- Further moieties comprising at least two functional groups of which at least one has a positive and one has a negative electrical charge (zwitterion groups) that may be used as side chains in the polymers described herein are described in Ichikawa T., Polymer Journal, 2017, 49, 413-421, Cardoso J. et al., J. Phys. Chem., 2010, 114, 14261-14268, and Fei Z. et al., Chem. Eur. J., 2004, 10, 4886-4893, the entire contents of which are herein incorporated by reference in their entirety.

The second polymer is a p-type polymer, having a low ionization potential, comprising one or more repeat units comprising one or more heteroaryl groups substituted with one or more moieties comprising at least one -alkylene-O- unit. Preferably, the moiety comprising at least one -alkylene-O unit is linked via an O atom.

Preferably, the second polymer comprises ethylene glycol side chains which may be oxidised (i.e., charged with holes) in aqueous MX salt electrolytes or organic solvents (e.g. DMF, DMSO, THF or acetonitrile) at voltages between -0.5 V and +1.5 V vs Ag/AgCl. M is M^+ , e.g., alkali metal cations, organic cations, or M^{2+} , e.g., alkaline earth metal ions; and X

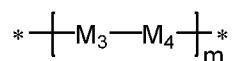
is a halide, organic anion, sulfates or carboxylates. For example, the second polymer may have an ionisation potential (IP) of about 6 eV to 4 eV.

The second polymer may be a conjugated homo or co-polymer comprising the formula
5 (II):

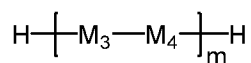


wherein, M_3 is a repeat unit comprising one or more heteroaryl groups, optionally substituted with one or more moieties comprising at least one -alkylene-O- units, and M_4 is absent or a repeat unit comprising a heteroaryl group, optionally substituted with one or
10 more moieties comprising at least one -alkylene-O- units.

The second polymer may consist essentially of a structure of the formula:



with termination of the polymer at the position marked *. A skilled person will appreciate
15 that termination may be with any suitable moiety such that a stable polymer is formed. For example, termination may be with H or a heteroaryl group, such that a stable polymer is formed. For example, the first polymer may consist essentially of:



20 Preferably the second polymer is a homopolymer (i.e., where M_4 is absent). An exemplary p-type second polymer is a homo alkoxy-substituted bithiophene polymer. Alkoxy-substituted bithiophenes represent electron rich structures with small dihedral angles where the oxygen atoms in the 3,3' position of the bithiophene may allow the formation of non-covalent sulfur oxygen interactions which planarize the bithiophene
25 compared to unsubstituted bithiophene structures. The alkoxy side chain may also increase the electron density through the overlap of the oxygen's lone pairs with the aromatic thiophene system, lowering the ionization potential and shifting the oxidation potential to lower voltages.

30 As used herein, the terms "donor" or "donating" and "acceptor", "accepting" or "withdrawing" will be understood to mean an electron donor or electron acceptor, respectively. "Electron donor" will be understood to mean a chemical entity that donates electrons to another compound or another group of atoms of a compound more than a hydrogen atom would if it occupied the same position. "Electron acceptor" will be
35 understood to mean a chemical entity that accepts electrons transferred to it from another

compound or another group of atoms of a compound more than a hydrogen atom would if it occupied the same position. (See also U.S. Environmental Protection Agency, 2009, Glossary of technical terms, <http://www.epa.gov/oust/cat/TUMGLOSS.HTM>, or "Glossary of terms used in physical organic chemistry (IUPAC recommendations 1994)" in Pure and Applied Chemistry, 1994, 66, 1077, pages 1109-1110).

The electron-donating or electron-withdrawing properties of several hundred of the most common substituents, reflecting all common classes of substituents have been determined, quantified, and published. The most common quantification of electron-donating and electron-withdrawing properties is in terms of Hammett σ values. Hydrogen has a Hammett σ value of zero, while other substituents have Hammett σ values that increase positively or negatively in direct relation to their electron-withdrawing or electron-donating characteristics. Substituents with negative Hammett σ values are considered electron-donating, while those with positive Hammett σ values are considered electron-withdrawing. See Lange's Handbook of Chemistry, 12th ed., McGraw Hill, 1979, Table 3-12, pp. 3-134 to 3-138, which lists Hammett σ values for a large number of commonly encountered substituents.

Examples of electron-withdrawing groups include, but are not limited to, halogen or halo (e.g., F, Cl, Br, I), $-\text{NO}_2$, $-\text{CN}$, $-\text{NC}$, $-\text{S}(\text{R}^\circ)_2^+$, $-\text{N}(\text{R}^\circ)_3^+$, $-\text{SO}_3\text{H}$, $-\text{SO}_2\text{R}^\circ$, $-\text{SO}_3\text{R}^\circ$, $-\text{SO}_2\text{NHR}^\circ$, $-\text{SO}_2\text{N}(\text{R}^\circ)_2$, $-\text{COOH}$, $-\text{COR}^\circ$, $-\text{COOR}^\circ$, $-\text{CONHR}^\circ$, $-\text{CON}(\text{R}^\circ)_2$, C_{1-40} haloalkyl groups, C_{6-14} aryl groups, and 5-14 membered electron-poor heteroaryl groups; where R° is a C_{1-20} alkyl group, a C_{2-20} alkenyl group, a C_{2-20} alkynyl group, a C_{1-20} haloalkyl group, a C_{1-20} alkoxy group, a C_{6-14} aryl group, a C_{3-14} cycloalkyl group, a 3-14 membered cycloheteroalkyl group, and a 5-14 membered heteroaryl group, each of which can be optionally substituted as described herein. For example, each of the C_{1-20} alkyl group, the C_{2-20} alkenyl group, the C_{2-20} alkynyl group, the C_{1-20} haloalkyl group, the C_{1-20} alkoxy group, the C_{6-14} aryl group, the C_{3-14} cycloalkyl group, the 3-14 membered cycloheteroalkyl group, and the 5-14 membered heteroaryl group can be optionally substituted with 1-5 small electron-withdrawing groups such as F, Cl, Br, $-\text{NO}_2$, $-\text{CN}$, $-\text{NC}$, $-\text{S}(\text{R}^\circ)_2^+$, $-\text{N}(\text{R}^\circ)_3^+$, $-\text{SO}_3\text{H}$, $-\text{SO}_2\text{R}^\circ$, $-\text{SO}_3\text{R}^\circ$, $-\text{SO}_2\text{NHR}^\circ$, $-\text{SO}_2\text{N}(\text{R}^\circ)_2$, $-\text{COOH}$, $-\text{COR}^\circ$, $-\text{COOR}^\circ$, $-\text{CONHR}^\circ$, and $-\text{CON}(\text{R}^\circ)_2$.

Examples of electron-donating groups include $-\text{OH}$, $-\text{OR}^\circ$, $-\text{NH}_2$, $-\text{NHR}^\circ$, $-\text{N}(\text{R}^\circ)_2$, and 5-14 membered electron-rich heteroaryl groups, where R° is a C_{1-20} alkyl group, a C_{2-20} alkenyl group, a C_{2-20} alkynyl group, a C_{6-14} aryl group, or a C_{3-14} cycloalkyl group.

Various unsubstituted heteroaryl groups can be described as electron-rich (or π -excessive) or electron-poor (or π -deficient). Such classification is based on the average electron density on each ring atom as compared to that of a carbon atom in benzene. Examples of electron-rich systems include 5-membered heteroaryl groups having one heteroatom such as furan, pyrrole, and thiophene; and their benzofused counterparts such as benzofuran, benzopyrrole, and benzothiophene. Examples of electron-poor systems include 6-membered heteroaryl groups having one or more heteroatoms such as pyridine, pyrazine, pyridazine, and pyrimidine; as well as their benzofused counterparts such as quinoline, isoquinoline, quinoxaline, cinnoline, phthalazine, naphthyridine, quinazoline, phenanthridine, acridine, and purine. Mixed heteroaromatic rings can belong to either class depending on the type, number, and position of the one or more heteroatom(s) in the ring. See Katritzky, A. R and Lagowski, J. M., *Heterocyclic Chemistry* (John Wiley & Sons, New York, 1960).

The expressions p- and n-type in this context are not associated with an intrinsic doping of the polymers but simply indicate their relative energetic 'ease' for oxidation and reduction, respectively. As used herein, the term "n-type" or "n-type semiconductor" will be understood to mean an extrinsic semiconductor in which the conduction electron density is in excess of the mobile hole density, and the term "p-type" or "p-type semiconductor" will be understood to mean an extrinsic semiconductor in which mobile hole density is in excess of the conduction electron density (see also, J. Thewlis, *Concise Dictionary of Physics*, Pergamon Press, Oxford, 1973).

As used herein, the term "conjugated" will be understood to mean a compound (for example a small molecule or a polymer) that contains mainly C atoms with sp^2 -hybridisation (or optionally also sp -hybridisation), and wherein these C atoms may also be replaced by hetero atoms. In the simplest case this is for example a compound with alternating C—C single and double (or triple) bonds, but is also inclusive of compounds with aromatic units like for example 1,4-phenylene. The term "mainly" in this connection will be understood to mean that a compound with naturally (spontaneously) occurring defects, which may lead to interruption of the conjugation, is still regarded as a conjugated compound. In the original meaning a conjugated system is a molecular entity whose structure may be represented as a system of alternating single and multiple bonds: e.g. $CH_2=CH-CH=CH_2$, $CH_2=CH-C\equiv N$. In such systems, conjugation is the interaction of one p-orbital with another across an intervening σ -bond in such structures. (In appropriate molecular entities d-orbitals may be involved.) The term is also extended to the analogous interaction involving a p-orbital containing an unshared electron pair, e.g. $:Cl-CH=CH_2$.

Accordingly, a conjugated system is a system of connected p-orbitals with delocalized electrons in molecules with alternating single and multiple bonds. A conjugated system has a region of overlapping p-orbitals, bridging the adjacent single bonds. They allow a delocalization of electrons across all the adjacent aligned p-orbitals. The conjugated
 5 system may be cyclic, acyclic, linear, branched or mixed. A conjugated system according to the present invention is a system which may be partly or completely conjugated.

The term "halide", "halo" and "halogen" are used interchangeably and, as used herein mean a fluorine atom, a chlorine atom, a bromine atom, an iodine atom and the like,
 10 preferably a fluorine atom, a bromine atom or a chlorine atom, and more preferably a fluorine atom.

As used herein, an alkyl group is a straight chain or branched, substituted or unsubstituted group (preferably unsubstituted) containing from 1 to 40 carbon atoms. An alkyl group
 15 may optionally be substituted at any position. The term "alkenyl," as used herein, denotes a group derived from the removal of a single hydrogen atom from a straight- or branched-chain aliphatic moiety having at least one carbon-carbon double bond. The term "alkynyl," as used herein, refers to a group derived from the removal of a single hydrogen atom from a straight- or branched-chain aliphatic moiety having at least one carbon-carbon triple
 20 bond.

The term 'alkyl', 'aryl', 'heteroaryl' etc also include multivalent species, for example alkylene, arylene, 'heteroarylene' etc. Examples of alkylene groups include ethylene (-CH₂-CH₂-), and propylene (-CH₂-CH₂-CH₂-). An exemplary arylene group is phenylene (-C₆H₄-), and an exemplary heteroarylene group is pyridinylene (-C₅H₃N-).
 25

As used herein, the term alkylene glycol refers to a group comprising a moiety of formula -alkylene-O-. As used herein, the term polyalkylene glycol refers to a group having 2-50 (preferably 2-30, 2-20, 2-10 or 2-5) alkylene (preferably ethylene or propylene, preferably
 30 ethylene) glycol repeat units of the following formula -(alkylene-O-)_n-R[‡], wherein R[‡] is H or methyl, preferably methyl, and n is an integer representing the number of repeat units. The alkylene of each -(alkylene-O)- unit may be the same or different (preferably the same) and may, for example, be C₂₋₆, C₂₋₄ or C₂₋₃ alkylene. The polyalkylene glycol may be polyethylene glycol or polypropylene glycol. A polyethylene glycol has repeat units of
 35 the following formula -(CH₂-CH₂-O-)_n-R[‡]. A polypropylene glycol has repeat units of the following formula -(CH₂-CH₂-CH₂-O-)_n-R[‡]. A polyalkylene glycol substituent may be linked to another moiety via an oxygen linker (e.g., to form a structure of formula -O-

(alkylene-O-)_n-R[±]). This structure is encompassed within the term “polyalkylene glycol” as referenced herein.

As used herein, a crown ether is a cyclic oligomer of a C₁₋₆alkylene oxide having repeat unit –C₁₋₆alkylene-O– (preferably ethylene oxide having repeat unit –CH₂CH₂O–).

Preferably a crown ether comprises 4 to 6 repeat units. Exemplary crown ethers include 12-crown-4, 15-crown-5, 18-crown-6 ether.

Aromatic rings are cyclic aromatic groups that may have 0, 1, 2 or more, preferably 0, 1 or 2 ring heteroatoms. Aromatic rings may be optionally substituted and/or may be fused to one or more aromatic or non-aromatic rings (preferably aromatic), which may contain 0, 1, 2, or more ring heteroatoms, to form a polycyclic ring system.

Aromatic rings include both aryl and heteroaryl groups. Aryl and heteroaryl groups may be mononuclear, i.e. having only one aromatic ring (like for example phenyl or phenylene), or polynuclear, i.e. having two or more aromatic rings which may be fused (like for example naphthyl or naphthylene), individually covalently linked (like for example biphenyl), and/or a combination of both fused and individually linked aromatic rings. Preferably the aryl or heteroaryl group is an aromatic group which is substantially conjugated over substantially the whole group. Aryl groups may contain from 5 to 40 ring carbon atoms, from 5 to 25 carbon atoms, from 5 to 20 carbon atoms, or from 5 to 12 carbon atoms. Heteroaryl groups may be from 5 to 40 membered, from 5 to 25 membered, from 5 to 20 membered or from 5 to 12 membered rings, containing 1 or more ring heteroatoms selected from N, O, S and P. An aryl or heteroaryl may be fused to one or more aromatic or non-aromatic rings (preferably an aromatic ring) to form a polycyclic ring system.

Aryl and heteroaryl preferably denote a mono-, bi- or tricyclic aromatic or heteroaromatic group with up to 25 ring atoms that may also comprise condensed rings and is optionally substituted.

Preferred aryl groups include, without limitation, benzene, biphenylene, triphenylene, [1,1':3',1'']terphenyl-2'-ylene, naphthalene, anthracene, binaphthylene, phenanthrene, pyrene, dihydropyrene, chrysene, perylene, tetracene, pentacene, benzopyrene, fluorene, indene, indenofluorene, spirobifluorene, etc.

Preferred heteroaryl groups include, without limitation, 5-membered rings like pyrrole, pyrazole, silole, imidazole, 1,2,3-triazole, 1,2,4-triazole, tetrazole, furan, thiophene,

selenophene, oxazole, isoxazole, 1,2-thiazole, 1,3-thiazole, 1,2,3-oxadiazole, 1,2,4-oxadiazole, 1,2,5-oxadiazole, 1,3,4-oxadiazole, 1,2,3-thiadiazole, 1,2,4-thiadiazole, 1,2,5-thiadiazole, 1,3,4-thiadiazole, 6-membered rings like pyridine, pyridazine, pyrimidine, pyrazine, 1,3,5-triazine, 1,2,4-triazine, 1,2,3-triazine, 1,2,4,5-tetrazine, 1,2,3,4-tetrazine, 1,2,3,5-tetrazine, and fused systems like carbazole, indole, isoindole, indolizine, indazole, benzimidazole, benzotriazole, purine, naphthimidazole, phenanthrimidazole, pyridimidazole, pyrazinimidazole, quinoxalinimidazole, benzoxazole, naphthoxazole, anthroxazole, phenanthroxazole, isoxazole, benzothiazole, benzofuran, isobenzofuran, dibenzofuran, quinoline, isoquinoline, pteridine, benzo-5,6-quinoline, benzo-6,7-quinoline, benzo-7,8-quinoline, benzoisoquinoline, acridine, phenothiazine, phenoxazine, benzopyridazine, benzopyrimidine, quinoxaline, phenazine, naphthyridine, azacarbazole, benzocarboline, phenanthridine, phenanthroline, thieno[2,3b]thiophene, thieno[3,2b]thiophene, dithienothiophene, dithienopyridine, isobenzothiophene, dibenzothiophene, benzothiadiazothiophene, 2,5-dihydropyrrolo[3,4-c]pyrrol-1,4-dione (diketopyrrolopyrrole, DPP), 2-oxo-1H-indol-3-ylidene, [3,3'-bipyrrolo[2,3-b]pyridinylidene]-2,2'(1H,1'H)-dione (pyridine isoindigo) and (3E)-3-(2-oxo-1H-indol-3-ylidene)-1H-indol-2-one (isoindigo), or combinations thereof. The heteroaryl groups may be substituted with alkyl, alkoxy, thioalkyl, fluoro, fluoroalkyl or further aryl or heteroaryl substituents. Preferably a heteroaryl group is thiophene.

20

As used herein, the term "fused" refers to a cyclic group, for example an aryl or heteroaryl group, in which two adjacent ring atoms, together with additional atoms, form a fused ring to give a polycyclic (for example, a bicyclic or tricyclic) ring system.

25 The term "cycloalkyl" as used herein refer to a saturated cyclic aliphatic monocyclic or polycyclic (including fused, bridging and spiro-fused) ring system which has from 3 to 20 carbon atoms. Preferably, an cycloalkyl group has from 3 to 15, more preferably from 3 to 12, even more preferably from 3 to 10, even more preferably from 3 to 8 carbon atoms, even more preferably from 3 to 6 carbons atoms. The term "cycloalkyl" also includes

30 aliphatic rings that are fused to one or more aromatic or non-aromatic rings, such as tetrahydronaphthyl rings, where the point of attachment is on the cycloalkyl ring. A cycloalkyl group may be polycyclic, e.g. bicyclic or tricyclic. Specifically, examples of cycloalkyls include cyclopropane, cyclobutane, cyclopentane, cyclohexane, bicycle[2,2,1]heptane, spiro[4.5]decane, cycloheptane, adamantane and cyclooctane.

35

A heterocycloalkyl is a cycloalkyl group as described above, which additionally contains one or more heteroatoms. Heterocycloalkyl groups preferably contain from 2 to 21 atoms,

preferably from 2 to 16 atoms, more preferably from 2 to 13 atoms, more preferably from 2 to 11 atoms, more preferably from 2 to 9 atoms, even more preferably from 2 to 7 atoms, wherein at least one atom is a carbon atom. Particularly preferred heteroatoms are selected from O, S, N, P and Si. When heterocycloalkyl groups have two or more
5 heteroatoms, the heteroatoms may be the same or different. Heterocycloalkyl groups may be substituted or unsubstituted, branched or unbranched.

A haloalkyl group is an alkyl group substituted with at least one halogen atom. The term "haloalkyl" encompasses fluorinated or chlorinated groups, including perfluorinated
10 compounds. Specifically, examples of "haloalkyl group" include fluoromethyl group, difluoromethyl group, trifluoromethyl group, fluoroethyl group, difluoroethyl group, trifluoroethyl group, chloromethyl group, bromomethyl group, iodomethyl group and the like.

15 A haloaryl group is an aryl group substituted with at least one halogen atom.

An alkoxy group is an alkyl group that is bonded via an oxy group. Specifically, examples of "alkoxy group" include methoxy group, ethoxy group, n-propoxy group, iso-propoxy group, n-butoxy group, iso-butoxy group, sec-butoxy group, tert-butoxy group, n-pentyloxy
20 group, iso-pentyloxy group, sec-pentyloxy group, n-hexyloxy group, iso-hexyloxy group, n-hexyloxy group, n-heptyloxy group, n-octyloxy group, n-nonyloxy group, n-decyloxy group, n-undecyloxy group, n-dodecyloxy group, n-tridecyloxy group, n-tetradecyloxy group, n-pentadecyloxy group, n-hexadecyloxy group, n-heptadecyloxy group, n-octadecyloxy group, n-nonadecyloxy group, n-eicosyloxy group, 1,1-dimethylpropoxy group, 1,2-
25 dimethylpropoxy group, 2,2-dimethylpropoxy group, 2-methylbutoxy group, 1-ethyl-2-methylpropoxy group, 1,1,2-trimethylpropoxy group, 1,1-dimethylbutoxy group, 1,2-dimethylbutoxy group, 2,2-dimethylbutoxy group, 2,3-dimethylbutoxy group, 1,3-dimethylbutoxy group, 2-ethylbutoxy group, 2-methylpentyloxy group, 3-methylpentyloxy group and the like.

30

An alkylthio group is an alkyl group that is bonded via a thio (-S-) group.

As used herein, the term "optionally substituted" means that one or more of the hydrogen atoms in the optionally substituted moiety is replaced by a suitable substituent. Unless
35 otherwise indicated, an "optionally substituted" group may have a suitable substituent at each substitutable position of the group, and when more than one position in any given structure may be substituted with more than one substituent selected from a specified

group, the substituent may be either the same or different at every position. Combinations of substituents envisioned by this invention are preferably those that result in the formation of stable compounds. The term "stable", as used herein, refers to compounds that are chemically feasible and can exist for long enough at room temperature (i.e. 16-
5 25°C) to allow for their detection, isolation and/or use in chemical synthesis.

Any of the above groups (for example, those referred to herein as "optionally substituted", including alkyl, aryl and heteroaryl groups) may optionally comprise one or more substituents, preferably selected from silyl, sulfo, sulfonyl, formyl, amino, imino, nitrilo,
10 mercapto, cyano, nitro, halogen, -NCO, -NCS, -OCN, -SCN, -C(=O)NR⁰R⁰⁰, -C(=O)X⁰, -C(=O)R⁰, -NR⁰R⁰⁰, C₁₋₁₂alkyl, C₁₋₁₂alkenyl, C₁₋₁₂alkynyl, C₆₋₁₂aryl, C₃₋₁₂cycloalkyl, heterocycloalkyl having 4 to 12 ring atoms, heteroaryl having 5 to 12 ring atoms, C₁₋₁₂alkoxy, hydroxy, C₁₋₁₂alkylcarbonyl, C₁₋₁₂alkoxy-carbonyl, C₁₋₁₂alkylcarbonyloxy or C₁₋₁₂alkoxycarbonyloxy wherein one or more H atoms are optionally replaced by F or Cl and/or
15 combinations thereof; wherein X⁰ is halogen and R⁰ and R⁰⁰ are, independently, H or optionally substituted C₁₋₁₂alkyl. The optional substituents may comprise all chemically possible combinations in the same group and/or a plurality of the aforementioned groups (for example amino and sulfonyl if directly attached to each other represent a sulfamoyl radical).

20

Throughout the description and claims of this specification, the words "comprise" and "contain" and variations of the words, for example "comprising" and "comprises", mean "including but not limited to", and are not intended to (and do not) exclude other components. In any of the embodiment described herein, reference to "comprising" also
25 encompasses "consisting essentially of".

It will be appreciated that variations to the foregoing embodiments of the invention can be made while still falling within the scope of the invention. Each feature disclosed in this specification, unless stated otherwise, may be replaced by alternative features serving the
30 same, equivalent or similar purpose. Thus, unless stated otherwise, each feature disclosed is one example only of a generic series of equivalent or similar features.

All of the features disclosed in this specification may be combined in any combination, except combinations where at least some of such features and/or steps are mutually
35 exclusive. In particular, the preferred features of the invention are applicable to all aspects of the invention and may be used in any combination. Likewise, features described in non-essential combinations may be used separately (not in combination).

It will be appreciated that many of the features described above, particularly of the preferred embodiments, are inventive in their own right and not just as part of an embodiment of the present invention. Independent protection may be sought for these features in addition to or alternative to any invention presently claimed.

EXAMPLES

Column chromatography with silica gel from VWR Scientific was used for flash chromatography. Microwave experiments were carried out in a Biotage Initiator V 2.3. ¹H and ¹³C NMR spectra were recorded on a Bruker AV-400 spectrometer at 298 K and are reported in ppm relative to TMS. UV-Vis absorption spectra were recorded on UV-1601 (λ_{max} 1100 nm) UV-VIS Shimadzu spectrometers. The IR spectra were recorded on a PerkinElmer Spectrum 100 FT-IR spectrometer with an ATR sampling unit. MALDI TOF spectrometry was carried out in positive reflection mode on a Micromass MALDI⁺TOF with trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]-malononitrile (DCTB) as the matrix.

Cyclic voltammograms for the values in Table 1 were recorded on an Autolab PGSTAT101 with a standard three-electrode setup with ITO coated glass slides, a Pt counter electrode and a Ag/AgCl reference electrode (calibrated against ferrocene (Fc/Fc⁺)). The measurements were either carried in an anhydrous, degassed 0.1 M tetrabutylammonium hexafluorophosphate TBAPF₆ acetonitrile solution or in a 0.1 M NaCl aqueous solution as the supporting electrolyte with a scan rate of 100 mV/s. The cyclic voltammetry measurements for the values in the accompanying figures were performed with an Ivium CompactStat potentiostat in a 0.1M NaCl aqueous solution.

Gel permeation chromatography (GPC) measurements were performed on an Agilent 1260 infinity system operating in DMF with 5 mM NH₄BF₄ with 2 PLgel 5 μ m mixed-C columns (300 $\times$ 7.5mm), a PLgel 5 mm guard column (50 $\times$ 7.5mm) at 50 °C with a refractive index detector as well as a variable wavelength detector. The instrument was calibrated with linear narrow poly(methyl methacrylate) standards in the range of 0.6 to 47kDa.

Dialysis was carried out in a dialysis kit Thermo Scientific Slide-A-Lyzer Cassette with a molecular weight cut off of 2K. The deionised water was replaced every 6 h.

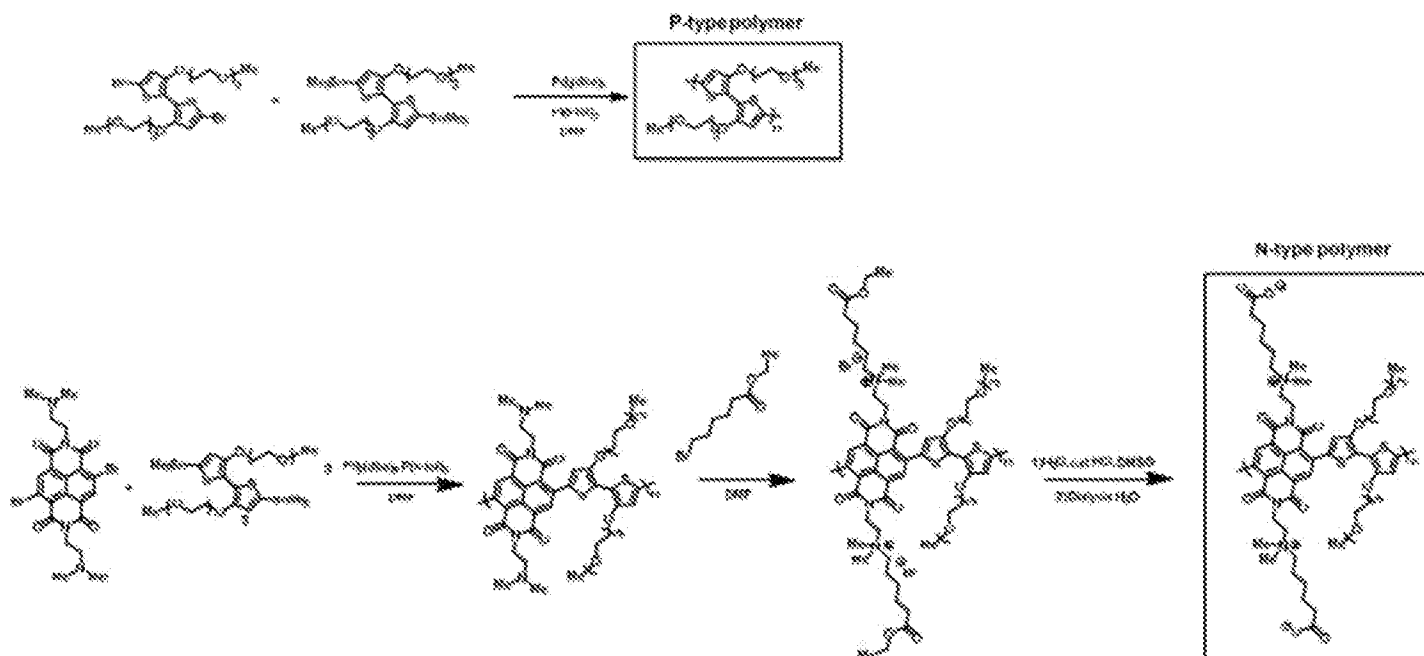
End-capping procedure: After the reaction was cooled to room temperature, 0.1 mL of a solution made of 1.00 mg of Pd₂(dba)₃ and 0.1 mL of 2-(Tributylstannyl)thiophene in 0.5

mL of anhydrous degassed DMF was added and heated for 1 h to 100 °C, then 0.1 mL of a solution made of 1.00 mg of Pd₂(dba)₃ and 0.1 mL of 2-bromothiophene in 0.5 mL of anhydrous degassed DMF was added and heated to 100 °C.

5 Example 1: Synthesis of polymers

- As previously reported, the attachment of polar side chains on n-type polymers enables reversible ion penetration which is important for highly reversible redox reactions in aqueous electrolytes (Giovannitti, A. *et al.*, Nat. Commun., 2016, 7, 13066). Based on this observation, we provided an n-type polymer p(g7NDI-gT2) with polyethylene glycol side chains attached to both the NDI M₁ and the bithiophene M₂ monomers of the polymer backbone. For a further n-type polymer, a zwitterion side chain was attached as the side chain of the NDI M₁ acceptor monomer to decrease the interaction of the side chain and allowing positive ions to penetrate into the film during electrochemical charging/discharging reactions. In addition, the advantage of a zwitterion side chain is that ions of opposite charge are included within the chemical structure of the same side chain. As a result, these ions are not able to migrate away from the active layer during operation which could affect the stability during charging of the polymers as well as avoiding the possible exchange of the mobile ions.
- A alkoxybithiophene M₂ monomer was provided with tri(ethylene glycol) side chains, which helps increase the solubility of the polymer in organic solvents and enables the use of solution processing techniques for the deposition of the materials.

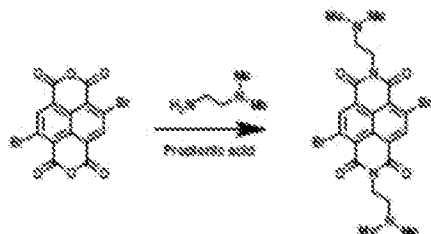
The syntheses of the p-type and n-type polymers are illustrated in Scheme 1.



Scheme 1: Synthesis of p(gT2) and p(ZI-NDI-gT2).

Monomer synthesis

(DMA)-NDI-Br₂



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A 150 ml two neck round bottom flask was dried and purged with argon. 2,6-dibromonaphthalene-1,4,5,8-tetracarboxylic dianhydride (512 mg, 1.20 mmol, 1.0 eq.) was suspended in propionic acid (20 ml) and N,N-dimethylethane-1,2-diamine (0.23 mg, 2.33 mmol) was added. The reaction mixture was heated to 120°C for 2 h. The reaction was monitored by NMR and after full conversion of the starting material, 100 mL of water and 100 mL of chloroform were added (product is water soluble). The aqueous layer was first washed with chloroform (2 x 100 mL). Then, 200 mL of chloroform was added and a 2 M NaHCO₃ solution was added until a pH value of 8 - 9 was reached. The organic layer was washed with water (3 x 100 mL) and dried over MgSO₄. The solvent was removed and the red solid was washed with methanol and acetone. Finally, the solid was washed with hot acetone and dried to obtain 250 mg (0.44 mmol) of an orange solid with a yield of 37 %.

¹H-NMR (400 MHz, trifluoroacetic acid -*d*₁) : 9.00 (s, 2H), 4.68 (t, 4H), 3.68 (t, 4H), 3.13 (s, 12H) ppm. ¹³C-NMR (100 MHz, trifluoroacetic acid -*d*₁) : 165.5, 142.5, 132.5, 130.2, 127.0, 126.6, 60.42, 46.3, 38.9 ppm. HRMS (ES-ToF): 565.0090 [M-H⁺] (calc. 565.0086).

5 *3,3'-bisalkoxy(TEG)-2,2'-bithiophene*

A 250 mL two neck RBF was dried and purged with argon. 3,3'-Dibromo-2,2'-bithiophene (6.48 g, 20 mmol), triethylene glycol monomethyl ether (11.5 g, 70 mmol), ^tBuOK (6.73 g, 60 mmol) and CuI (1.52 g, 8.0 mmol) were suspended in anhydrous tert-butanol (100 mL). The reaction mixture was degassed with argon for 15 min and heated to reflux with stirring for 16 h. After the reaction was finished, water was added and the aqueous layer was extracted with ethyl acetate (200 mL). The organic phase was washed with DI water (3 x 100 mL), dried over MgSO₄ and concentrated *in vacuo* to afford the crude product as a dark yellow oil. Purification by column chromatography on silica gel with a solvent mixture of ethyl acetate : hexane 3:1 with 1 % of triethylamine afforded the target molecule as a yellow waxy solid (3.2 g, 6.52 mmol, 33% yield). ¹H NMR (400 MHz, CDCl₃) δ: 7.08 (d, J = 5.6 Hz, 2H), 6.85 (d, J = 5.6 Hz, 2H), 4.25 (t, J = 4.9 Hz, 4H), 3.90 (t, J = 5.0 Hz, 4H), 3.78 – 3.75 (m, 4H), 3.69 – 3.66 (m, 4H), 3.66 – 3.64 (m, 4H), 3.55 – 3.53 (m, 4H), 3.37 (s, 6H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ: 151.9, 122.0, 116.7, 114.9, 72.1, 71.5, 71.1, 70.9, 70.7, 70.2, 59.2 ppm. HRMS (ES-ToF): 491.1774 [M-H⁺] (calc. C₂₂H₃₅O₈S₂ 491.1773).

5,5'-dibromo-3,3'-bis(TEG)-2,2'-bithiophene

A two neck RBF was dried under vacuum and purged with argon. 3,3'-bis(TEG)-2,2'-bithiophene (1.83 g, 2.24 mmol) was dissolved in anhydrous THF (200 mL), degassed with argon and cooled to - 20 °C. NBS (0.83 g, 4.66 mmol) was added in the dark and the reaction mixture was stirred for 10 min (reaction control indicated full conversion after 10 min). The reaction was quenched by the addition of 100 mL of 1 M NaHCO₃ aqueous solution, followed by the addition of 150 mL of ethyl acetate. The organic layer was washed with water (3 x 100 mL), dried over MgSO₄ and the solvent was removed under reduced pressure. Purification of the crude product was carried out by column chromatography on silica gel with a solvent mixture of hexane : ethyl acetate in the ration of 1 : 1 and 1 % of triethylamine. Finally, the product was recrystallised from diethyl ether/hexane to afford the product as a yellow solid with a yield of 60 %. (1.45 g, 2.24mmol). ¹H NMR (400 MHz, CDCl₃) δ: 6.85 (s, 2H), 4.21 – 4.18 (m, 4H), 3.88 – 3.85 (m, 4H), 3.75 – 3.73 (m, 4H), 3.70 – 3.68 (m, 4H), 3.68 – 3.65 (m, 4H), 3.57 – 3.54 (m, 4H), 3.38 (s, 6H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ: 150.3, 119.8, 116.0, 111.2, 72.1, 71.8, 71.1, 70.9,

70.8, 70.3, 59.2 ppm. HRMS (ES-ToF): 646.9964 [M-H⁺] (calc. C₂₂H₃₃Br₂O₈S₂ 646.9983).

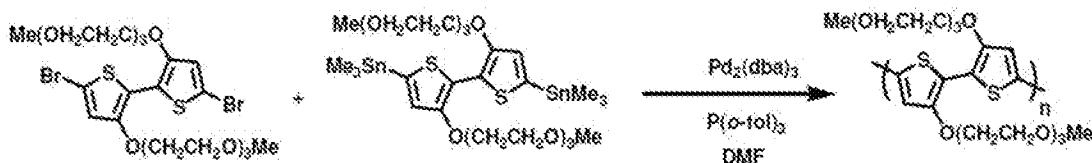
(3,3'-bis(TEG)-[2,2'-bithiophene]-5,5'-diyl)bis(trimethylstannane)

- 5 A 250 mL two neck RBF was dried and purged with argon. 1.01 g of 5,5'-dibromo-3,3'-bis(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-2,2'-bithiophene (1.56 mmol, 1.0 eq.) was dissolved in 150 mL of anhydrous THF. The reaction mixture was cooled to -78 °C and 2.5 mL of n-BuLi (2.5 M in hexane, 6.23 mmol, 4.0 eq.) was added slowly. A yellow solution was formed which was stirred at -78 °C for 3 h. Then, 7.8 mL of trimethyltin chloride (1 M
- 10 in hexane, 7.8 mmol, 5.0 eq.) was added and the reaction mixture was warmed to room temperature. 150 mL of diethyl ether was added and the organic phase was washed with water (3 x 100 mL) and dried over Na₂SO₄. The solvent was removed and the obtained solid was dissolved in 100 mL of acetonitrile which was then washed with hexane (3 x 100 mL). The solvent was removed and the product was recrystallised from diethyl ether to
- 15 obtain the product as yellow needles with a yield of 64 % (810 mg, 0.99 mmol).
¹H NMR (400 MHz, acetone-d₆) δ: 8.99 (s, 2H), 4.28 – 4.26 (m, 4H), 3.88 – 3.85 (m, 4H), 3.71 – 3.69 (m, 4H), 3.62 – 3.56 (m, 8H), 3.46 – 3.44 (m, 4H), 3.27 (s, 6H), 0.37 (s, 18 H) ppm. ¹³C NMR (100 MHz, acetone-d₆): 154.9, 134.9, 125.3, 121.1, 72.8, 72.4, 71.8, 71.3, 71.0, 59.0, 8.24 ppm. HRMS (ES-ToF): 819.1069 [M-H⁺] (calc. 819.1084).

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Polymer synthesis

Poly(TEG-alkoxybithiophene)

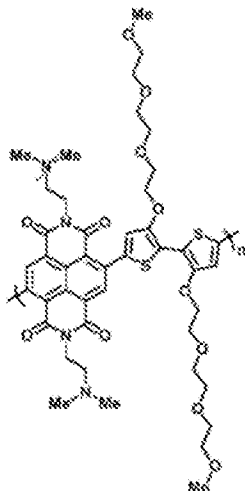


- In a dried 5.0 mL microwave vial, 79.4 mg of (3,3'-bis(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-[2,2'-bithiophene]-5,5'-diyl)bis(trimethylstannane) (97.3 μmol) and 63.1 mg of 5,5'-dibromo-3,3'-bis(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-2,2'-bithiophene (97.3 μmol) were dissolved in 3.0 mL of anhydrous, degassed DMF. Pd₂(dba)₃ (1.78 mg, 1.95 μmol) and P(o-tol)₃ (2.37 mg, 7.78 μmol) were added and the vial was sealed and heated to 100 °C for 16 h. After the polymerisation has finished,
- 30 the end-capping procedure was carried out. Then, the reaction mixture was cooled to room temperature and precipitated in methanol. A blue solid was formed which was filtered into a glass fibre-thimble and Soxhlet extraction was carried out with methanol, ethyl acetate, acetone, hexane, and chloroform. The polymer was dissolved in chloroform

and the solvent was removed. The polymer was dissolved in a minimum amount of chloroform and precipitated in methanol. The collect solid was filtered and dried under high vacuum. A blue solid was obtained with a yield of 74 % (70 mg, 71.6 μ mol).

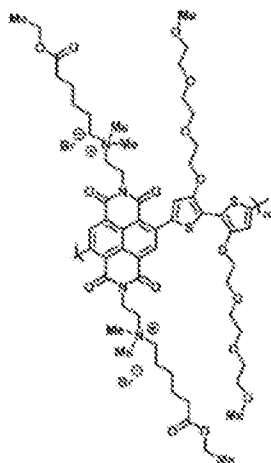
GPC (DMF, 50 °C) Mn = 56 kDa, Mw = 306 kDa. ^1H NMR (CDCl_3 , 400 MHz) δ : 6.96 (br s, 2 H), 4.35 (br s, 4 H), 4.01 – 3.92 (m, 4 H), 3.81 – 3.79 (m, 4 H), 3.72 – 3.70 (m, 4 H), 3.66 – 3.63 (m, 4 H), 3.53 – 3.50 (m, 4 H), 3.34 (s, 6 H) ppm.

p((DMA)-NDI-gT2)



- 10 In a 5.0 mL microwave vial, 38.76 mg of 4,9-dibromo-2,7-bis(2-(dimethylamino)-ethyl) benzo[*lmn*][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone (68.45 μ mol, 1.0 eq.), 55.86 mg of (3,3'-bis(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-[2,2'-bithiophene]-5,5'-diyl)-bis (trimethylstannane) (68.45 μ mol, 1.0 eq.), 1.4 mg of $\text{Pd}_2(\text{dba})_3$ (1.52 μ mol, 2 mol%) and 1.87 mg of $\text{P}(\text{o-tol})_3$ (6.12 μ mol, 8 mol%) were dissolved in 1.5 mL of anhydrous,
- 15 degassed DMF and the vial was heated to 85 °C for 16 h. The colour changed from yellow to green. After the polymerisation has finished, the end-capping procedure was carried out. Then, the reaction mixture was cooled to room temperature and the dark green reaction mixture was precipitated in ethyl acetate. The precipitate was filtered and Soxhlet extraction was carried out with ethyl acetate, methanol, acetone, hexane and chloroform.
- 20 The polymer was soluble in hot chloroform. Polymer *p*(2-(dimethylamino)ethyl-NDI-gT2) was obtained as a green solid with a yield of 79 % (48.4 mg, 54.1 μ mol). GPC (CHCl_3 , 50 °C) Mn = 5.3 kDa, Mw = 8.9 kDa. ^1H -NMR (400 MHz, CHCl_3) δ : 8.82 (br s, 2H), 7.26 (br s, 4H), 4.42 (br s, 4H), 4.35 (br s, 4H), 4.26 (br s, 4H), 3.91 – 3.83 (m, 4H), 3.83 – 3.75 (m, 4H), 3.75 – 3.64 (m, 4H), 3.64 – 3.54 (m, 4H), 3.54 – 3.45 (m, 4H), 3.39 – 3.28 (m, 6H), 2.69 – 2.58 (m, 4H), 2.40 – 2.22 (m, 12H) ppm.
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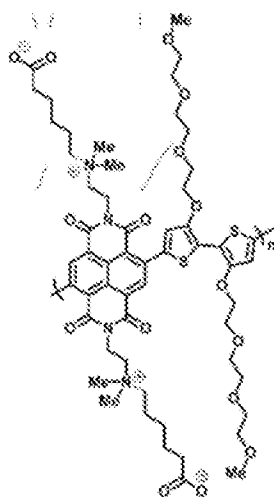
p((DMA-Br)-NDI-gT2)



A 5.0 mL microwave vial was dried and purged with argon, 14.3 mg p(2-(dimethylamino) ethyl-NDIgT2) (15.9 μ mol) was suspended in 4.00 ml anhydrous DMF and 0.5 ml Ethyl-6-bromohexanoate (2.8 mmol) was added. The reaction mixture was heated to 120°C for 5 1.5 h and a green solution was formed. The reaction mixture was cooled to room temperature and the solvent was removed under reduced pressure. The green solid was suspended in 3 mL of methanol and precipitated in acetone followed by the addition of hexane. The solution was filtered and the green solid was washed with chloroform and acetone. Finally, the polymer was dried under high vacuum for 16 h. 20.6 mg (15.4 10 μ mol) of the polymer was obtained as a green solid with a yield 97%.

GPC (DMF, 50 °C) Mn = 38 kDa, Mw = 60 kDa. $^1\text{H-NMR}$ (500 MHz, DMSO- d_6) δ : 8.64 – 8.57 (m, 2H), 7.81 – 7.48 (m, 4H), 4.49 – 4.24 (m, 8H, signals overlapping), 4.07 – 3.98 (m, 4H, COCH₂), 3.98 – 3.89 (m, 4H), 3.68 – 3.62 (m, 4H), 3.57 – 3.50 (m, 8H), 3.47 – 3.40 (m, 8H), 3.22 – 3.11 (m, 12H), 2.95 – 2.86 (m, 4H), 3.98 – 3.89 (m, 4H), 2.37 – 2.29 15 (m, 4H), 1.80 – 1.70 (m, 4H), 1.62 – 1.54 (m, 4H), 1.37 – 1.27 (m, 4H), 1.18 – 1.13 (m, 6H) ppm.

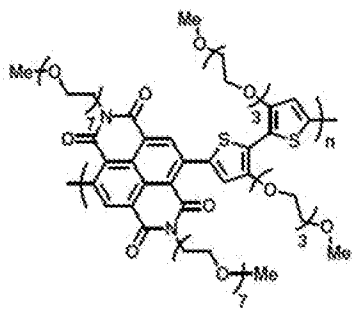
p(ZI-NDI-gT2)



In a 7.0 mL microwave, 10 mg p(2-(dimethylammonium-ethylhexanoate)ethyl-NDI-gT2) (8.46 μ mol, 1.00 eq.) was dissolved in 2 mL of DMSO and 2 mL of water. 0.1 mL of conc. HCl was added and the reaction mixture was heated to 75 °C for 16 h. Then, the reaction mixture was cooled to room temperature and the solution was transferred into a dialyses
 5 kit (molecular weight cut off 2kDa) and the system was stirred in DI water for 2 days, exchanging the water every 6 h. Finally, solvent was removed and the polymer was dried at 60 °C for 16 h. 9.2 mg (8.19 μ mol) of a green polymer was obtained with a yield of 97 %.

GPC (DMF, 50 °C) M_n = 24 kDa, M_w = 53 kDa. $^1\text{H-NMR}$ (500 MHz, DMSO- d_6) δ : 8.67 –
 10 8.55 (m, 2H), 7.73 – 7.45 (m, 4H), 4.48 – 4.30 (m, 8H, signals overlapping), 3.61 – 3.56 (m, 8H, signals overlapping), 3.55 – 3.52 (m, 4H), 3.46 – 3.40 (m, 8H), 3.40 – 3.24 (m, 4H, overlap with water peak), 3.23 – 3.12 (m, 12H), 2.30 – 2.21 (m, 4H), 1.81 – 1.70 (m, 4H), 1.62 – 1.54 (m, 4H), 1.37 – 1.28 (m, 4H) ppm.

15 Polymer p(g7NDI-gT2)



In a 7.0 mL microwave vial, 72.25 mg of g7NDI-Br2 (67.6 μ mol, 1.0 eq.) and 55.17 mg of 5,5'-bis(trimethylstannyl)-2,2'-bis(3,3'-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)) bithiophene (67.6 μ mol, 1.0 eq.) were dissolved in 2.0 mL of anhydrous, degassed chlorobenzene.
 20 1.36 mg of $\text{Pd}_2(\text{dba})_3$ (1.35 μ mol, 2 mol%) and 1.78 mg of $\text{P}(\text{o-tol})_3$ (5.4 μ mol, 8 mol%) were added and the vial was heated to 135 °C for 16 h. After the polymerisation has finished, the end-capping procedure at 135 °C was carried out. Then, the reaction mixture was cooled to room temperature and the dark green reaction mixture was precipitated in ethyl acetate followed by addition of hexane. Soxhlet extraction was carried out with
 25 hexane, ethyl acetate, MeOH, acetone, THF and chloroform. The polymer was soluble in hot chloroform. Polymer p(g7NDI-gT2) was obtained as a dark green solid with a yield of 76 % (48 mg, 0.05 mmol).

GPC (CHCl_3 :DMF; 5:1, 50 °C) M_n = 14 kDa, M_w = 26 kDa. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ :
 30 8.82 (s, 2H), 7.31 – 7.16 (m, 4H), 4.44 – 4.34 (m, 4H), 4.34 – 4.25 (m, 4H), 4.02 – 3.93 (m, 4H), 3.89 – 3.75 (m, 4H), 7.31 – 7.16 (m, 4H), 3.70 – 3.52 (m, 60H), 3.52 – 3.49 (m, 4H), 3.36 (br s, 12H).

Example 2: Electrochemical properties of polymers

The p(ZI-NDI-gT2) polymer can be solution processed by spin and drop casting or doctor blade coating and the resulting films are stable in aqueous solution after annealing at 150 °C for about 10 minutes. The (ionization potentials (IPs) and electron affinities (EAs) of the polymers were measured by cyclic voltammetry and are summarized in Table 1. We observe that the IPs are only slightly affected by choice of the side chain (4.8 eV- 5.0 eV for the n-type polymers), also consistent with PESA measurements. We note that the EAs of the n-type polymer increases after alkylation of the dimethylamine group from 3.8 eV to 4.0 eV.

Table 1. Summary of the polymers' properties

Polymer	IP ^[A] [eV]	IP ^[B] [eV]	EA ^[B] [eV]	Mn ^[D]	Mw ^[D]
p(gT2)	4.48	4.2	-	56 kDa	306 kDa
p((DMA)-NDI-gT2)	5.08	4.9	3.8	5.3 kDa ^[F]	8.9 kDa ^[F]
p((DMA-Br)-NDI-gT2)	5.13	4.9	4.0	38 kDa	60 kDa
p(ZI-NDI-gT2)	5.15	5.0	4.0	24 kDa	53 kDa
p(g7NDI-gT2)	4.95	4.8	4.1	14 kDa ^[E]	26 kDa ^[E]

^[A] Photoelectron spectroscopy in Air (PESA)

^[B] CV measurements in acetonitrile (0.1 M NBu₄PF₆, 100 mV/s)

^[C] Measurements were carried out in degassed 0.1 M NaCl aqueous solution vs Ag/AgCl.

^[D] GPC measurements were carried out in DMF with NBu₄BF₄.

^[E] GPC measurements were carried out in a solvent mixture chloroform:DMF 5:1.

^[F] GPC measurements were carried out in chloroform.

We investigated the simultaneous electrochemical and optical response of each of the p-type and n-type polymer in order to characterise their electrochemical charging behaviour. The materials were deposited on fluorine doped tin oxide (FTO) conducting glass substrates and used as working electrode of a three electrode electrochemical cell with 0.1 NaCl:DIW used as supporting electrolyte.

p-type polymer

Figure 1 shows cyclic voltammograms with corresponding simultaneous optical transmission spectra of a 40 nm thick p-type p(gT2) polymer film. Figure 1a displays the oxidation characteristics of the p(gT2) polymer for the first 4 cycles. The measurement shows a current profile with large area, which is desirable for efficient energy storage, with

two peaks at potentials of about -0.1V and 0.15V vs Ag/AgCl. These processes are attributed to charging of the film via injection of holes from the FTO substrate into the polymer and ionic charge compensation which occurs via exchange of ions from the electrolyte and the polymer film. The scans show high reversibility with coulombic efficiency, defined as the ratio between the extracted charge and the injected charge, close to 100% at a scan rate of 50 mV s⁻¹ and only a slight variation in peak position after the first cycle.

Figure 1b shows the optical spectral evolution related to the electrochemical charging of the p-type polymer. We observe complete quenching of the absorption feature in the visible (peak at about 645nm), which we attribute to the polymer neutral state absorption, and formation of a new species absorbing in the NIR. Further oxidation results in a drop of the absorption band in the NIR for $V > 0.2V$ vs Ag/AgCl suggesting that further conversion occurs. We ascribe this behavior to the formation of polarons, followed by formation of bipolarons. We calculated spectra of the trimer (gT2)₃ using TDDFT. The features that we obtain from theory support our interpretation of the charging behavior and formation of bipolarons in the electrode. Similar observation were also reported for the optical characterization of P3HT polymer films upon electrochemical charging.

Importantly, the spectral evolution suggests complete conversion of neutral polymers into the charged state, indicating that the full volume of the electrode undergoes charging. When scanning to more positive potential, a higher level of charging can be achieved, although this may compromise the coulombic efficiency of the electrode.

n-type polymer

Figure 2 shows the spectroelectrochemical measurements for the n-type polymers p(g7NDI-gT2) (glycol side chains) and p(ZI-NDI-gT2) (zwitterion side chain) where charging of the film occurs via reduction, i.e. injection of electrons from the FTO contact into the film. In this case counter ionic charge is also expected to be exchanged with the electrolyte.

For n-type polymers we find that removal of oxygen from the electrochemical cell is crucial in order to observe reversible charging of the material. For p(g7NDI-gT2), we observe a reversible reduction peak around -0.4V vs Ag/AgCl (see Figure 2a). When scanning the potential to more negative voltage, we observe a second peak. This peak is however not reversible and it is not present in any of the following scans suggesting irreversible

changes to the polymer film. Also the reversibility of the first peak is affected when scanning to more negative potentials than about -0.55V vs Ag/AgCl.

From the optical spectra displayed in Figure 2c, we can note similar behavior to the p-type polymer, where charging of the chains results in a decrease in the neutral state absorption band and the appearance of polaron and bipolaron bands. Figure 2b and d present spectroelectrochemical measurements performed on a p(ZI-NDI-gT2) polymer thin film. In this case the spectroelectrochemical data suggest reduction of the polymer chains resulting in the formation of an electron polaron at a potential of -0.4V and bipolaron between -0.4V and -0.75 vs Ag/AgCl. Both these processes are reversible over multiple cycles, implying the ability for the (zwitterion) p(ZI-NDI-gT2) polymer to reversibly exchange a potentially higher density of charge compared to the (glycolated) p(g7NDI-gT2) polymer, as shown by the greater area enclosed by the cyclic voltammetry scans on p(ZI-NDI-gT2). The calculated absorbance spectra (normalized) shown in Figure 2 e and f support our interpretation. The relative position of the absorption peaks calculated for the monomers in the neutral and charged states qualitatively match the experimental observation, confirming that bipolaron formation is possible on both polymers, although only the (zwitterion) p(ZI-NDI-gT2) enables reversible and complete conversion of polymer chains from neutral state to negative bipolarons.

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Specific capacity, stability and power density performance

Cyclic voltammetry measurements were performed to estimate the capacity and the stability of the p-type and n-type polymers for films of different thicknesses. The reversible charge measured from scans at 50 mV s⁻¹ showed a linear dependence on thickness showing achievable charge density values in the range of 25 to 36 mAh cm⁻³ for the p(gT2) and the p(ZI-NDI-gT2) polymer respectively up to ~200 nm thick films. Due to its reversibility limitations, the p(g7NDI-gT2) polymer showed only about 10 mAh cm⁻³ specific capacity. Continuous cycling at 50 mV s⁻¹ in water of the polymers showed that 75%, 80% and 70% of the initial (2nd scan) capacity is retained after 1000 cycles for the p(gT2) the p(g7NDI-gT2) and the pZI-NDI-gT2) polymers respectively. The p(g7NDI-gT2) polymer was scanned only up to voltages corresponding to the 1st reduction peak which shows good reversibility according to Figure 2a, while for the p(gT2) and the p(ZI-NDI-gT2) polymers a wider electrochemical potential range was considered in the measurement.

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We investigated the dynamic response of polymer electrodes using galvanostatic charging-discharging cycling, spectroelectrochemistry and impedance spectroscopy.

Figure 3 shows measurements of charge density injected in and extracted from thin films of p(gT2) and p(ZI-NDI-gT2) during galvanostatic measurements performed at different charging and discharging rates. The data show the ability of these polymer thin films deposited on FTO to exchange the maximum amount of charge that can be stored in their volume with an external circuit in timescales faster than seconds. The coulombic efficiency η_{coul} of p(gT2) is close to 1 for a wide range of C-rates and shows only a slight decrease at the slower rate tested here. p(ZI-NDI-gT2) shows similarly good charging and discharging rate performance.

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Spectrochronocoulometry and impedance measurements were performed for p(gT2) or p(ZI-NDI-gT2) to assess the timescale and the mechanism of charging and discharging. For the first type of measurement, a step potential was applied to the film and both the transient current and the transient optical absorption were measured on the millisecond to second timescale. Nearly mono-exponential changes as a function of time were observed for absorbance at wavelengths corresponding to the neutral and the charged state absorption window. Time constants in the order of 0.1s to 10s for films of about 15 to 200 nm thickness were extracted for both polymers. The impedance spectra of the polymer electrode at different potentials could be fitted using an equivalent circuit which did not include any transport resistance element. This result suggests that the rate capabilities measured for these materials in this work are limited mainly by the FTO series resistance (in the order of 50 Ω) and an interfacial charge transfer resistance.

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Example 3: Aqueous-based electrochemical energy storage device

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We used the p-type p(gT2) and n-type p(ZI-NDI-gT2) polymer films as the cathode and anode electrodes of a complete two-electrode electrochemical energy storage device. We deposited the two polymers on separate FTO glass slides and immersed them in the same electrochemical cell filled with 0.1M NaCl:DIW, used as electrolyte.

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Figure 4a and b show the spectroelectrochemical characterization of the polymer battery. The CV measurements do not show significant changes in shape over 4 consecutive cycles. The spectral analysis in Figure 4b also shows that charging of both polymers occurs to similar extent to what presented in the previous sections. Based on the optical characterization of the individual electrodes shown in Figure 1 and 2 we can conclude that the electrochemical charging of the two polymer films in the battery configuration results in the formation of bipolaron for both films. This is also consistent with the applied potential of 1.4 V which is the total potential range used for the characterization of the two polymers

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(p-type polymer is measured up to 0.5 V vs Ag/AgCl and n-type polymer is measured down to -0.9 V vs Ag/AgCl). Notably, the fraction of the total maximum stored charge that can be extracted at positive voltages is in the order of 80% to 94% (depending on rate of discharge) indicating that the device effectively implements the function of energy storage.

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Figure 4c shows galvanostatic stability measurements on the device, illustrating that about 60% of the battery specific capacity is maintained after about 1600 cycles (the capacity is normalized to the 1st discharging cycle). The measurement was performed using galvanostatic cycling at approximately 300 C-rate (inset showing the first and last cycles of the experiment). This is a promising result compared to other organic materials tested as battery electrodes. The degradation observed here is not solely related to decrease in capacity of the electrodes but also to charge retention issues. We found that scanning the cell to a negative potential of -1 V after continuous cycling results in significant recovery in capacity.

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Figure 5a shows that the dynamic properties of the battery reflect the high rate capabilities measured for the single electrodes, with measured specific capacity above 15 mAh cm⁻³ at up to >1000 C-rates. Note that the specific capacity mentioned here accounts for both electrodes' volume and it is therefore about half of the values referred to the individual polymers reported in the previous sections. Better sealing and removal of oxygen from the cell for the measurement shown in Figure 5a results in better coulombic efficiency than the one measured for the n-type polymer in a three-electrode cell. The fast charging/discharging capabilities are also confirmed by the relatively unchanged shape of CV scans run at up to 200 mV s⁻¹ (see Figure 5b) and the linear dependence of the peak current from scan rate up to 2000 mV s⁻¹. The shift in the peaks of the cyclic voltammograms at fast scan rate and the drop in capacity at fast C-rate (see inset in Figure 5a) are again consistent with the presence of a series resistance due to the two FTO layers in the order of 100Ω.

30 In conclusion, we have presented a strategy for material design that enables the fabrication of solution processable p-type and n-type polymers that can be employed as cathode and anode of aqueous-based electrochemical energy storage devices.

The use of polar side chains is identified as a successful solution to improve the ion penetration within the conjugated polymer films. We show that sacrificing volume density of redox sites to include a more favourable medium for ion transport within the battery

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electrode can be a 'good investment' to achieve fast rates of reversible charging/discharging of the polymer chains.

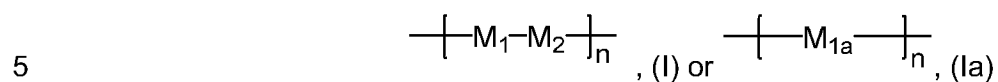
Specific capacity of the electrodes in the order of 30 mAh cm^{-3} and $<30\%$ drop in capacity over >1000 cycles were observed. We show that the process of charging and discharging occurs on the second timescale (C-rate > 1000) for both p(gT2) and p(ZI-NDI-gT2) polymers with thickness up to about 100 nm, expected to be limited by contact series resistance. These p-type and n-type polymers were coupled in a two terminal structure with a neutral NaCl aqueous supporting electrolyte to form a battery with $> 15 \text{ mAh g}^{-1}$ specific capacity, which was measured up to > 2000 C-rate.

The design of the polymers' backbone structure resulted in favorable energetics and ultimately in operational voltage of the battery up to 1.4V. This study shows that conjugated polymers with polar side chains can be used as electrodes of battery devices where these materials implement the transport of both the electronic and the ionic charges within their bulk as well as the redox behavior, enabling high levels of power density. These polymers are also solution processable, and therefore compatible with printing techniques and roll to roll high throughput fabrication. In addition, the use of sodium chloride and water at neutral pH values as electrolyte is a promising demonstration for a potentially inexpensive and safe electrochemical energy storage solution.

Embodiments of the invention have been described by way of example only. It will be appreciated that variations of the described embodiments may be made which are still within the scope of the invention.

CLAIMS

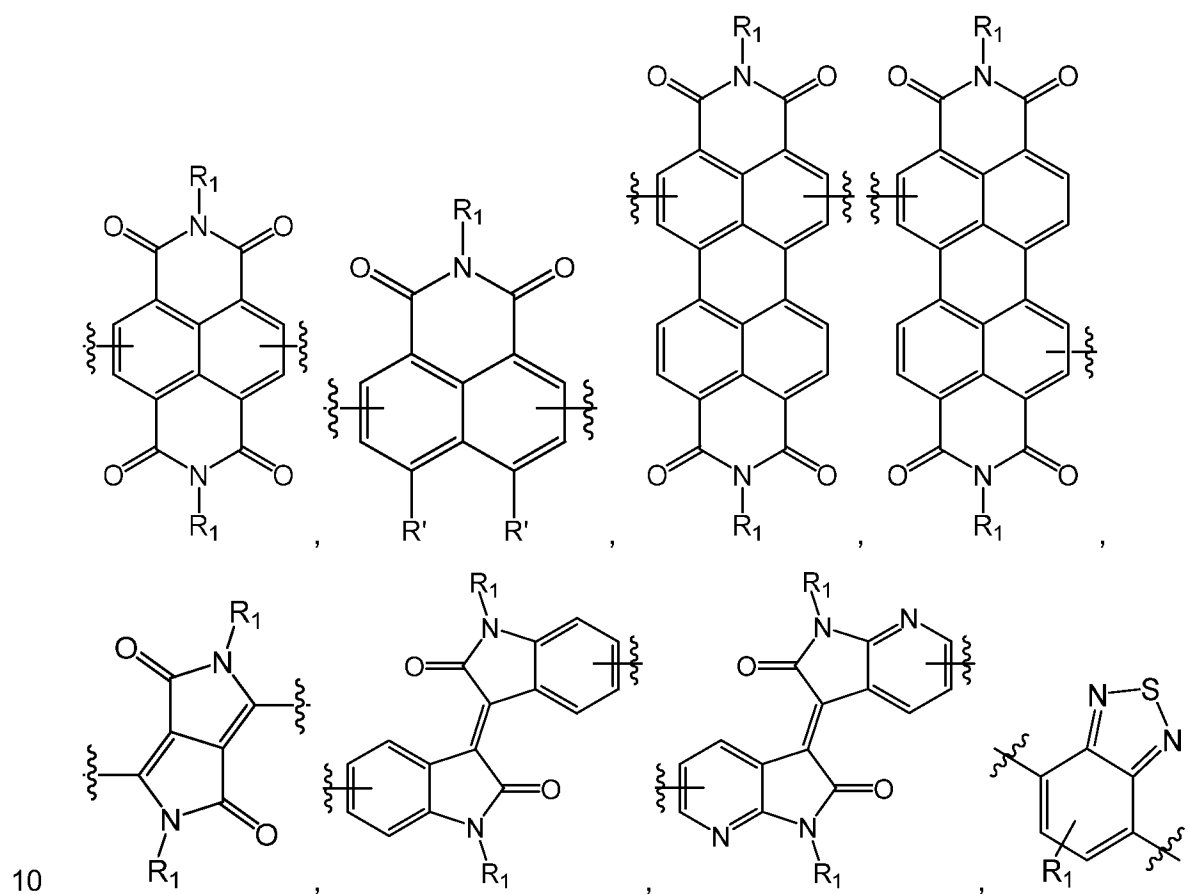
1. An electrochemical cell comprising:
a first electrode comprising a first polymer comprising the formula (I) or (Ia):

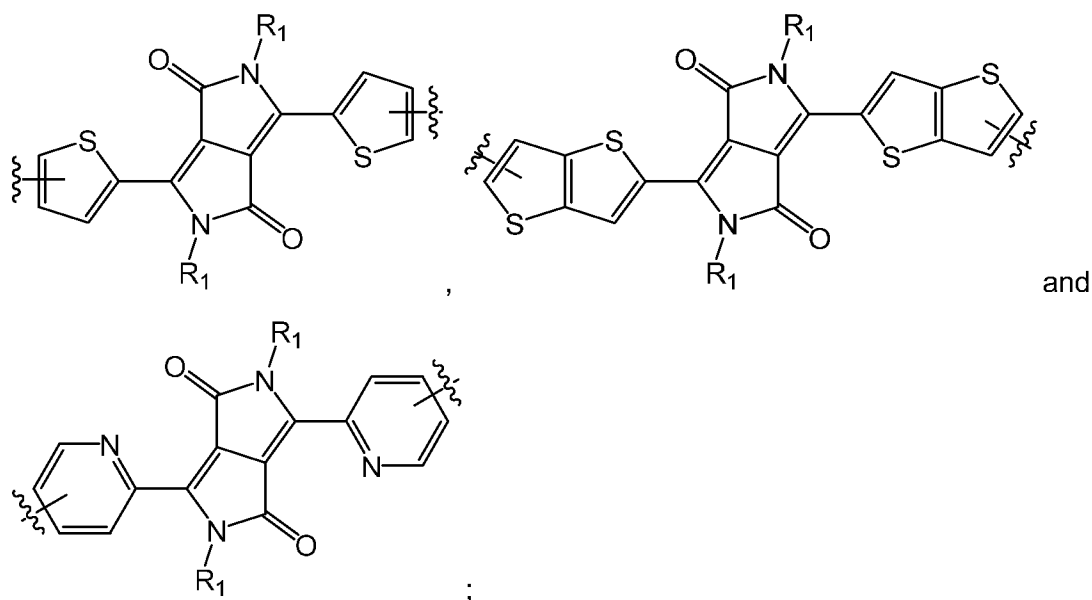


wherein:

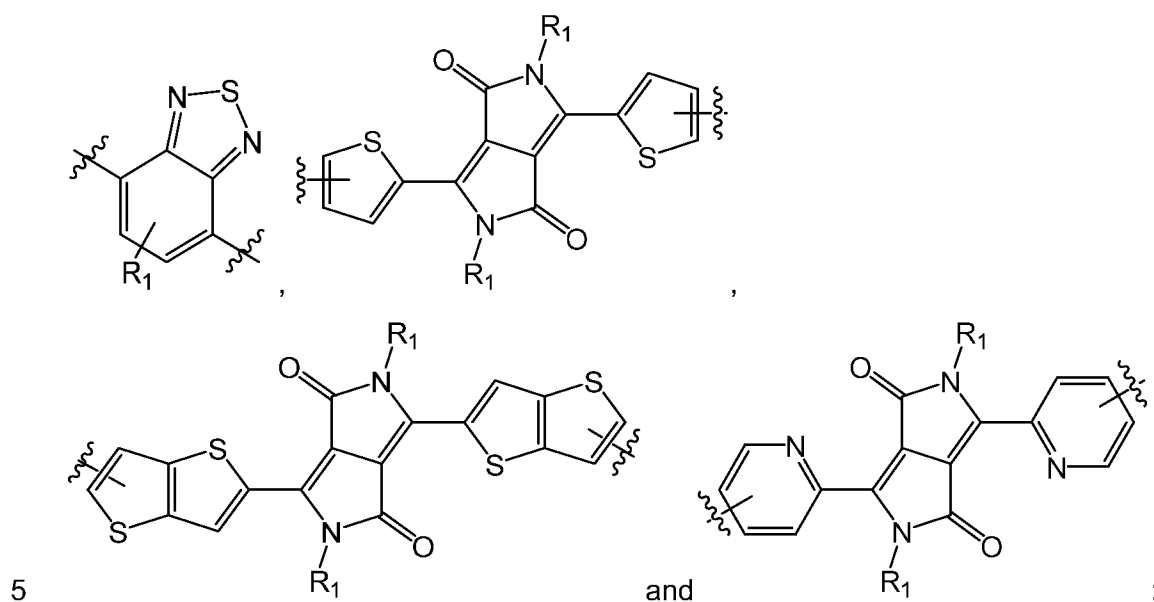
each M_1 is

independently selected from:





each M_{1a} is independently selected from:



wherein R_1 , at each occurrence, is independently a moiety comprising at least one -alkylene-O- unit or a moiety comprising at least two functional groups of which at least one has a positive and one has a negative electrical charge;

R' , at each occurrence, is independently selected from H, an electron-withdrawing group, a C_{1-40} alkyl group optionally substituted with 1-5 electron-withdrawing groups, a moiety comprising at least one -alkylene-O- unit or a moiety comprising at least two functional groups of which at least one has a positive and one has a negative electrical charge;

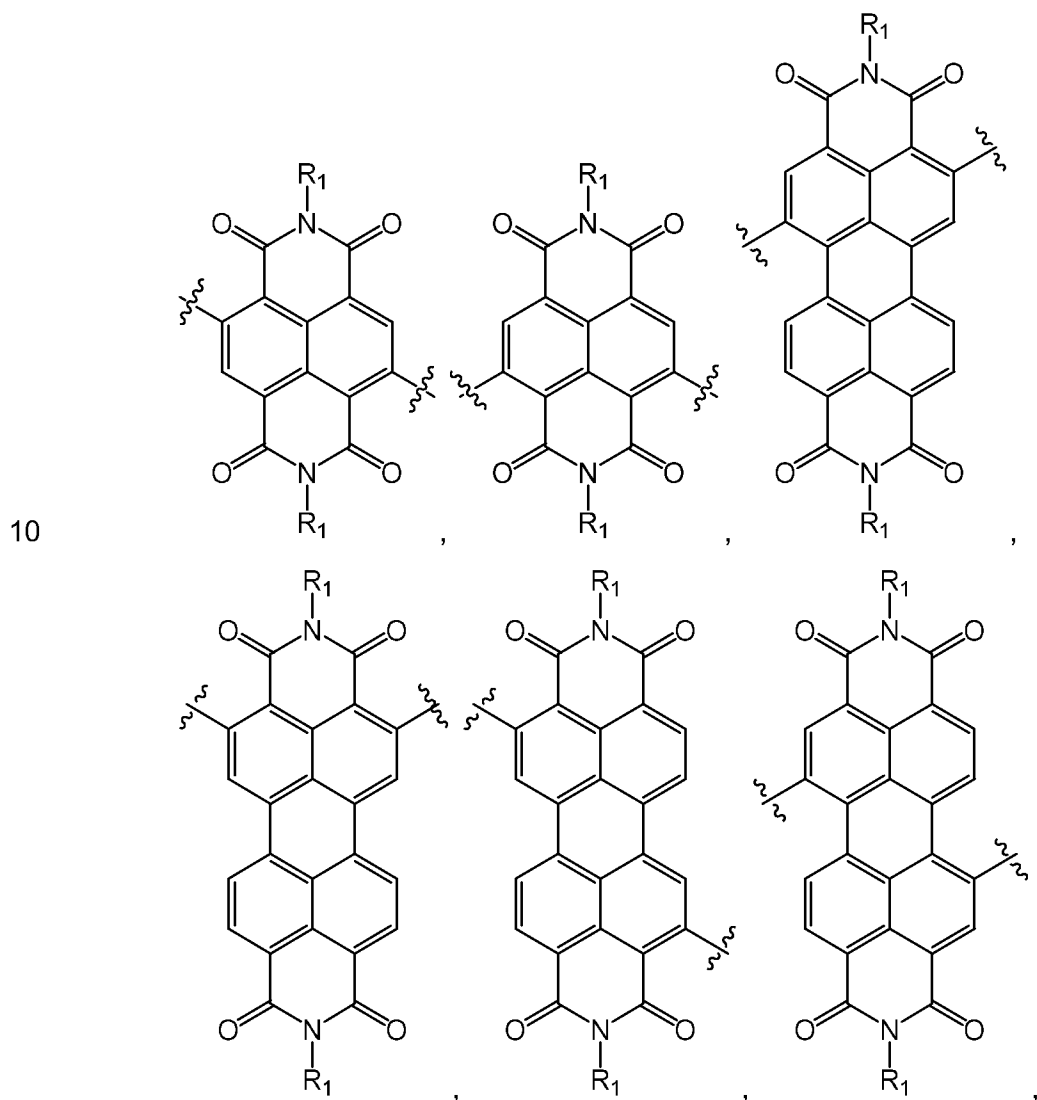
each M_2 is independently a repeat unit comprising one or more heteroaryl groups optionally substituted with one or more groups selected from a moiety comprising at least

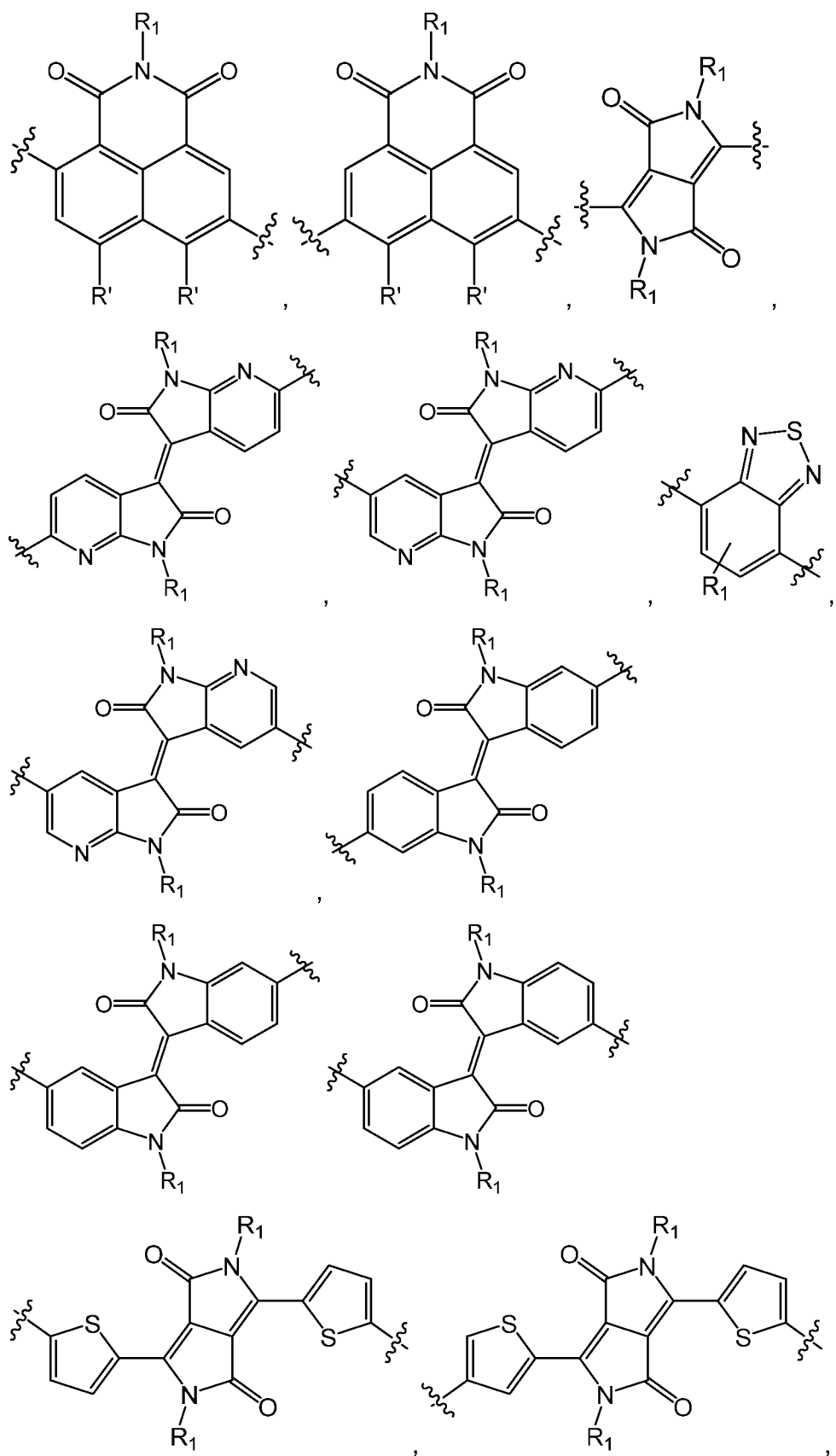
one -alkylene-O- unit and a moiety comprising at least two functional groups of which at least one has a positive and one has a negative electrical charge; and

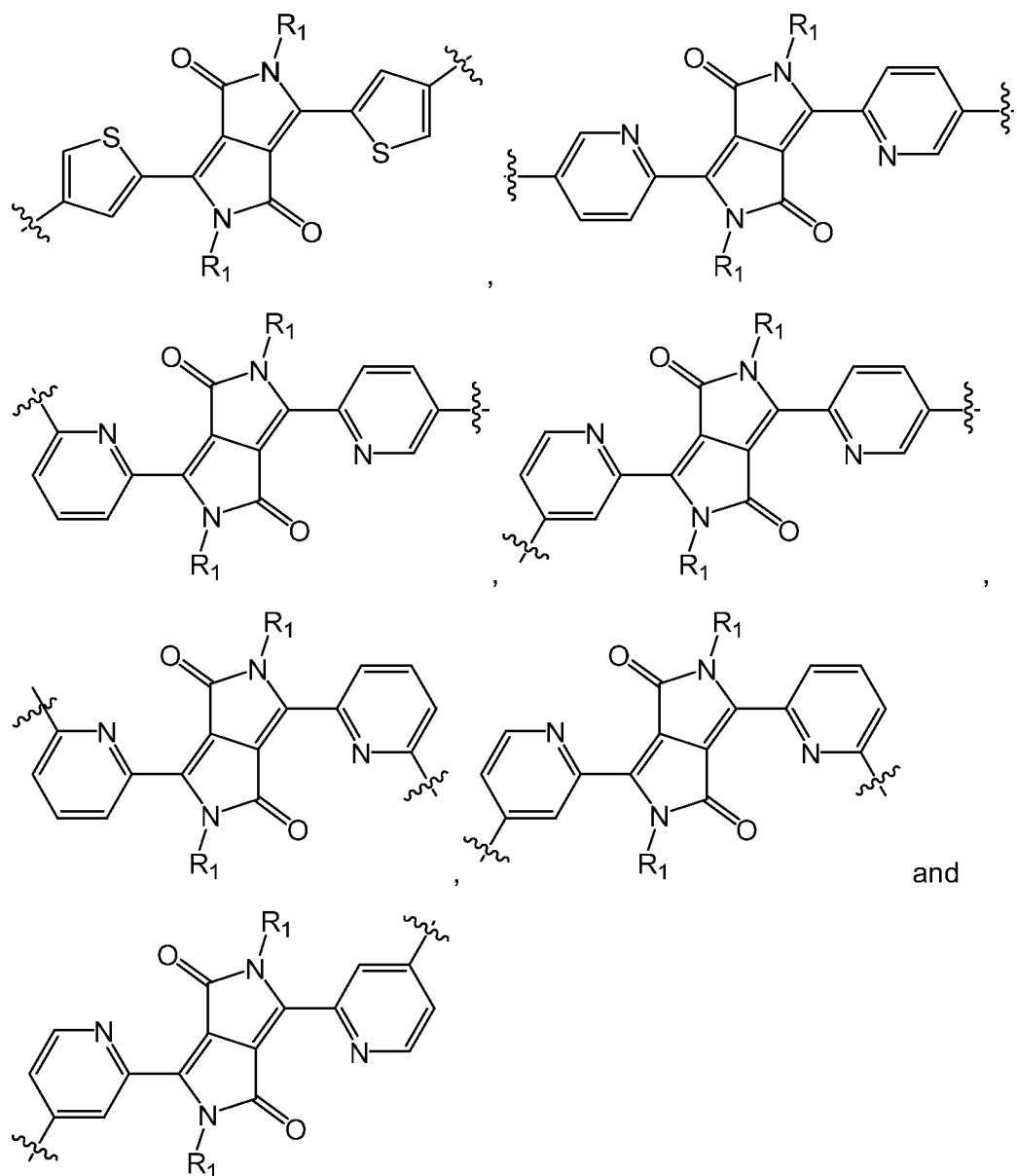
n is an integer of at least 2, optionally between 2 and 5,000; and

a second electrode comprising a second polymer comprising one or more repeat units comprising one or more heteroaryl groups substituted with one or more moieties comprising at least one -alkylene-O- unit.

2. The electrochemical cell of claim 1, wherein each M_1 is independently selected from:





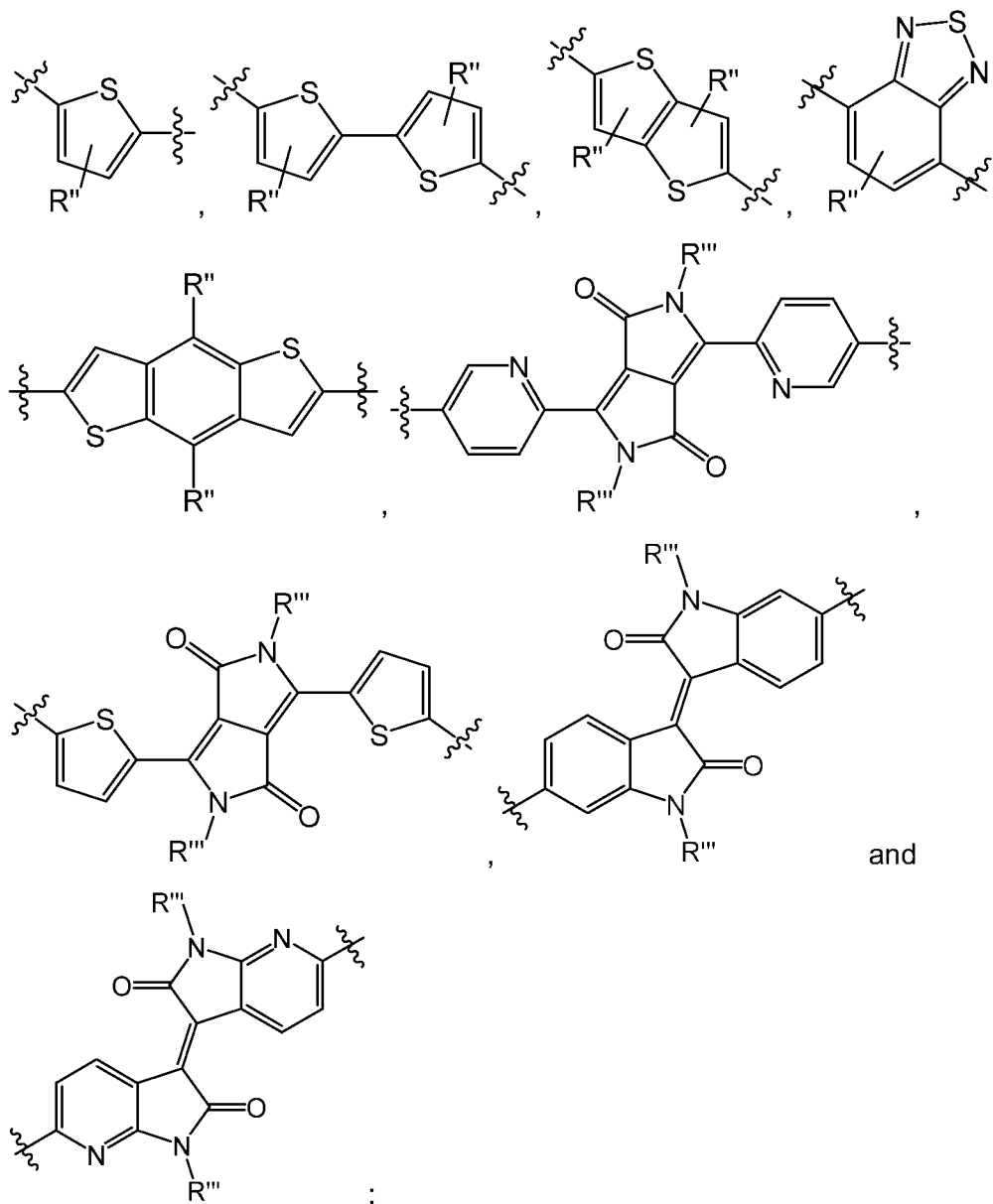


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3. The electrochemical cell of any preceding claim, wherein each M_2 is independently a repeat unit comprising one or more heteroaryl groups wherein the heteroaryl group is selected from thiophene, 2,5-dihydropyrrolo[3,4-c]pyrrol-1,4-dione (diketopyrrolopyrrole, DPP) and (3E)-3-(2-oxo-1H-indol-3-ylidene)-1H-indol-2-(isoindigo), and [3,3'-bipyrrolo[2,3-b]pyridinylidene]-2,2'(1H,1'H)-dione (pyridine isoindigo), preferably thiophene, bithiophene, 3,6-alkoxy- thieno[3,2-b]thiophene, thieno[3,2-b]thiophene, 3,3'-alkoxybithiophene, 2,5-dihydropyrrolo[3,4-c]pyrrol-1,4-dione (diketopyrrolopyrrole, DPP), (3E)-3-(2-oxo-1H-indol-3-ylidene)-1H-indol-2-one (isoindigo) and [3,3'-bipyrrolo[2,3-b]pyridinylidene]-2,2'(1H,1'H)-dione (pyridine isoindigo).

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4. The electrochemical cell of any preceding claim, wherein each M_2 is independently selected from:



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and

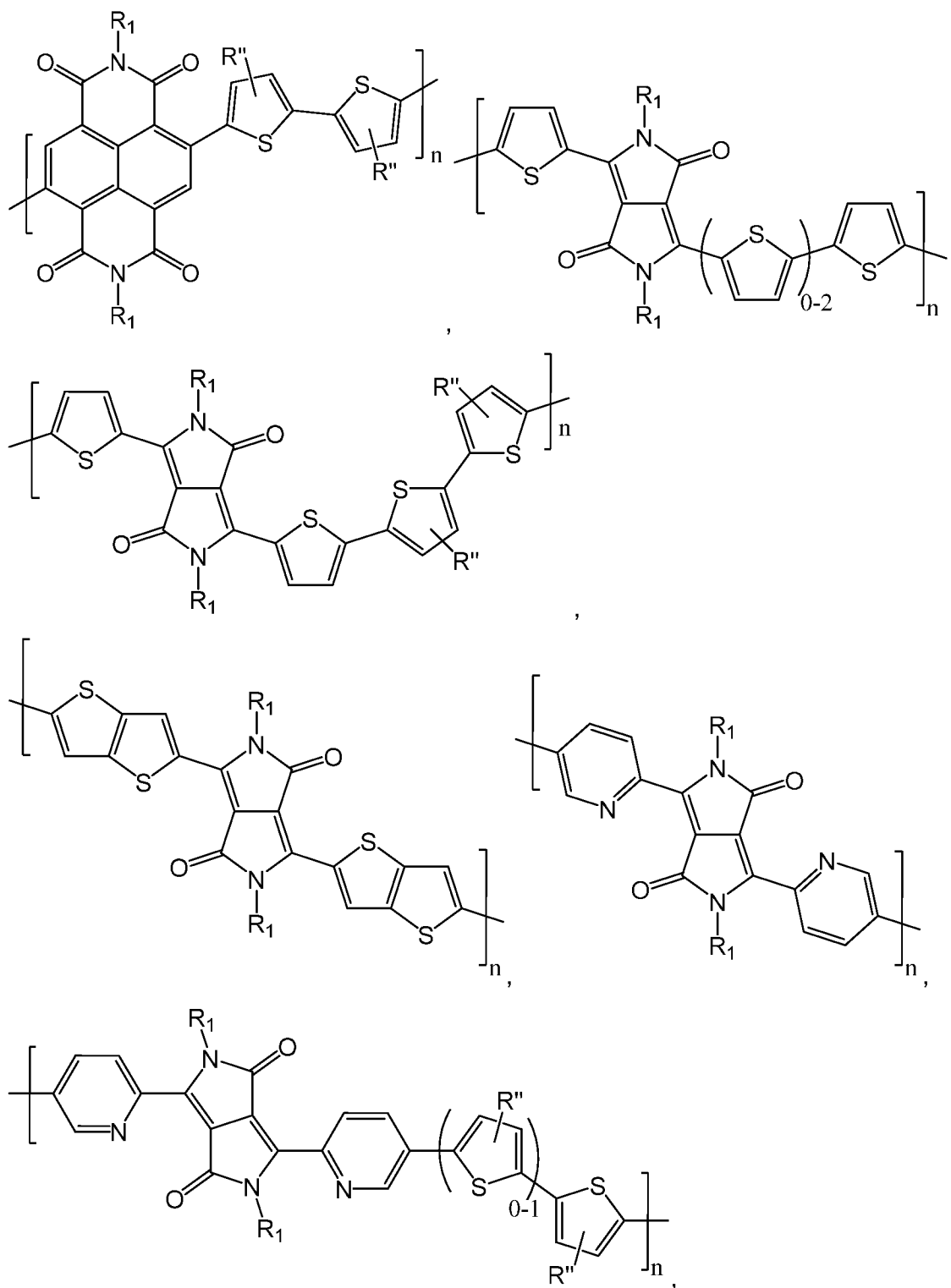
wherein:

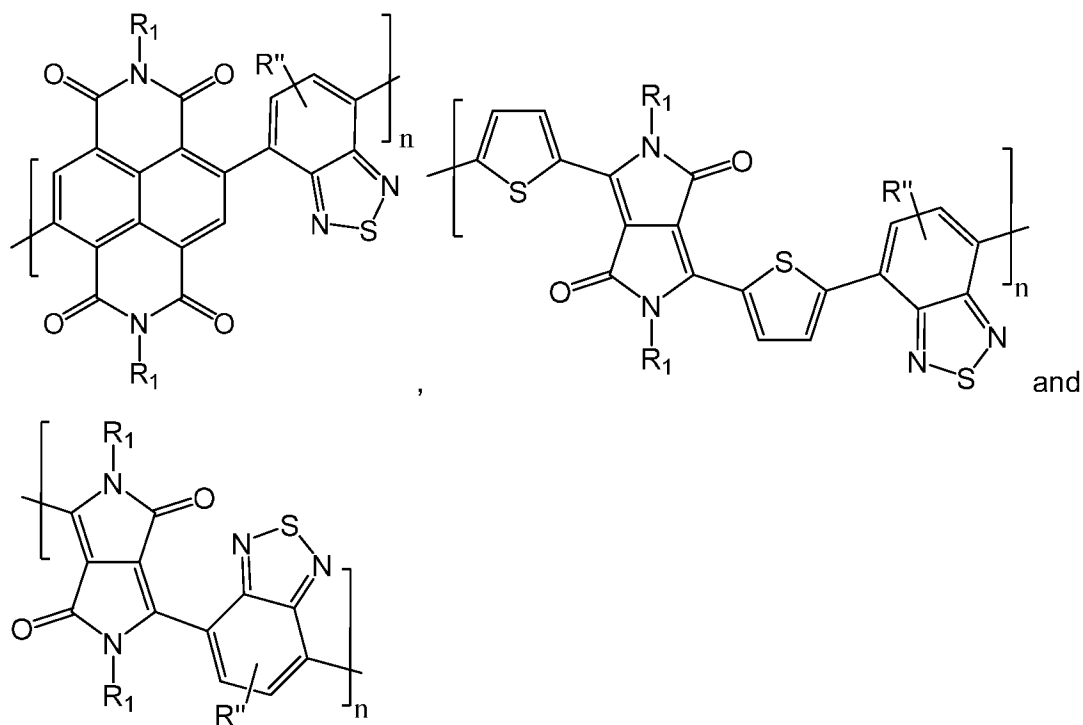
R'' , at each occurrence, is independently selected from H, $-O-C_{1-6}$ alkyl, $-COOH$, $-C(O)O-C_{1-6}$ alkyl, a (poly)alkylene glycol chain having 1-30 alkylene glycol units, a C_{3-6} alkyl group substituted with one or more (poly)alkylene glycol chains having 1-30 alkylene glycol units, C_{1-6} alkyl substituted with a crown ether or a moiety comprising at least two functional groups of which at least one has a positive and one has a negative electrical charge; and

R''' , at each occurrence, is independently selected from a (poly)alkylene glycol chain having 1-30 alkylene glycol units, a C_{3-6} alkyl group substituted with one or more (poly)alkylene glycol chains having 1-30 alkylene glycol units, and C_{1-6} alkyl substituted

with a crown ether or a moiety comprising at least two functional groups of which at least one has a positive and one has a negative electrical charge.

5. The electrochemical cell of any preceding claim, wherein the first polymer is
5 selected from:





6. The electrochemical cell of any preceding claim, wherein in each M₁ group each R₁ is the same.

7. The electrochemical cell of any preceding claim, wherein each R₁ is independently selected from:

- (i) a group of formula -A-[alkylene-O]_{n'}-X, wherein n' is 1-30; A is absent, an alkyl linker or O; and X is hydrogen, alkyl, -alkyl-SO₃H, -alkyl-COOH or haloalkyl; and
- (ii) a group of formula -W-X-Y-Z, wherein W and Y are each independently a linker moiety selected from alkylene, arylene, heteroarylene or a moiety comprising at least one -alkylene-O- unit (optionally a moiety of formula -[alkylene-O]_{n'}-, wherein n' is 1-30), or a combination thereof; one of X and Z is a positively charged moiety and the other is a negatively charged moiety, optionally wherein a positively charged moiety is a moiety comprising a cationic nitrogen group (e.g., quaternary ammonium, protonated amine, azomethine, amidine, guanidene or a cationic nitrogen containing heteroaryl, such as pyridinium or imidazolium), or a sulfonium or phosphonium cation, and a negatively charged moiety is a moiety comprising a phosphate, sulfonate, carboxylate, phosphonate, phosphinante, sulfate, alkoxydicyanobenzenolate, boronate, phenolate, sulfonamide or sulfonimide anion; and

(iii) a group of formula $-W'-X'(Z')-Y'$, wherein W' is a linker moiety selected from alkylene, arylene, heteroarylene or a moiety comprising at least one -alkylene-O- unit (optionally a moiety of formula $[-alkylene-O-]_{n'}$, wherein n' is 1-30), or a combination thereof; Y' is absent, H or a linker moiety selected from alkylene, 5 arylene, heteroarylene or a moiety comprising at least one -alkylene-O- unit (optionally a moiety of formula $[-alkylene-O-]_{n'}$, wherein n' is 1-30); X' is a positively charged moiety or a negatively charged moiety and Z' is a mobile counter ion, optionally wherein a positively charged moiety is a moiety comprising a cationic nitrogen group (e.g., quaternary ammonium, protonated amine, 10 azomethine, amidine, guanidene or a cationic nitrogen containing heteroaryl, such as pyridinium or imidazolium), or a sulfonium or phosphonium cation, and a negatively charged moiety is a moiety comprising a phosphate, sulfonate, carboxylate, phosphonate, phosphinante, sulfate, alkoxydicyanobenzenolate, boronate, phenolate, sulfonamide or sulfonimide anion.

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8. The electrochemical cell of any preceding claim, wherein each R_1 is independently selected from:

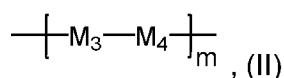
- (i) a group of formula $-A-[-ethylene-O-]_{n'}-X$, wherein n' is 1-30; A is absent or O; and X is methyl, $-alkyl-SO_3H$, $-alkyl-COOH$ or haloalkyl;
- 20 (ii) a group of formula $-W-X-Y-Z$, wherein W and Y are each independently a linker moiety selected from C_{1-30} alkylene, phenylene, pyridylene or a moiety of formula $[-ethylene-O-]_{n'}$, wherein n' is 1-30, or a combination thereof; X is a positively charged moiety selected from quaternized ammonium, protonated amine, pyridinium and imidazolium, and Z is a negatively charged moiety selected 25 from a phosphate anion, a phosphonate anion, a sulfonate anion and a carboxylate anion; and
- (iii) a group of formula $-W'-X'(Z')-Y'$, wherein W' is a linker moiety selected from C_{1-30} alkylene, phenylene, pyridylene or a moiety of formula $[-ethylene-O-]_{n'}$, wherein n' is 1-30, or a combination thereof; Y' is absent, H or a linker moiety 30 selected from C_{1-30} alkylene, phenylene, pyridylene or a moiety of formula $[-ethylene-O-]_{n'}$, wherein n' is 1-30), or a combination thereof; X' is a positively charged moiety or a negatively charged moiety, wherein a positively charged moiety is a moiety selected from quaternized ammonium, protonated amine, pyridinium and imidazolium, and a negatively charged moiety is a moiety selected 35 from a phosphonate anion, a phosphate anion, a sulfonate anion and a carboxylate anion; and Z' is a mobile counter ion selected from H^+ , M^+ or a halide anion, wherein M^+ is a metal cation (optionally an alkali metal cation).

9. The electrochemical cell of any preceding claim, wherein R', at each occurrence, is independently selected from H, a halogen, -CN, C₁₋₁₀haloalkyl, a moiety comprising at least one -alkylene-O unit and a moiety comprising at least two functional groups of which
 5 at least one has a positive and one has a negative electrical charge.

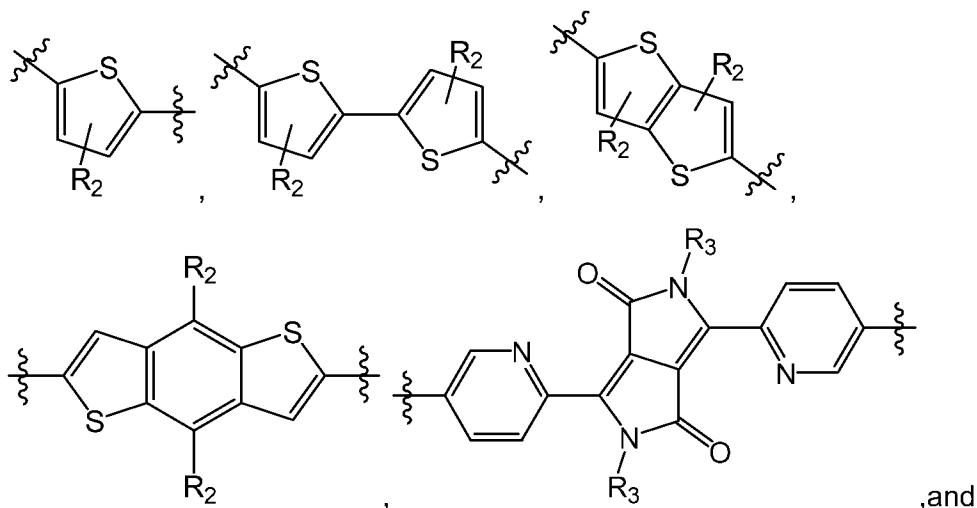
10. The electrochemical cell of any preceding claim, wherein:

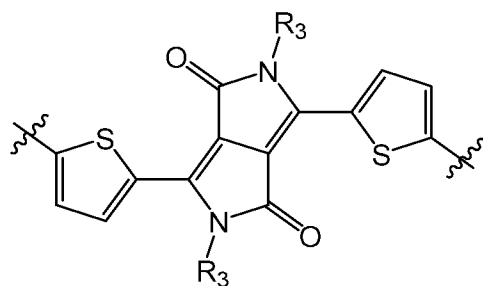
- a) each R'' is independently selected from H, a C₁₋₄₀alkoxy group, a (poly)alkylene glycol chain having 1-30 alkylene glycol units, and a C₃₋₆alkyl group substituted with one
 10 or more (poly)alkylene glycol chains having 1-30 alkylene glycol units; and/or
- b) each R''' is independently selected from a (poly)alkylene glycol chain having 1-30 alkylene glycol units, and a C₃₋₆alkyl group substituted with one or more (poly)alkylene glycol chains having 1-30 alkylene glycol units.

11. The electrochemical cell of any preceding claim, wherein the second polymer is a polymer comprising the formula (II):

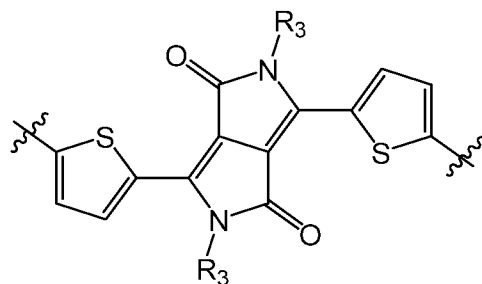
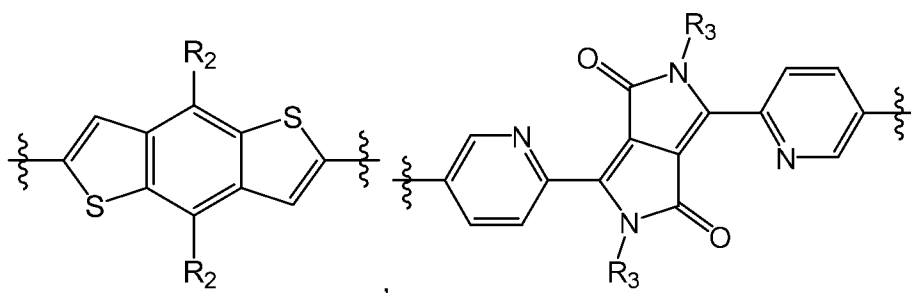
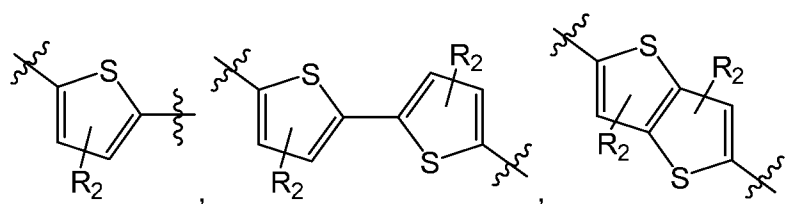


wherein, M₃ is a repeat unit comprising one or more heteroaryl groups, optionally substituted with one or more moieties comprising at least one -alkylene-O- units, and M₄ is
 20 absent or a repeat unit comprising one or more heteroaryl groups, optionally substituted with one or more moieties comprising at least one -alkylene-O- units, optionally wherein each M₃ group is independent selected from:





; and

each M₄ group is independently selected from:

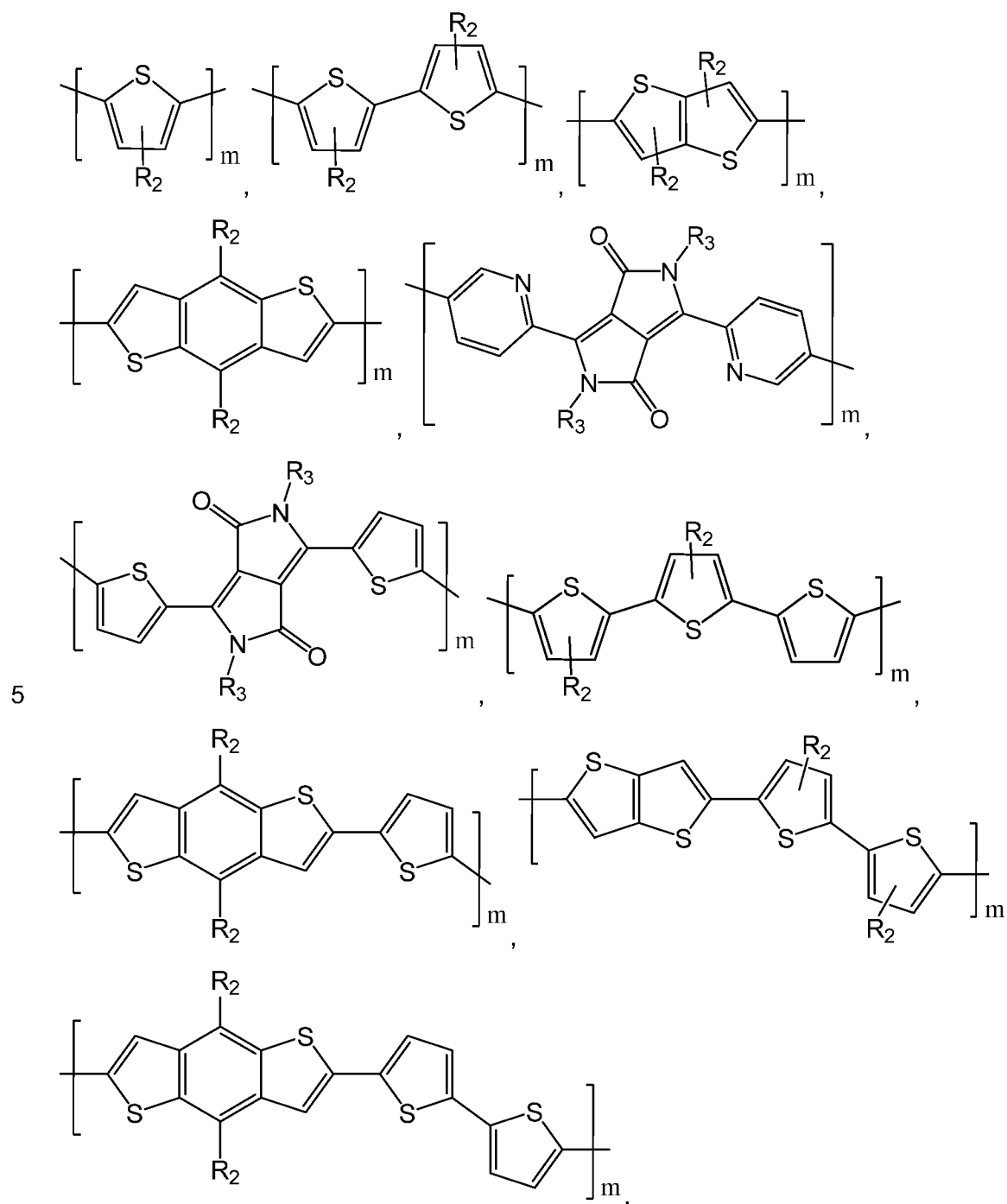
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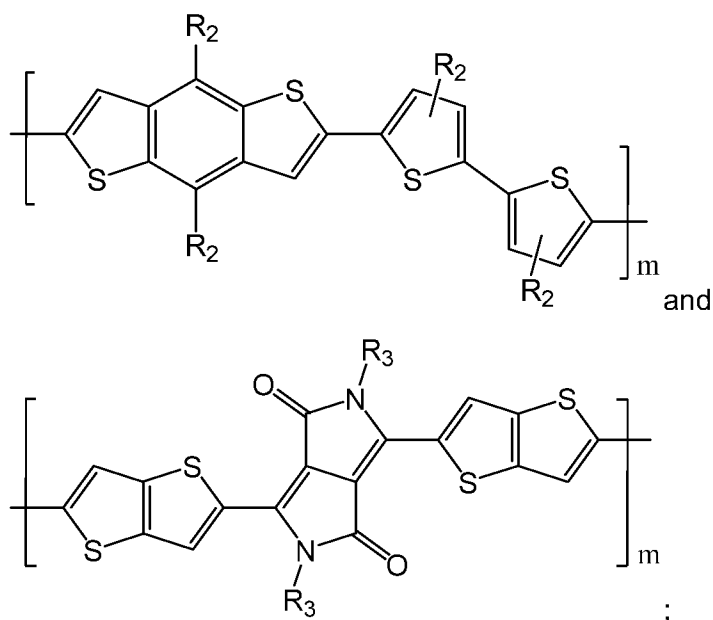
and absent;

wherein R₂ and R₃ are each independently a moiety comprising at least one -alkylene-O- unit.

12. The electrochemical cell of any preceding claim, wherein the second polymer
 10 comprises a repeat unit comprising one or more heteroaryl groups selected from
 thiophene, 2,5-dihydropyrrolo[3,4-c]pyrrol-1,4-dione (diketopyrrolopyrrole, DPP) and (3E)-
 3-(2-oxo-1H-indol-3-ylidene)-1H-indol-2-(isoindigo), and [3,3'-bipyrrolo[2,3-
 b]pyridinylidene]-2,2'(1H,1'H)-dione (pyridine isoindigo), preferably thiophene,
 bithiophene, thieno[3,2-b]thiophene, 3,6-alkoxy- thieno[3,2-b]thiophene, 3,3'-
 15 alkoxybithiophene 2,5-dihydropyrrolo[3,4-c]pyrrol-1,4-dione (diketopyrrolopyrrole, DPP),
 (3E)-3-(2-oxo-1H-indol-3-ylidene)-1H-indol-2-one (isoindigo) and [3,3'-bipyrrolo[2,3-
 b]pyridinylidene]-2,2'(1H,1'H)-dione (pyridine isoindigo).

13. The electrochemical cell of any preceding claim, wherein the second polymer is selected from:





wherein R_2 and R_3 are each independently a moiety comprising at least one -alkylene-O- unit; and

5 m is an integer of at least 2, optionally between 2 and 5,000.

14. The electrochemical cell of any one of claims 11-13, wherein:

each R_2 is independently a moiety comprising at least one -alkylene-O- unit linked via an O atom, optionally wherein each R_2 is independently a moiety of formula -O-[-alkylene-O-] m' -X, wherein m' is 1-30 and X is hydrogen, alkyl, -alkyl-SO₃H, -alkyl-COOH
10 or haloalkyl, optionally wherein alkylene is ethylene; and/or

each R_3 is independently a moiety comprising at least one -alkylene-O- unit linked via a C atom, optionally wherein each R_3 is independently a moiety of formula -[-alkylene-O-] m'' -X, wherein m'' is 1-30 and X is alkyl, -alkyl-SO₃H, -alkyl-COOH or haloalkyl,
15 optionally wherein alkylene is ethylene, optionally alkylene is ethylene.

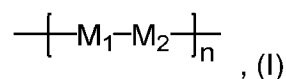
15. The electrochemical cell of any preceding claim, wherein the first and/or second polymer has a number average molecular weight of about 1 to about 500 kD, optionally about 5 to about 50 kD.

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16. The electrochemical cell of any preceding claim, wherein the first electrode comprises a substrate with the first polymer deposited thereon, and/or the second electrode comprises a substrate with the second polymer deposited thereon.

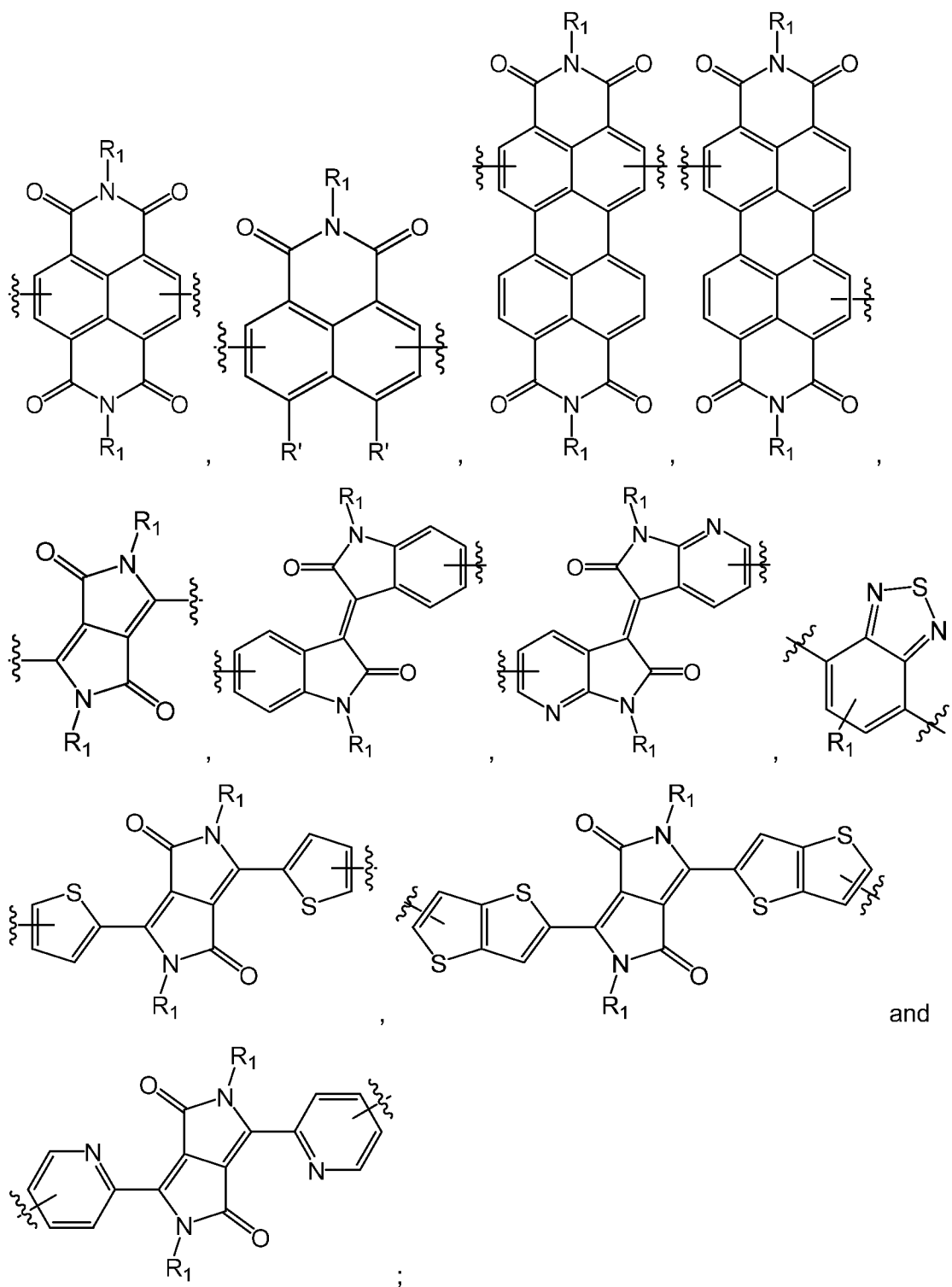
25 17. The electrochemical cell of claim 16, wherein the first and/or second polymer is provided in the form of a bulk material or a film, optionally a film.

18. The electrochemical cell of any preceding claim, wherein the electrochemical cell is an energy storage device, optionally a battery or a supercapacitor.
- 5 19. The electrochemical cell of any preceding claim, further comprising an electrolyte, optionally wherein the electrolyte is an aqueous electrolyte.
20. The electrochemical cell of any preceding claim, wherein the first electrode is the anode and the second electrode is the cathode, or wherein the first electrode is the
- 10 cathode and the second electrode is the anode.
21. A process for producing a device as claimed in any preceding claim, comprising providing a first substrate and a second substrate;
dispersing a first polymer according to any one of claims 1-10 or 15 in a liquid
- 15 medium to form a first composition;
depositing the first composition on a surface of the first substrate to form a first electrode;
dispersing a second polymer according to any one of claims 1 or 11-15 in a liquid medium to form a second composition; and
- 20 depositing the second composition on a surface of the second substrate to form a second electrode;
optionally further comprising immersing both the first and second electrodes in a electrolyte.
- 25 22. A polymer comprising the formula (I):



wherein:

each M_1 is independently selected from:



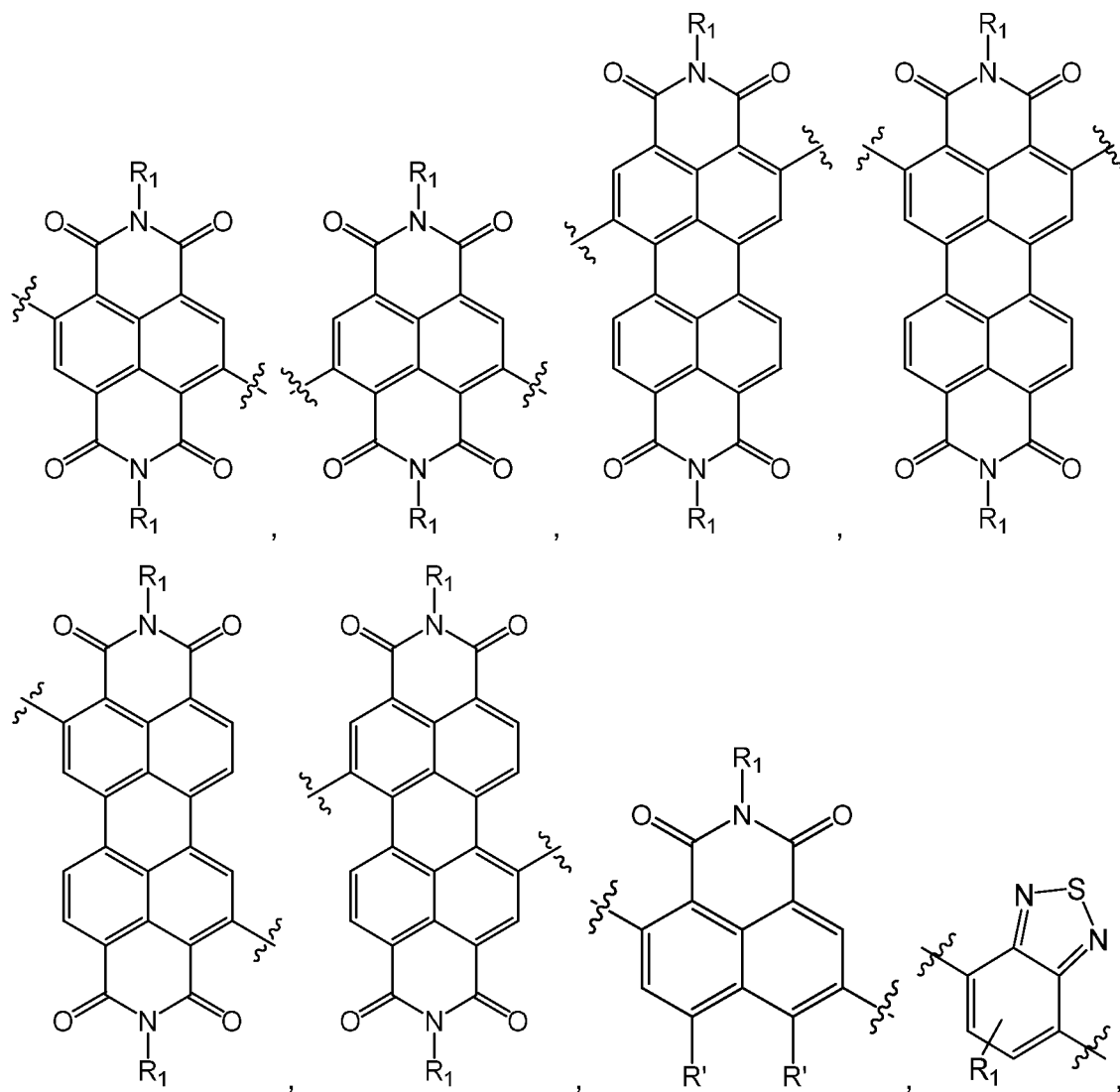
5 R', at each occurrence, is independently selected from H, an electron-withdrawing group, a C₁₋₄₀alkyl group optionally substituted with 1-5 electron-withdrawing groups, a moiety comprising at least one -alkylene-O- unit or a moiety comprising at least two functional groups of which at least one has a positive and one has a negative electrical charge; and

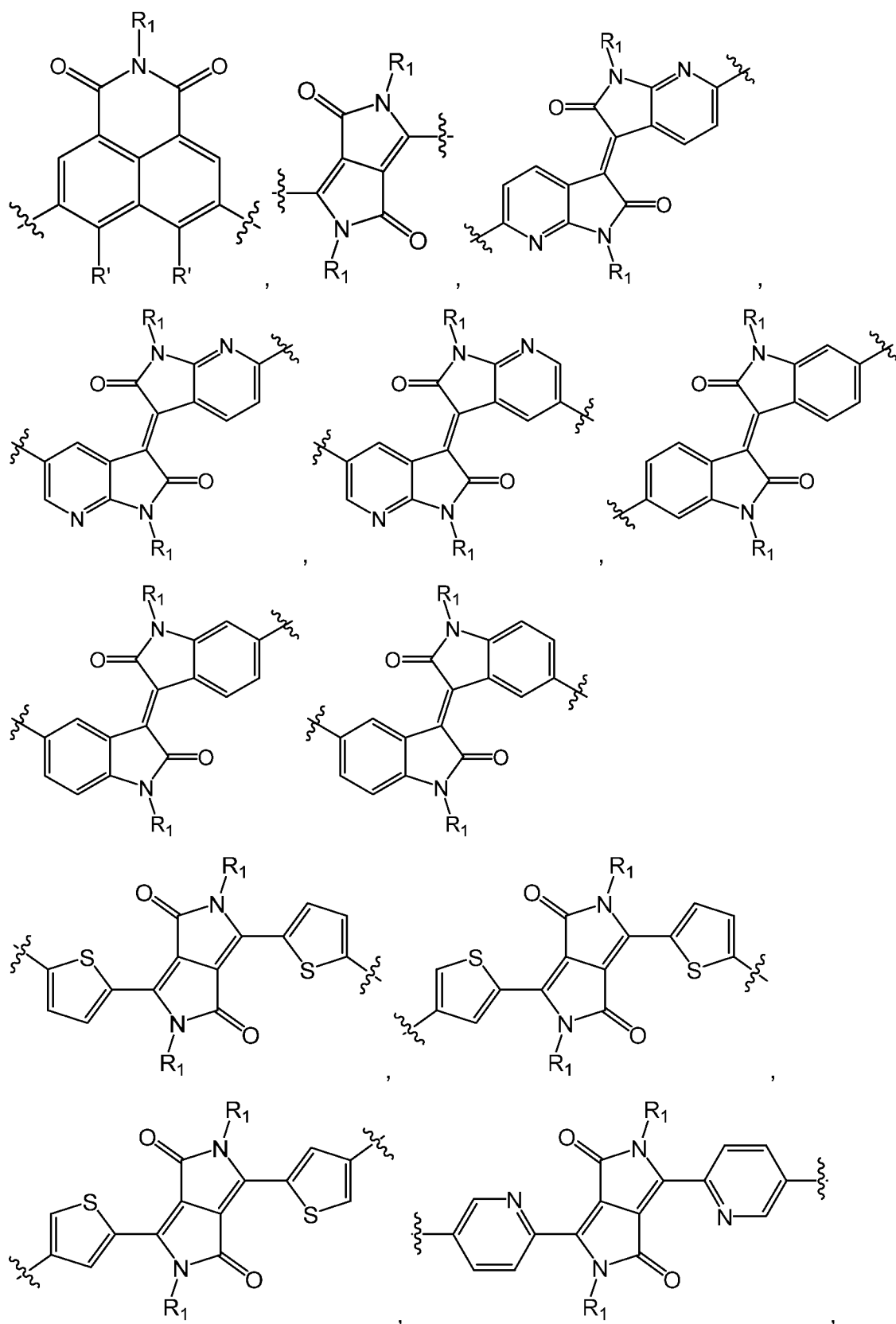
10 wherein R₁, at each occurrence, is independently a moiety comprising at least one -alkylene-O- unit and each M₂ is independently a repeat unit comprising one or more

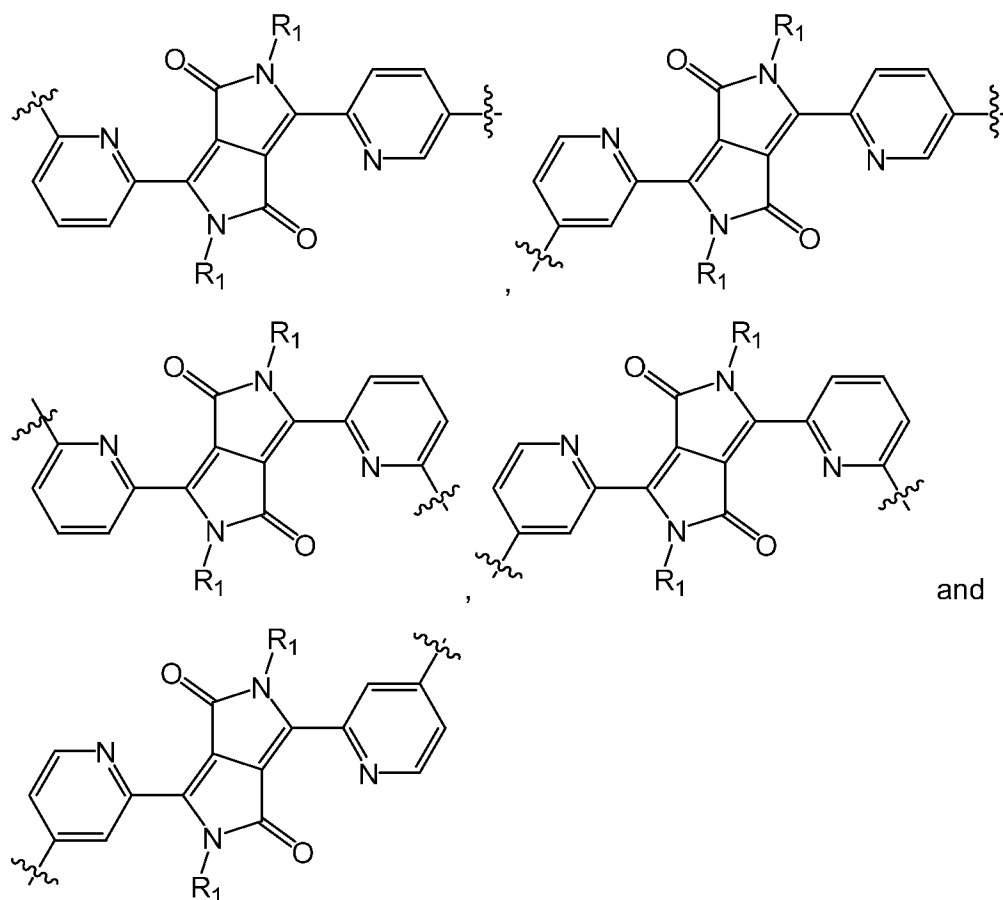
heteroaryl groups substituted with one or more groups selected from a moiety comprising at least one -alkylene-O- unit and a moiety comprising at least two functional groups of which at least one has a positive and one has a negative electrical charge; or

- wherein R_1 , at each occurrence, is independently a moiety comprising at least two functional groups of which at least one has a positive and one has a negative electrical charge and each M_2 is independently a repeat unit comprising one or more heteroaryl groups optionally substituted with one or more groups selected from a moiety comprising at least one -alkylene-O- unit and a moiety comprising at least two functional groups of which at least one has a positive and one has a negative electrical charge; and
- n is an integer of at least 2, optionally between 2 and 5,000.

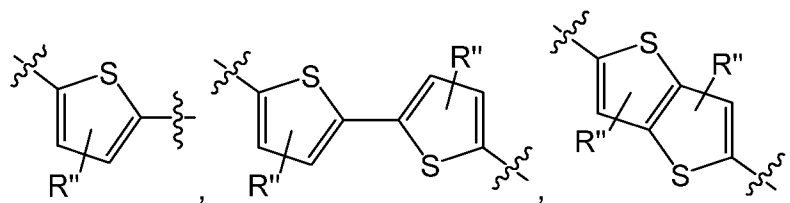
23. The polymer of claim 22, wherein each M_1 is independently selected from:

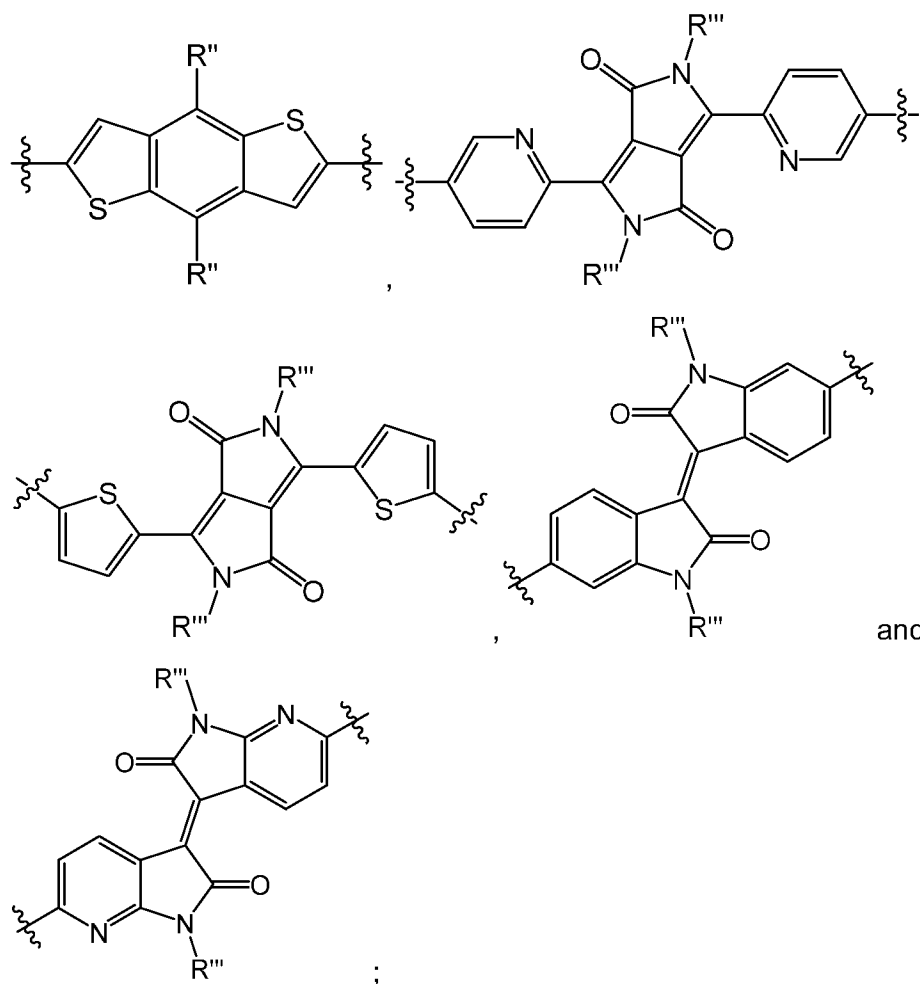






- 5 24. The polymer of any one of claims 22-23, wherein each M₂ is independently a repeat unit comprising one or more heteroaryl groups wherein the heteroaryl group is selected from thiophene, 2,5-dihydropyrrolo[3,4-c]pyrrol-1,4-dione (diketopyrrolopyrrole, DPP) and (3E)-3-(2-oxo-1H-indol-3-ylidene)-1H-indol-2-(isoindigo), and [3,3'-bipyrrolo[2,3-b]pyridinylidene]-2,2'(1H,1'H)-dione (pyridine isoindigo), preferably thiophene,
- 10 bithiophene, 3,6-alkoxy-thieno[3,2-b]thiophene, thieno[3,2-b]thiophene, 3,3'-alkoxybithiophene 2,5-dihydropyrrolo[3,4-c]pyrrol-1,4-dione (diketopyrrolopyrrole, DPP), (3E)-3-(2-oxo-1H-indol-3-ylidene)-1H-indol-2-one (isoindigo) and [3,3'-bipyrrolo[2,3-b]pyridinylidene]-2,2'(1H,1'H)-dione (pyridine isoindigo).
- 15 25. The polymer of any one of claims 22-23, wherein each M₂ is independently selected from:



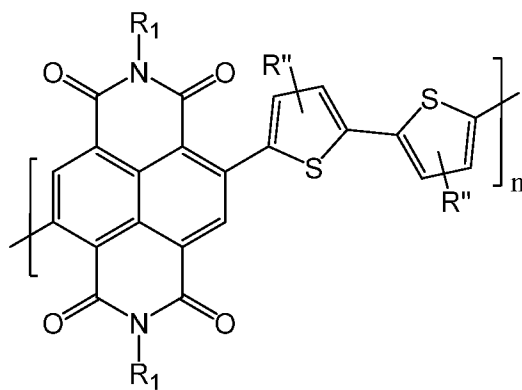


wherein:

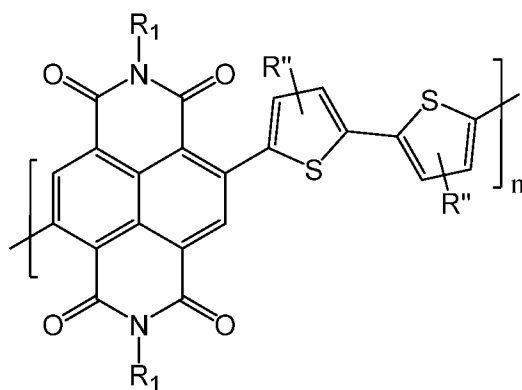
- 5 R'' , at each occurrence, is independently selected from H, $-O-C_{1-6}$ alkyl, $-COOH$, $-C(O)O-C_{1-6}$ alkyl, a (poly)alkylene glycol chain having 1-30 alkylene glycol units, a C_{3-6} alkyl group substituted with one or more (poly)alkylene glycol chains having 1-30 alkylene glycol units, C_{1-6} alkyl substituted with a crown ether or a moiety comprising at least two functional groups of which at least one has a positive and one has a negative electrical
- 10 charge; and

- R''' , at each occurrence, is independently selected from a (poly)alkylene glycol chain having 1-30 alkylene glycol units, a C_{3-6} alkyl group substituted with one or more (poly)alkylene glycol chains having 1-30 alkylene glycol units, and C_{1-6} alkyl substituted with a crown ether or a moiety comprising at least two functional groups of which at least
- 15 one has a positive and one has a negative electrical charge.

26. The polymer of any one of claims 22-25, wherein the polymer is selected from:



wherein R_1 is a moiety comprising at least two functional groups of which at least one has a positive and one has a negative electrical charge; and R_2 is H or a moiety comprising at least one -alkylene-O- unit or a moiety comprising at least two functional groups of which at least one has a positive and one has a negative electrical charge; or



wherein R_1 is a moiety comprising at least one -alkylene-O- units; and R_2 is a moiety comprising at least one -alkylene-O- unit or a moiety comprising at least two functional groups of which at least one has a positive and one has a negative electrical charge.

27. The polymer of any one of claims 22-26, wherein in each M_1 group each R_1 is the same.

28. The polymer of any one of claims 22-27, wherein each R_1 is independently selected from:

- (i) a group of formula $-A-[-alkylene-O-]_{n'}-X$, wherein n' is 1-30; A is absent, an alkyl linker or O; and X is hydrogen, alkyl, -alkyl-SO₃H, -alkyl-COOH or haloalkyl; and
- (ii) a group of formula $-W-X-Y-Z$, wherein W and Y are each independently a linker moiety selected from alkylene, arylene, heteroarylene or a moiety comprising at least one -alkylene-O- unit (optionally a moiety of formula $-[-alkylene-O-]_{n'}-$, wherein n' is 1-30), or a combination thereof; one of X and Z is a

- positively charged moiety and the other is a negatively charged moiety, optionally wherein a positively charged moiety is a moiety comprising a cationic nitrogen group (e.g., quaternary ammonium, protonated amine, azomethine, amidine, guanidine or a cationic nitrogen containing heteroaryl, such as pyridinium or imidazolium), or a sulfonium or phosphonium cation, and a negatively charged moiety is a moiety comprising a phosphate, sulfonate, carboxylate, phosphonate, phosphinante, sulfate, alkoxydicyanobenzenolate, boronate, phenolate, sulfonamide or sulfonimide anion; and
- (iii) a group of formula $-W'-X'(Z')-Y'$, wherein W' is a linker moiety selected from alkylene, arylene, heteroarylene or a moiety comprising at least one -alkylene-O- unit (optionally a moiety of formula $-[-alkylene-O-]_{n'}$, wherein n' is 1-30), or a combination thereof; Y' is absent, H or a linker moiety selected from alkylene, arylene, heteroarylene or a moiety comprising at least one -alkylene-O- unit (optionally a moiety of formula $-[-alkylene-O-]_{n'}$, wherein n' is 1-30); X' is a positively charged moiety or a negatively charged moiety and Z' is a mobile counter ion, optionally wherein a positively charged moiety is a moiety comprising a cationic nitrogen group (e.g., quaternary ammonium, protonated amine, azomethine, amidine, guanidine or a cationic nitrogen containing heteroaryl, such as pyridinium or imidazolium), or a sulfonium or phosphonium cation, and a negatively charged moiety is a moiety comprising a phosphate, sulfonate, carboxylate, phosphonate, phosphinante, sulfate, alkoxydicyanobenzenolate, boronate, phenolate, sulfonamide or sulfonimide anion.

29. The polymer of any one of claims 22-28, wherein each R_1 is independently selected from:

- ((i) a group of formula $-A-[-ethylene-O-]_{n'}-X$, wherein n' is 1-30; A is absent or O; and X is methyl, $-alkyl-SO_3H$, $-alkyl-COOH$ or haloalkyl;
- (ii) a group of formula $-W-X-Y-Z$, wherein W and Y are each independently a linker moiety selected from C_{1-30} alkylene, phenylene, pyridylene or a moiety of formula $-[-ethylene-O-]_{n'}$, wherein n' is 1-30, or a combination thereof; X is a positively charged moiety selected from quaternized ammonium, protonated amine, pyridinium and imidazolium, and Z is a negatively charged moiety selected from a phosphate anion, a phosphonate anion, a sulfonate anion and a carboxylate anion; and
- (iii) a group of formula $-W'-X'(Z')-Y'$, wherein W' is a linker moiety selected from C_{1-30} alkylene, phenylene, pyridylene or a moiety of formula $-[-ethylene-O-]_{n'}$, wherein n' is 1-30, or a combination thereof; Y' is absent, H or a linker moiety

selected from C₁₋₃₀alkylene, phenylene, pyridylene or a moiety of formula $[-\text{ethylene-O-}]_{n'}$, wherein n' is 1-30), or a combination thereof; X' is a positively charged moiety or a negatively charged moiety, wherein a positively charged moiety is a moiety selected from quaternized ammonium, protonated amine, pyridinium and imidazolium, and a negatively charged moiety is a moiety selected from a phosphonate anion, a phosphate anion, a sulfonate anion and a carboxylate anion; and Z' is a mobile counter ion selected from H⁺, M⁺ or a halide anion, wherein M⁺ is a metal cation (optionally an alkali metal cation).

30. The polymer of any one of claims 22-29 wherein R', at each occurrence, is independently selected from H, a halogen, -CN, C₁₋₁₀haloalkyl, a moiety comprising at least one -alkylene-O- unit and a moiety comprising at least two functional groups of which at least one has a positive and one has a negative electrical charge.

31 The polymer of any one of claims 22-30, wherein:

a) each R'' is independently selected from H, a C₁₋₄₀alkoxy group, a (poly)alkylene glycol chain having 1-30 alkylene glycol units, and a C₃₋₆alkyl group substituted with one or more (poly)alkylene glycol chains having 1-30 alkylene glycol units; and/or

b) each R''' is independently selected from a (poly)alkylene glycol chain having 1-30 alkylene glycol units, and a C₃₋₆alkyl group substituted with one or more (poly)alkylene glycol chains having 1-30 alkylene glycol units.

32. The polymer of any one of claims 22-31, wherein the polymer has a number average molecular weight of about 1 to about 500 kD, optionally about 5 to about 50 kD.

33. The polymer of any one of claims 22-32, wherein the polymer is provided in the form of a bulk material or a film, optionally a film.

34. Use of the polymer of any one of claims 22-33 in an optical or electronic device, in non-linear optics or as an antifouling coating.

35. The use of claim 34, wherein the device is an electrochemical energy storage device (optionally a battery, capacitor or supercapacitor), an electrochromic energy storage device, a photovoltaic cell (optionally an organic solar cell), an organic transistor (optionally an organic electrochemical transistor or an organic field effect transistor), a light emitting diode, a photodetector or a photocatalytic device, optionally wherein the device is an electrochemical energy storage device.

36. The use of claim 34 or 35, wherein the polymer forms an electrode or an active layer, optionally an electrode.
- 5 37. The use of any one of claims 34-36, wherein the device is battery comprising an electrode comprising the polymer according to any one of claims 22-33.
38. An electrochemical cell, polymer, device or process as substantially described herein with reference to or as illustrated in one or more of the examples or accompanying
10 figures.

Figure 1

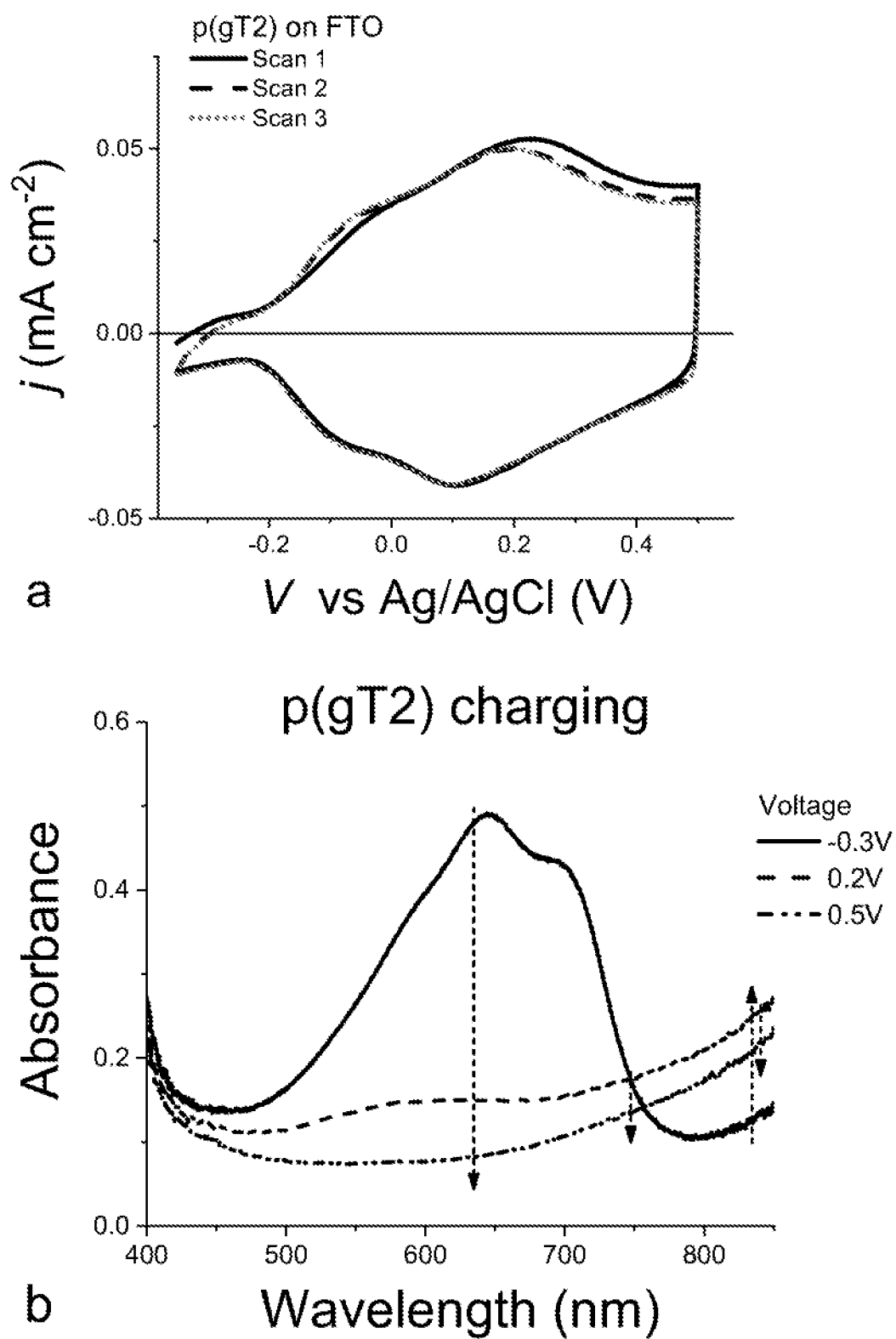
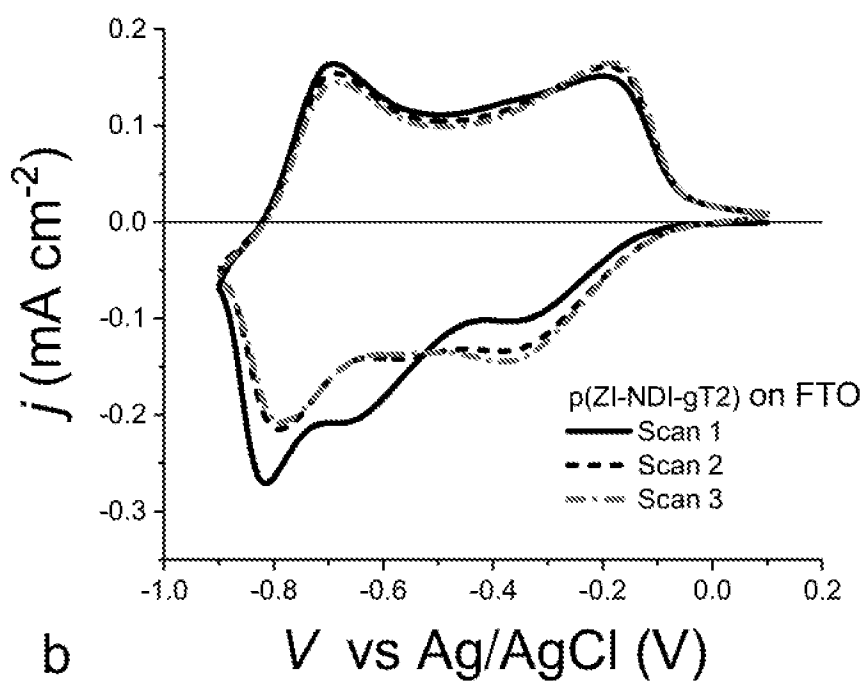
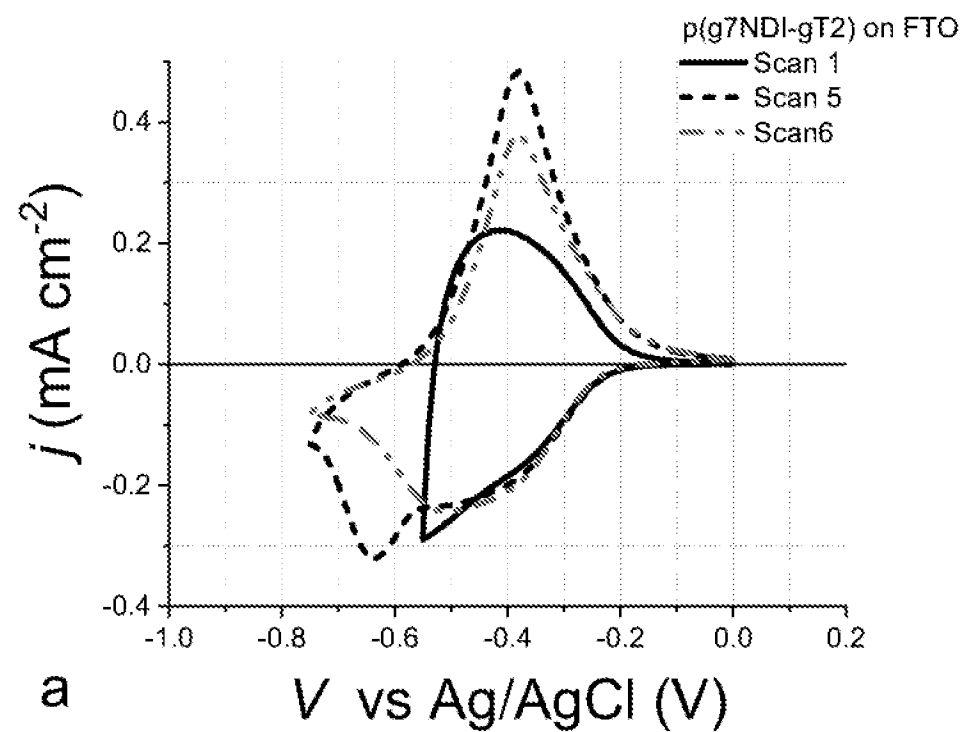


Figure 2



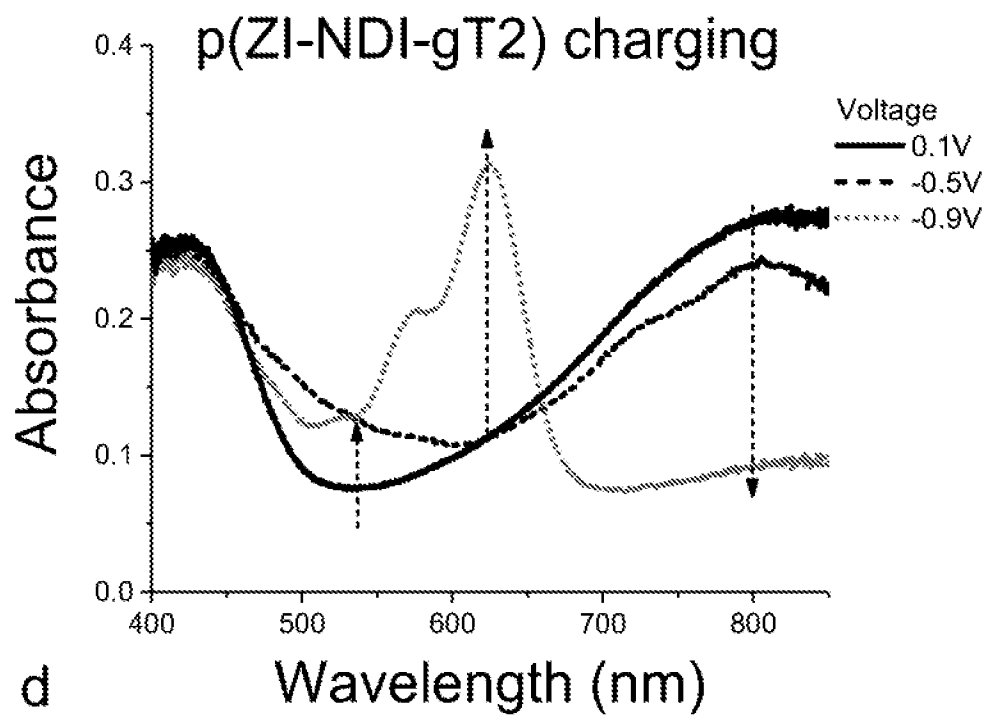
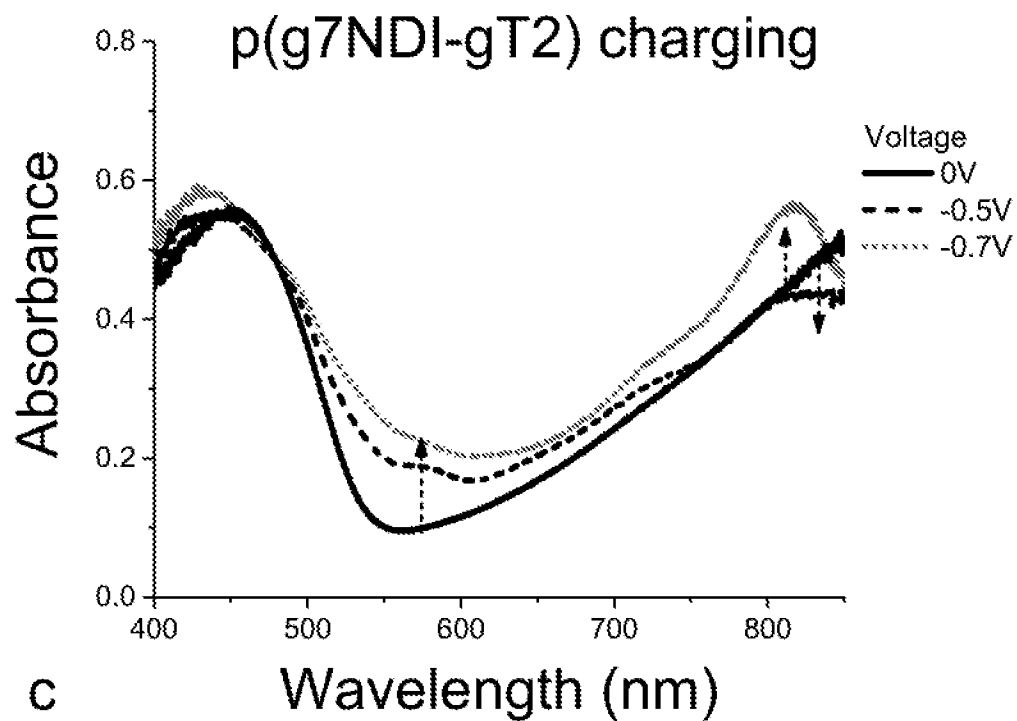


Figure 3

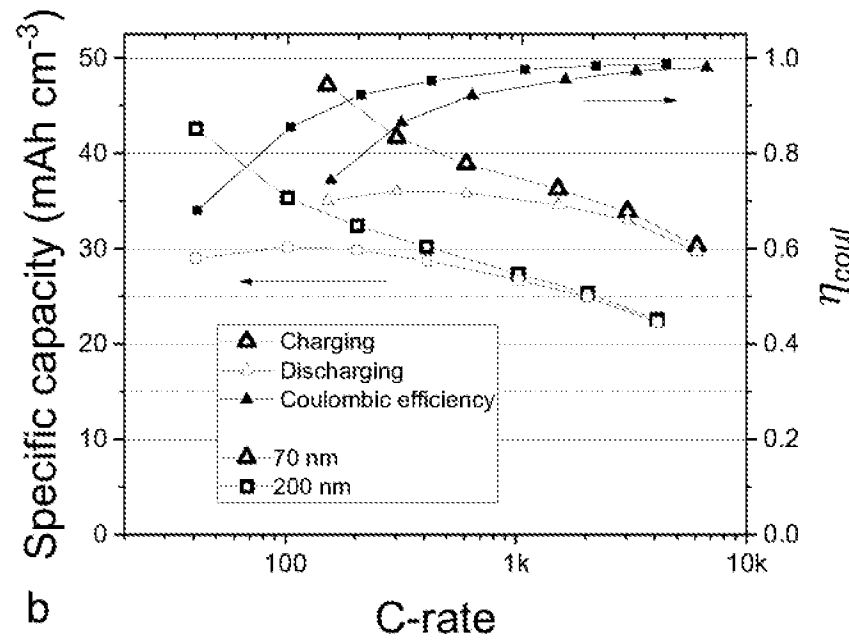
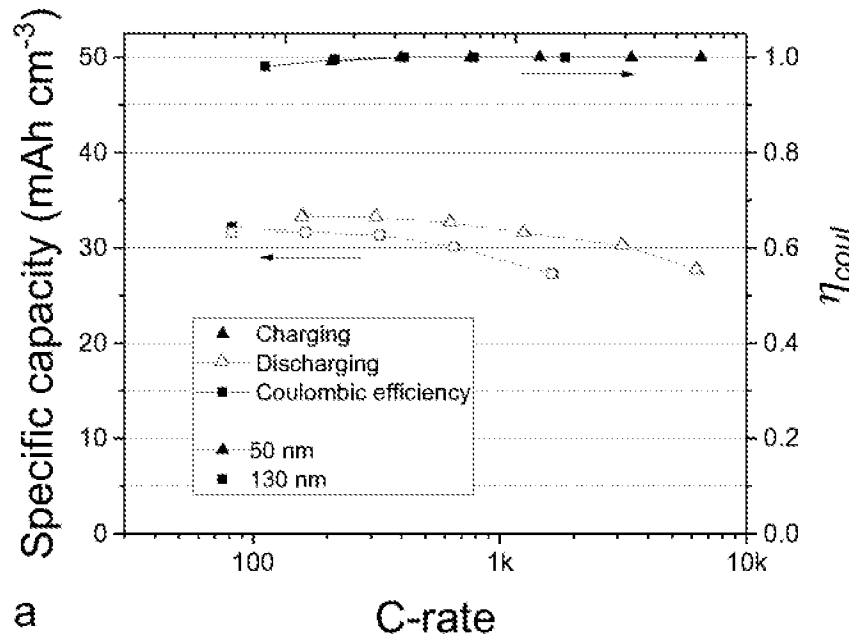


Figure 4

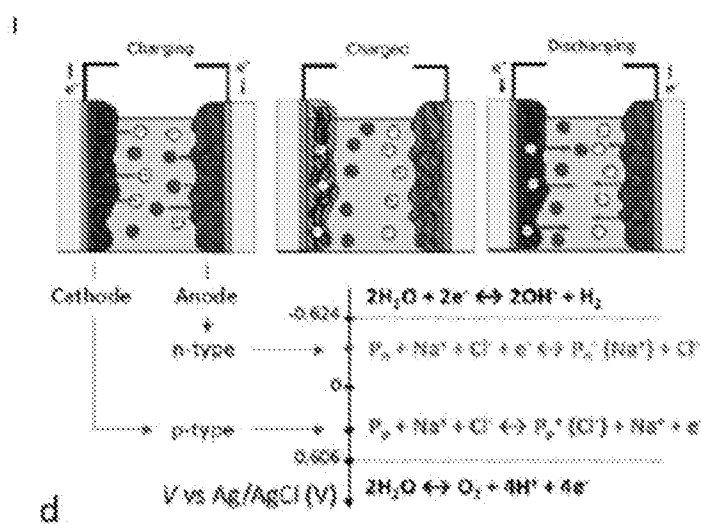
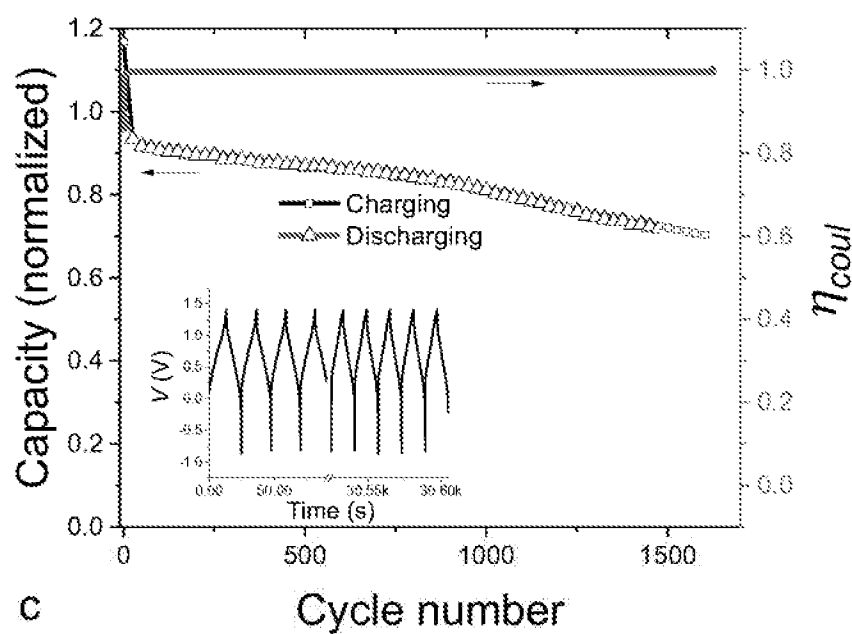
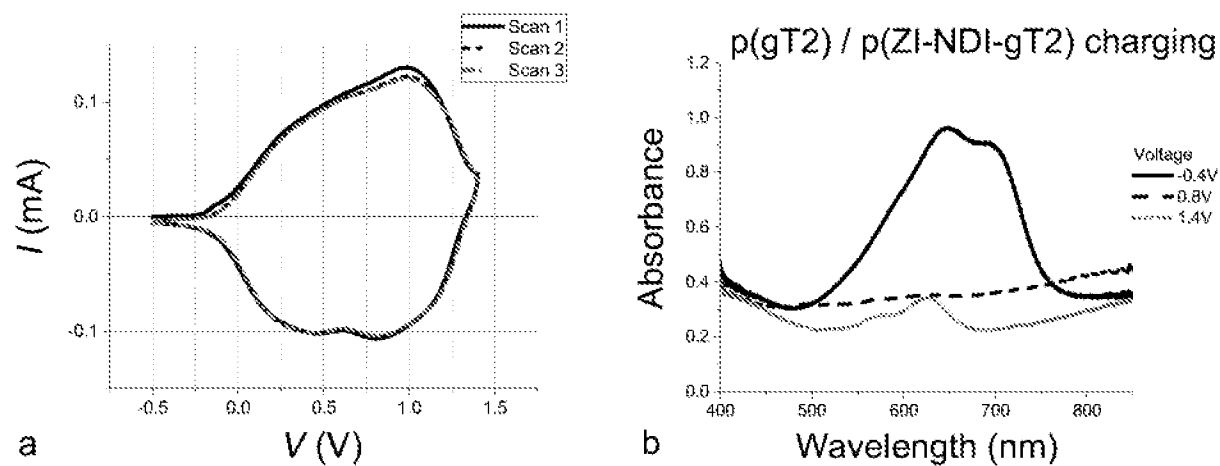
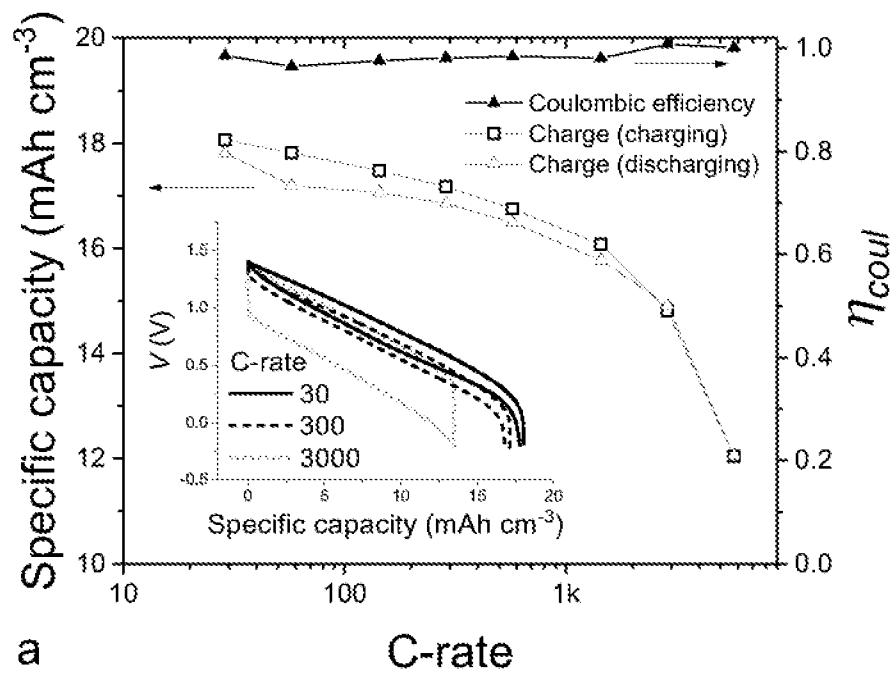
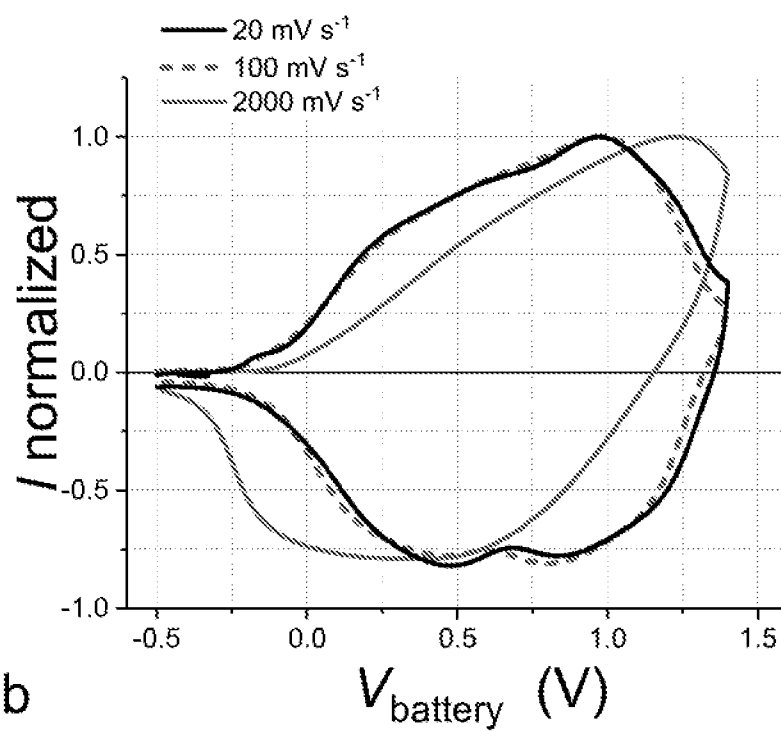


Figure 5



a



b

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2018/053329A. CLASSIFICATION OF SUBJECT MATTER
INV. H01M4/60 H01M14/00
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	ALEXANDER GIOVANNITTI ET AL: "N-type organic electrochemical transistors with stability in water", NATURE COMMUNICATIONS, vol. 7, no. 1, 7 October 2016 (2016-10-07) , XP055557228, DOI: 10.1038/ncomms13066 page 2 - page 6 ----- -/--	1-38



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

18 February 2019

Date of mailing of the international search report

26/02/2019

Name and mailing address of the ISA/

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Authorized officer

Götz, Heide

INTERNATIONAL SEARCH REPORT

International application No

PCT/GB2018/053329

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	HIROAKI BENTEN ET AL: "Recent research progress of polymer donor/polymer acceptor blend solar cells", JOURNAL OF MATERIALS CHEMISTRY A, vol. 4, no. 15, 1 January 2016 (2016-01-01), pages 5340-5365, XP055557175, GB	1-4, 6-25, 27-38
A	ISSN: 2050-7488, DOI: 10.1039/C5TA10759H page 5345 page 5347	5,26
X	----- RONG-HO LEE ET AL: "Synthesis of di(ethylene glycol)-functionalized diketopyrrolopyrrole derivative-based side chain-conjugated polymers for bulk heterojunction solar cells", RSC ADVANCES, vol. 7, no. 2, 1 January 2017 (2017-01-01), pages 1016-1025, XP055557208, ISSN: 2046-2069, DOI: 10.1039/C6RA26245G	1-25, 27-38
A	page 1017 - page 1019 -----	26