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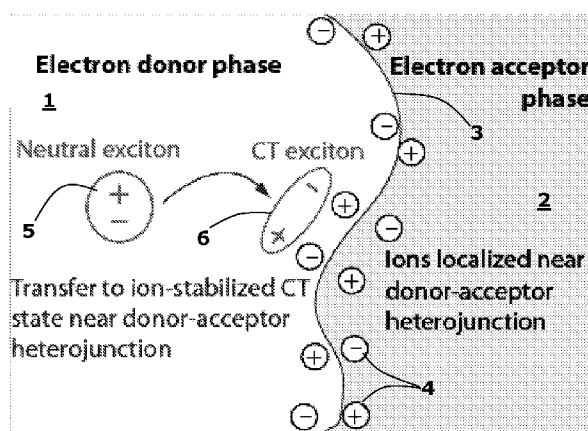


Figure 1

(57) Abstract: A photovoltaic (PV) device having an electron donor region and electron acceptor region, the donor and acceptor regions comprising conjugated polymers and/or molecular semiconductors, ion pairs being, preferably preferentially, located at, near or towards the interface between the donor and acceptor regions.

PHOTOVOLTAIC DEVICES COMPRISING ION PAIRS

This invention relates to polymeric semiconductors and, in particular,
5 although not exclusively, to polymeric semiconductors which are usable in
photovoltaic or photoresponsive devices.

Semiconducting polymers make remarkably effective substitutes for
conventional inorganic semiconductors in a range of optoelectronic devices
10 including light emitting diodes (LEDs), photovoltaic (PV) diodes, field effect
transistors (FETs), and lasers. Conjugated polymers offer considerable
material advantages over inorganic semiconductors including chemically
tunable optoelectronic properties and low-temperature, solution-based
processing suitable for printed electronics. However, their additional
15 functional potential has not been so widely recognized until recently. One
functional advantage offered by conjugated polymers is their capacity to
employ both electronic and ionic charge carriers in device operation.
Whereas solid state inorganic semiconductors are typically impermeable and
unstable towards extrinsic ions, ion transport is at the heart of energy
20 conversion and signaling in the soft functional materials found in nature.

Benefits of using ionic charge carriers have been demonstrated in polymer
light emitting devices (LEDs). In that case, efficient polymer LEDs have
been fabricated by blending the active layer with electrolytes, or
25 substituting it with single-component conjugated polyelectrolytes (CPEs)
that have ion pairs tethered to the sidechains. The added ions were
originally believed to facilitate electrochemical doping under applied bias,
however mounting experimental evidence supports an electrodynamic
model whereby the redistribution of mobile ions enhances the field locally at
30 the electrodes, leading to facile and balanced electronic carrier injection.
However, solid-state photoluminescence (PL) efficiencies of CPEs are found
to be considerably lower than their neutral counterparts and dependent on
the nature and size of counterions present. Accordingly, CPEs are deployed

most effectively as thin injection layers between the electrodes and highly emissive neutral conjugated polymers. Extrinsic In^{3+} and Cl^- ions have also been found to induce PL quenching in films of neutral polymers without evidence of any electrochemical doping.

5

It is desirable to utilize the properties of CPEs in photoresponsive devices.

Polymer solar cells may comprise a layer or film of active layer, the donor layer, and a layer or film of acceptor molecules sandwiched between a pair
10 of contacts. The donor layer may comprise conjugated polymer species which possess delocalized π electrons which can be excited by light (usually visible light) from the highest occupied molecular orbital (HOMO) to the molecules lowest unoccupied molecular orbital (LUMO), a π - π^* transition. The band gap between the HOMO and LUMO corresponds to the energy of
15 the light which can be absorbed.

In polymers the exciton electron-hole pairs created by such light absorption are strongly bound. However, the exciton pair can be dissociated by providing an interface across which the chemical potential of the electrons
20 decreases. After dissociation, the electron will pass to the donor layer and be collected as a contact, whereas the hole will be collected by its respective contact. Of course, if the charge carrier mobility of either donor or acceptor layer is too low or not sufficiently high the charge carriers will not reach the contacts. For instance, the charge carriers may recombine at
25 trap sites or remain in the respective layer or remain in the device as undesirable space charges that oppose the drift of new carriers.

A prior art polymer solar cell comprises a polyethylene terephthalate (PET) substrate, upon which is provided successive layers of indium tin oxide
30 (ITO), Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS), an active layer which may be a polymer:fullerene blend, and an aluminium layer. In such a solar cell device architecture the polymer chain is the electron donor layer and fullerene is the electron acceptor layer.

It is a non-limiting object of the present invention to provide a new species for use in solar cells and a corresponding solar cell architecture which will, or may, lead to performance enhancements over prior art solar cell architectures.

Accordingly, a first aspect of the invention provides a photoresponsive device including a semiconducting polymer comprising redox inert ions.

The semiconducting polymer may be a copolymer.

A second aspect of the invention provides a solar cell having an electron donor region and electron acceptor region, the donor and acceptor regions comprising conjugated polymers, ion pairs being, preferably preferentially, located at, near or towards the interface between the donor and acceptor regions.

The cation and anion pairs may be located at either side of the interface or the cations one side and anions the other.

Further exploitation of ions in polymer optoelectronic devices will be enabled by better understanding the interactions between ions and electronic excitations, particularly the origin of the observed luminescence quenching. The difficulty of uncovering the inherent photophysical interactions arises, in part, because ions tethered to conjugated polymers introduce amphiphilic character which can induce rigid ordered backbone conformations and the formation of aggregates and interchain states. This prompted us to investigate the solid state photophysics of a derivative of poly(9,9'-dioctylfluorene-*alt*-benzothiadiazole) (F8BT) with a low density of ions that are tethered statistically. This arrangement was chosen to minimize the likelihood of ion-induced ordering while ensuring that ions are distributed with sufficient density to interact with electronic excitations in the film.

By time resolving emission and absorption spectra of excitons encountering ions in our CPE films, we show that, contrary to existing views, ions do not destroy optical excitations but rather induce the formation of long-lived,
5 weakly emissive and immobile charge-transfer (CT) states via Coulombic interactions.

In order that the invention may be more fully understood, it will now be described, by way of example only, with reference to the accompanying
10 drawings, in which:

Figure 1 is a schematic diagram of a first interface in a solar cell according to the invention;

Figure 2 is a schematic diagram of a second interface in a solar cell
15 according to the invention;

Figure 3 is a schematic diagram of a first route to distribute ions at an interface;

Figure 4 is a schematic diagram of a second route to distribute ions at an interface;

Figure 5 is a schematic diagram of a third route to distribute ions at an interface;
20

Figure 6 is a reaction scheme according to the invention;

Figure 7 shows optical absorption spectra and photoluminescence spectra of FN-BF₄-7% and F8BT (comparative example);

Figure 8 shows a) time resolved photoluminescence spectra of F8BT (comparative example) and FN-BF₄-7% at <1 ns and 6 ns after 470 nm excitation. b) Time-resolved PL kinetics for F8BT (comparative example) detected at 540 nm and 640 nm, and for FN-BF₄-7% at the same wavelengths;
25

Figure 9 shows transient absorption spectra of F8BT (top) and FN-BF₄-7% (bottom) within 2 ns of excitation with integrated time regions indicated ($\lambda_{\text{exc}} = 490 \text{ nm}$, fluence $< 10^{14} \text{ photons/cm}^2$). The 1-2 ns spectrum is duplicated with a magnified scale in FN-BF₄-7% for
30

better comparison with early time spectra. Also shown is the spectrum of F8BT polaron pairs formed via exciton annihilation under significantly (>25 -fold) higher fluence;

Figure 10 shows a) temperature dependent PL spectra of FN-BF₄-7%.
 5 ($\lambda_{\text{exc}} = 470 \text{ nm}$); b) Temperature dependent PL Quantum efficiency (PLQE) of F8BT (comparative example) and FN-BF₄-7%; and c) Arrhenius plot of extracted non-radiative decay rate for F8BT (comparative example) and FN-BF₄-7%;

Figure 11 shows transient absorption polarization anisotropy kinetics
 10 ($\lambda_{\text{exc}} = 490 \text{ nm}$, fluence $< 10^{14} \text{ photons/cm}^2$, $\lambda_{\text{probe}} = 800 \text{ nm}$) for F8BT (comparative example) and FN-BF₄-7%.

Figure 12 shows a) Normalized GS recovery kinetics for F8BT (comparative example), FN-BF₄-7% and an F8BT/PFB blend (comparative example) ($\lambda_{\text{exc}} = 490 \text{ nm}$, fluence $= 6 \times 10^{13}$
 15 photons/cm^2 , $\lambda_{\text{probe}} = 490 \text{ nm}$). b) Relevant spectra to assess Förster transfer from an F8BT exciton donor to the following acceptors (with absorption shown in units of molar extinction coefficient); an F8BT exciton (comparative example), an FN-BF₄-7% charge pair and an F8BT/PFB charge pair (comparative example).

20 Referring first to Figure 1, there is shown an interface 3 between an electron donor 1 and an acceptor 2 phase in a solar cell. It will be appreciated that ion pairs 4 are located at, adjacent or near to the donor-acceptor heterojunction 3.

25 A neutral, bound, exciton 5 generated in the donor phase 2 will migrate towards the ionic region at the interface 3 and is aligned with the ion pairs to generate a stable charge-transfer (CT) state 6.

30 It is considered that because CT states are stabilized by the Coulomb field of ions means that the strength of interaction with a neutral photoexcitation can be extrinsically tuned by varying the nature (*i.e.*, size, valency) of the

added ions. The screening of the electron-hole electrostatic attraction will facilitate separation of the electron hole pair.

Referring now to Figure 2, there is shown an interface 3' between an
5 electron donor 1' and an acceptor 2' phase in a solar cell. It will be appreciated that ion pairs 4' are located at, adjacent or near to the donor-acceptor heterojunction 3'. However, in this instance the cations and anions are distributed along respective sides of the interface.

10 Under the influence of an external bias, ions are displaced to some degree and thus redistribute the electric field across the active layer of the polymer solar cell. Again, ions are localized at the interface between donor 1' and acceptor 2' phases so that the electric field is enhanced at charge-separating interfaces where it can affect the dissociation of geminate charge
15 pairs.

Ions 4' at donor-acceptor interfaces 3' are available to screen the mutual Coulomb attraction between photogenerated geminate electron-hole pairs
20 7, thus enhancing the likelihood of electronic charge-pairs escaping their binding radius and increasing the yield of free charges.

There are several ways to realize the intended ionic polymer solar cell architecture that localizes ion pairs 4, 4' near the interfaces 3, 3' between nanostructured donor 1, 1' and acceptor 2, 2' phases.

25 For example, and referring to Figure 3, block copolymers 10 could template the phase separation between ionic and non-ionic regions during film formation, using the relative block lengths and solvent affinities to tune the phase morphology of the resulting vesicle 11. Such a block copolymer 10
30 could have a uniform conjugated backbone structure but separate blocks defined by the ion-pairs 4, 4' tethered to the sidechains.

Alternatively, and referring to Figure 4, a triblock oligomer 20 comprised of electron donor 1, 1' and acceptor 2, 2' blocks spanning an ionic unit (donor 21, ion 22, acceptor 23) could be blended with homopolymers of the respective donor 1, 1' and acceptor 2, 2'. In this configuration, the oligomer 20 acts as a surfactant and localizes at the donor-acceptor interface 3, 3', enabling the interface 3, 3' to be engineered by the inclusion of ionic groups 4, 4'.

Additionally, and referring here to Figure 5, donor 1a and acceptor 2a polymers could be designed to incorporate complementary ion pairs 4a, 4b into their structure that will be enriched at donor-acceptor interfaces 3, 3' due to their favorable association of the ionically complementary species.

In order to further exemplify the invention, reference is made to the following non-limiting Example.

Example

Copolymerization of the bis(6-bromohexyl)-fluorenyl boronic ester **M1** and the 9,9-dioctylfluorene boronic ester **M2** with 4,7-dibromo-2,1,3-benzothiadiazol was achieved using palladium mediated Suzuki cross-coupling copolymerization (see Stork *et al*; *Adv. Mater.* **14** (2002) pp 361-366). The reaction route is outlined in Figure 6.

NMR analysis of **FNBr-7%** revealed that a 1:9 **M1:M2** feed ratio gave a copolymer containing 7% of the bis(6-bromohexyl)fluorine and 93% of **F8BT** repeats. The bromohexyl tails were treated with trimethylamine in THF to give the corresponding trimethylammonium derivatives with bromide counterions (**FNBr-7%**). The counter ions were then exchanged to tetrafluoroborate by dissolving the polymer in a THF and water solution containing an excess of NaBF₄. The solvent was then removed under reduced pressure, and the solid washed several times with deionized water to give the resulting polymer (**FN-BF₄-7%**) in 45% yield. The relatively low

density of ionic sidechains in FN-BF₄-7% ensures that the polymer is soluble in most of the same solvents used to process F8BT.

Figure 7 (top panel) shows the absorption and emission spectra of dilute chloroform solutions (10 mg/L) of FN-BF₄-7% (line B) compared with the non-ionic F8BT (line A). The spectral features are virtually identical. Moreover, time-resolved PL decays (not shown) are monoexponential and independent of wavelength, with nearly identical lifetimes for FN-BF₄-7% (τ = 2.8 ns) and F8BT (τ = 2.9 ns). The invariance of the photophysics indicates that the ionic sidechains and counterions do not interact with the conjugated backbone in dilute solution, nor do they induce aggregation or decomposition. Both effects have been found to lead to PL quenching in solutions of CPEs with exclusively ionic sidechains.

The bottom panel of Figure 7 shows the absorption and emission spectra of thin films of FN-BF₄-7% (line B') and F8BT (line A'). Again, the absorption spectra are virtually identical; however the PL intensity is significantly attenuated for the ionic copolymer FN-BF₄-7% compared with F8BT when measured under identical conditions. The integrated PL quantum efficiency is 6% for FN-BF₄-7% compared with 60% for F8BT. While the PL spectra are all peaked at λ_{em} = 540 nm, comparison of the normalized PL spectra shows that FN-BF₄-7% has slightly enhanced emission on the red tail of the spectrum.

The observation of PL quenching and subtle spectral shifts prompted us to undertake time-resolved measurements by the time-correlated single photon counting (TCSPC) method in order to better understand the perturbations induced by the ions in thin films. Figure 8a shows the time-resolved PL spectra for FN-BF₄-7% compared with F8BT. These spectra were obtained by reconstructing kinetic traces taken sequentially at 10-nm intervals throughout the spectrum. The F8BT PL decay kinetics (Figure 8b) are well fit by single exponential functions, with little variation in lifetime across the spectrum (τ (540 nm) = 1.41 ns, R^2 = 0.999; τ (640 nm) = 1.58

ns, $R^2 = 0.997$), also evident by the invariance of the PL spectra at <1 ns and 6 ns following excitation. The exciton decay is dominated by radiative relaxation, and the minimal wavelength dependence shows that there is little energetic disorder sampled on the timescale of the measurement. In contrast to this, the FN-BF₄-7% spectra (Figure 8a) exhibit strong quenching and a pronounced dynamic redshift. Within the first nanosecond after excitation, the PL spectrum ($\lambda_{\text{max}} = 540$ nm) closely resembles the excitonic F8BT emission. However, this feature is rapidly quenched ($\tau = 350 \pm 30$ ps, approaching the 130-ps instrument response function), largely accounting for the 10-fold reduction in the integrated PL quantum efficiency. A secondary red-shifted emission peak ($\lambda_{\text{max}} = 610$ nm) is clearly seen on longer timescales ($\tau = 2.0 \pm 0.2$ ns). The ions introduced in FN-BF₄-7% have the effect of quenching the primary exciton, while introducing a secondary emissive state that is stabilized by 0.3 eV with respect to the primary exciton. We note that spectral characteristics of the secondary red-shifted emission peak are reminiscent of the emissive interchain and intrachain CT states formed when F8BT is coupled with electron donors.

We turned to TA spectroscopy as a more direct probe of charge transfer (including non-emissive states), as shown in Figure 9. For reference, the TA spectrum of F8BT (comparative example, top panel), is characterized by a stimulated emission (SE) feature ($\Delta T/T > 0$) at wavelengths corresponding to the PL ($\lambda < 610$ nm), and a photoinduced absorption feature ($\Delta T/T < 0$) peaked at ~ 740 nm that is associated with the red-shifted absorption of the exciton. Aside from the small Stokes shift in the stimulated emission, the decay is broadly wavelength independent and proceeds on the same timescale as GS recovery shown in Figure 12a (we note that the signal is still decaying at the limit of our detection window). This is consistent with the simple decay of mobile emissive excitons to the ground state without the participation of any other intermediates, as has been shown in previous photophysical studies of F8BT at excitation intensities sufficiently low to avoid charge generation from exciton-exciton annihilation.

In the case of FN-BF₄-7% (Figure 9, bottom panel) measured under identical low-fluence conditions, the exciton spectrum 1 ps after excitation is virtually identical to that of F8BT, consistent with the conclusion from time-resolved PL that the primary exciton is not affected by the presence of a low density of ions. However, the TA signal of FN-BF₄-7% ceases to evolve after a few hundred picoseconds, and the spectrum of the residual long-lived population is characterized by a broadened photoinduced absorption feature peaked at 700-750 nm that extends into the 500-600-nm region where stimulated emission is otherwise expected. These spectral features are consistent with charge photogeneration.

For comparison, the TA spectrum of charge pairs in pristine F8BT was independently obtained by exciting the sample with a significantly higher (>25-fold) fluence, known to produce polaron pairs via exciton-exciton annihilation. Indeed, the resulting high-fluence F8BT polaron pair TA spectrum shown in Figure 9 has a broad visible absorption peaked at 730 nm and a lack of SE - strongly reminiscent of the long-lived TA signal measured in FN-BF₄-7% under low fluence.

Interchain and intrachain CT states derived from F8BT excitons coupled to electron-donating units have also been shown to give rise to weakened and red-shifted PL, longer radiative lifetimes, loss of SE, and broadened photoinduced absorption across the visible region. The TA and time-resolved PL spectra of FN-BF₄-7%, provide strong evidence that the added ions induce the photogeneration of CT states that have increased electron-hole separation compared with the emissive bound exciton. For brevity, our subsequent references to CT states will include both weakly emissive CT states and non-emissive polaron pairs.

Ionic charges have the potential to stabilize CT states in conjugated polymers by establishing local Coulomb fields that perturb the HOMO and LUMO orbital energies. For example, an anion will raise the energy levels of HOMO and LUMO orbitals of neighboring chains, thus attracting holes and

repelling electrons, while a cation will have the reverse effect. The distribution of both anions and cations in the conjugated polymer film is thus expected to lead to local configurations where electron-hole pairs are separated under the influence of ions. The electronic structure of F8BT
5 enhances the interaction with the Coulomb field of ions. The alternating fluorene (donor) and benzothiadiazole (acceptor) units give rise to CT character in the lowest energy excitonic states of F8BT, and consequently solvatochromism in the absorption and emission spectra.

10 In solid films of FN-BF₄-7%, CT excitons are stabilized when BF₄⁻ counter anions interact with a partially positive fluorene donor unit, whereas destabilization will occur if the BF₄⁻ ions interact with the partially negative benzothiadiazole (BT) units. Likewise, theoretical calculations show that quarternary amine cations attached to the polymer sidechains are poised to
15 undergo electrostatic interaction with electronegative BT units.

We can also eliminate several other possible causes of exciton quenching in FN-BF₄-7%. Firstly, the quarternary amine and BF₄⁻ ions are not redox active towards F8BT in either the ground state or the singlet exciton state,
20 thus limiting their role to a physical perturbation upon the polymer photophysics. Secondly, the absence of heavy atoms precludes the participation of triplet excited states because intersystem crossing operates on a timescale of ~40 ns in F8BT. Thirdly, the photophysics observed in FN-BF₄-7% is not consistent with the presence of chemical keto defects -
25 fluorenones that are found to appear as photo-oxidation products in some polyfluorenes. Fluorenone defects emit at significantly higher energy ($\lambda_{\text{max}} \sim 540$ nm) than the secondary emissive state we observe in FN-BF₄-7%, and are not considered to be important in fluorene copolymers such as F8BT with lower energy excited states. Additionally, spectroscopic measurements
30 on solid films were carried out under vacuum ($<10^{-5}$ Torr) to avoid the possibility of photo-oxidation.

Next we consider the possibility that tethered ions could induce conformational changes to the conjugated backbone, perhaps forming interchain aggregate states that act as recombination sites. Schwartz and coworkers (see *Annu. Rev. Phys. Chem.*; **54**; pp141-172 (2003)) have demonstrated that aggregates form when chains adopt extended conformations that permit close interchain contact, thus their formation depends strongly upon the nature of polymer sidechains and the solvent used for casting films. Aggregates display red-shifted absorption and emission spectra. As previously noted, the low density of tethered ions in FN-BF₄-7% and their statistical incorporation is not expected to cause significant ordering as it can in amphiphilic block copolymers or CPEs with ions attached to all sidechains. The invariance of GS absorption spectra and transient absorption polarization anisotropy decay strongly suggest that FN-BF₄-7% retains the same film morphology as F8BT. Additionally, previous studies that directly create and interrogate interchain interactions in F8BT provide little evidence that it could account for the photophysics observed in FN-BF₄-7%. It has been shown that thermal annealing increased the planarity of F8BT and changed the interchain packing from an eclipsed to an alternating packing structure with respect to F8 and BT units of adjacent chains (e.g. Donley *et. al.*; *J. Am.Chem.Soc.*; **127**; pp12890-12899 (2005))

Thermal annealing induced clear shifts in absorption and PL spectra, yet the corresponding ~10% variation in PL efficiencies shows that such changes in conformation and chain packing are insufficient to explain the strong quenching we observe in FN-BF₄-7%. Schmidtke *et. al.* (*Phys. Rev. Lett.*; **99**; pp167401 (2007)) probed interchain interactions by carrying out photophysical studies on F8BT films under high pressures. Red-shifted absorption and PL spectra at pressures up to 5 GPa were actually explained mostly by the intramolecular planarization of F8BT chains, showing that even highly compressed chain conformations do not represent the photophysics of FN-BF₄-7%.

A low density of ions could not induce such a pronounced perturbation of exciton decay without invoking exciton migration towards ionic sites. This mechanism is exploited for the amplification of exciton quenching via charge- or energy transfer in sensors, since excitons diffuse in three dimensions to sample a relatively large volume for the presence of an analyte. In FN-BF₄-7%, two ion pairs are attached to the alkyl sidechains of 7% of monomer units in a statistical fashion, and the volume occupied by each monomer unit in a film is estimated to be $\sim 1.3 \text{ nm}^3$ (based on the unit cell reported for F8BT films using x-ray diffraction techniques). Therefore, one would expect the mean distance between neighboring ion pairs to be $\sim 2.7 \text{ nm}$ if the ion pairs are randomly dispersed throughout the film, which is certainly within the exciton diffusion radius of F8BT ($>10 \text{ nm}$). Phase segregation between ionic and non-ionic regions could increase the size of pristine non-ionic regions, however the scope for phase segregation is expected to be rather constrained for a statistical copolymer with 7% ionic sidechains.

We undertook low temperature PL measurements in order to investigate the photophysical influence of dispersed ionic sites when exciton diffusion lengths are constrained due to insufficient energy for thermally activated exciton hopping. Figure 10a shows the temperature dependence of PL in FN-BF₄-7%. In addition to the predicted sharpening of vibronic peaks, the PL intensity clearly undergoes a substantial increase with decreasing temperature; the integrated PLQE of FN-BF₄-7% increases nearly ~ 3 -fold upon lowering the temperature from 300 K to 5 K, whereas F8BT only exhibits a 1.1-fold increase in PLQE over this range (Figure 10b), along with vibronic peak sharpening. Figure 10c reformulates the PLQE data as an Arrhenius plot in order to examine the activation energy associated with exciton trapping. In this plot, it is assumed that non-radiative relaxation channels account for most of the variation in PLQE, thus k_{nr} is extracted from each temperature in the series assuming that the radiative lifetime is equal for the two materials and independent of temperature (2.7 ns, based on the measured room temperature PLQE and lifetime of F8BT). While k_{nr} is

rather insensitive to temperature for F8BT, the ionic copolymer exhibits two distinct temperature regimes for variation in k_{nr} , corresponding to activation energies of 28 ± 4 meV (when fitting the range 200-300 K) and 0.1 ± 0.03 meV (when fitting $T < 100$ K). We do not attach any physical significance to the low energy component since it is lower than thermal energy, and likely to be susceptible to our assumption about the invariance of k_r . The 28-meV component accounts for most of the observed temperature variation of the PL intensity in FN-BF₄-7%, and we attribute this to the exciton hopping activation energy. The measured activation energy lies within the wide range of reported values *e.g.*, 170 meV for singlet exciton hopping in PPV, 60 meV for triplet exciton hopping in a Platinum poly-yne, and 7 meV for triplet exciton hopping in an Ir(PPy)-cored dendrimer. In these examples, the activation energy for exciton motion is noted to be very sensitive to the nature and strength of intermolecular interactions and the energetic disorder. The variable temperature measurements do not reveal the activation energy for exciton hopping in pristine F8BT due to the absence of quenching sites. Even at low temperature, the PLQE is considerably (~ 3.5 -fold) lower for FN-BF₄-7% than for non-ionic F8BT, indicating that exciton diffusion is not completely shut off at low temperature. Simple geometric considerations suggest that the exciton diffusion radius of FN-BF₄-7% decreases by a factor of 1.44 in going from 300 K to 5 K. This is consistent with the ~ 1.5 -fold contraction of the exciton diffusion radius reported for MEH-PPV at low temperature, where a temperature-independent exciton transfer regime persists.

Polarization anisotropy dynamics are a powerful probe of exciton motion in disordered chromophore materials. Figure 11 shows polarization resolved transient absorption (TA) kinetics for FN-BF₄-7% compared with F8BT (comparative example) probed in the photoinduced absorption region at 800 nm (*vide infra*). The polarization anisotropy decays with a time constant of ~ 8 ps in both materials, which corresponds to depolarization of excitons in just a few hops - significantly shorter than the timescale of exciton population decay (*vide infra*). The similarity of polarization

anisotropy decays indicates that the ionic substituents do not significantly alter the film morphology in FN-BF₄-7% compared with F8BT. Additionally, the initial polarization anisotropy levels ($r \sim 0.3$) are sufficiently high to suggest that there is negligible absorption into interchain aggregate states, which has been demonstrated cause depolarization on an ultrafast timescale. However, the polarization anisotropy does not quite decay to a zero baseline in FN-BF₄-7% as it does in F8BT. The non-zero anisotropy baseline corresponds to the residual population of long-lived excitations in the ionic copolymer, leading us to conclude that the residual population is immobile. The small magnitude of long-lived anisotropy is simply a consequence of rapid depolarization during the exciton hopping steps prior to trapping, thus only the fraction of excitons that were trapped in CT states within the first few hops are expected to retain polarization anisotropy.

Finally, we sought to quantify the fraction of excitations that form long-lived CT states (rather than decaying to the GS) by measuring the GS recovery kinetics by at a wavelength ($\lambda_{\text{probe}} = 490 \text{ nm}$) that is resonant with the GS absorption band and too high in energy to induce excited state absorption or stimulated emission. Figure 12a shows the normalized kinetics of GS recovery for FN-BF₄-7% and F8BT. Low excitation fluences ($6 \times 10^{13} \text{ ph/cm}^2$) were used to preclude the effect of exciton-exciton interactions. When considering the first 400 ps of the kinetics trace, the ionic copolymer undergoes significantly faster GS recovery compared with F8BT. Beyond this time, a residual signal is retained out to the maximum time delay of 1.7 ns, whereas the F8BT continues to proceed toward complete GS recovery. The residual signal in FN-BF₄-7% corresponds to $\sim 15\%$ of the initial excited state population. This result appears to imply that the presence of ions primarily accelerates the decay of most excitons to the ground state non-radiatively, with only small residual ($< 15\%$) trapped as CT states to contribute to the red-shifted emission and transient absorption signal. However, we see no plausible mechanism that could readily account for such rapid non-radiative decay of excitons, as required to reconcile the

picosecond GS recovery kinetics with the low steady-state PLQE in the presence of redox-inert ions.

Instead, we consider whether excitons could be quenched by prior photogenerated charges at the excitation intensities used in the TA measurements. Singlet excitons are known to be efficiently quenched by polarons in conjugated organic materials, typically via Förster resonant energy transfer from an emissive exciton to an absorbing polaron. The enhanced visible absorption of charges relative to excitons means that this bimolecular decay channel can still be operative at excitation densities below the threshold of exciton-exciton annihilation. We calculated the Förster radius for resonant energy transfer from an F8BT exciton to an absorbing CT state. According to the application of Förster theory to conjugated polymers, the Förster radius (R_0) is given by;

$$R_0^6 = \frac{9Q_0(\ln 10)\kappa^2}{128\pi^5\eta^4 N_{Av}} \int f_D(\lambda)\epsilon_A(\lambda)\lambda^4 d\lambda \quad (1)$$

In equation 1, κ^2 is the orientational factor (taken to be 0.655 for the case where the donor and acceptor dipoles lie in the plane of the film) η is the refractive index of the medium (previously measured to be 1.8 by ellipsometry), N_{Av} is Avagadro's number, $f_D(\lambda)$ is the emission spectrum of the donor (in this case an F8BT singlet exciton) normalized such that $\int f_D(\lambda) d\lambda = 1$, and $\epsilon_A(\lambda)$ is the absorption spectrum of the acceptor (the CT state in this case) in units of molar extinction coefficient ($M^{-1}cm^{-1}$). The absorption spectrum is obtained in the appropriate units using;

$$\epsilon_A(\lambda) = \frac{\log_{10} e}{1000} N_{Av} \sigma(\lambda) \quad (2)$$

where $\sigma(\lambda)$ is the absorption cross-section calculated from the transient transmission spectrum using;

$$\sigma(\lambda) = \frac{1}{N} \ln 1 + \frac{\Delta T}{T} \lambda \quad (3)$$

In equation 3, the excitation density ($N = 4.7 \times 10^{17} cm^{-3}$) is determined from the product of the incident fluence ($6 \times 10^{13} ph/cm^2$), the absorption

efficiency at the excitation wavelength ($\eta_{490\text{ nm}} = 0.78$), the fraction of excitations that survive beyond 1 ns where the spectrum is measured ($\Phi = 0.15$, based in the red curve in Figure 12a), and the film thickness ($z = 150\text{ nm}$). A strong Förster overlap for quenching by CT states is evident in Figure 12b, corresponding to a Förster radius of 4.25 nm. This is considerably higher than the corresponding radius for quenching by another F8BT exciton (2.93 nm, black curve), corresponding to a 10-fold enhancement in the Förster transfer rate when the ratio is taken to the sixth power according to the Förster equation. It is clear from Figure 12b that the loss of SE and the extension of absorption into the PL region accounts for the enhanced Förster quenching by CT states. At the excitation densities employed for the TA studies, the mean distance between initial excitations ($r = \sqrt[3]{1/N_0} = 6.9\text{ nm}$) approaches the calculated Förster radius, indicating that photogenerated CT states in FN-BF₄-7% are indeed likely to rapidly quench nearby excitons at the fluences used. We note that comparing the Förster radius to the mean distance between excitations is overly simplistic for many reasons, including; i) the distribution of excitations is neither uniform nor static on the timescale of quenching (as demonstrated by the temperature dependent PL and the 8-ps exciton depolarization), ii) an exciton can undergo multiple pairwise interactions with quenching sites in a film, resulting in a cumulative quenching rate, iii) the point-dipole model that underpins Förster theory breaks down for the closely packed arrays of elongated chromophores encountered in conjugated polymers, and iv) additional (non-resonant) mechanisms could also contribute to charge-induced exciton quenching. Taking these corrections into account will enhance the predicted rate of exciton quenching by CT states.

Rather than attempting to quantify these corrections, we measured GS recovery kinetics under identical conditions for F8BT blended with PFB (poly(9,9-dioctylfluorene-co-bis-*N,N'*-(4-butylphenyl)-bis-*N,N'*-phenyl-1,4-phenylene-diamine), a combination that is known to readily facilitate charge photogeneration and photovoltaic behavior. We were able to prepare a

blended film morphology that exhibited F8BT exciton quenching on a comparable timescale to FN-BF₄-7% by casting the film (1:1 F8BT:PFB by weight) from a mixture of low- and high- boiling-point solvents, in this case chloroform:chlorobenzene (90:10 by volume). The conversion of excitons to long-lived charge-pairs is known to be very efficient in this blend under steady state excitation ($\Phi_{\text{exciton} \rightarrow \text{charge}} > 60\%$).

Therefore, if no additional quenching channels were operational, one would expect the blend to exhibit GS recovery kinetics similar to unblended F8BT, but with the decay arrested at >0.6 of the initial level corresponding to the charge population. However, we observe that the GS recovery kinetics are markedly accelerated in the blend and only $<10\%$ of excitations survive 2 ns after the excitation pulse (Figure 12a, blue curve). Figure 12a is taken as strong evidence that excitons are quenched by prior photogenerated charges in both the ionic polymer FN-BF₄-7%, and the donor-acceptor blend at fluences below the threshold for exciton-exciton annihilation. Accordingly, Figure 12c shows that the overlap integral for Förster quenching via interfacial charge-pairs in the F8BT:PFB blend ($R_0 = 4.24$ nm) is nearly identical to that of the CT state in FN-BF₄-7% ($R_0 = 4.25$ nm). Exciton quenching by photogenerated charges under pulsed excitation in FN-BF₄-7% causes us to underestimate the fraction of excitons that form CT states under steady state conditions. Comparison with GS recovery kinetics in the donor-acceptor blend implies that under steady state excitation, ions will induce the majority of excitons to convert to CT states in the CPE, potentially accounting for all of the observed PL quenching.

We have synthesized a CPE with a low density ionic sidechains and applied time-resolved spectroscopy techniques in order to isolate the inherent interactions between excitons and ionic charges in CPE films. Without wishing to be bound by any particular theory, we believe that time-resolved emission and absorption spectroscopy show that in films of FN-BF₄-7%, the primary exciton resembles that of the non-ionic counterpart (F8BT). Excitons then undergo activated hopping ($E_{\text{act}} = 28$ meV) until the majority

encounter a region where ions interact with the polymer backbone in FN-BF₄-7%. Beyond this timescale, the excited state population exhibits longer-lived emission that is stabilized by 0.3 eV, loss of stimulated emission, and a broadened photo-induced absorption signal. These spectral features
5 provide strong evidence for photogenerated CT states induced by the interaction of ions with bound excitons in CPEs.

These findings have significant implications for the design of conjugated polymer devices that incorporate ionic charge carriers. Unless the
10 interaction between ions and conjugated polymer backbone is well-controlled, morphologies must be optimized to exclude ions from exciton transporting domains. In the case of LEDs, it is notable that ions are most effectively deployed as a layer that is well-separated from the recombination zone where emissive excitons are generated.

15 Producing a favorable morphology that exploits mobile ionic charges to assist electronic charge separation in bulk heterojunction polymer PV devices is more challenging. Here, ions must be distributed on the nanometer lengthscale at donor-acceptor interfaces throughout the active
20 layer in order to assist charge separation, whilst being excluded from within exciton transporting domains. Our data demonstrates that excitons are effectively funneled towards ionic regions, thereby allowing us to direct the motion of excitons by controlling the spatial distribution of ions and their interaction strengths. We note that counter ions could be readily substituted
25 in order to tune the energetic balance between excitons and separated charges in CPEs.

Accordingly, the presented data demonstrates that CPE with low density ionic sidechains are eminently usable in PV devices and that the presence of
30 ions at the interface between donor and acceptor layers can lead to improved performance of such devices.

It will be readily appreciated by the skilled person, that other ionic species may be incorporated into the polymeric structure. It will be further appreciated that other CPEs and molecular semiconductors (*e.g.* fullerenes) may be used in the invention outlined herein.

5

It will be further appreciated that one or both of the species may have tethered ions as discussed above.

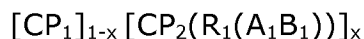
Claims

- 5 1. A photovoltaic (PV) device having an electron donor region and electron acceptor region, the donor and acceptor regions comprising conjugated polymers and/or molecular semiconductors, ion pairs being, preferably preferentially, located at, near or towards the interface between the donor and acceptor regions.
- 10 2. A PV device according to Claim 1, wherein the cation and anion pairs are located towards or at either side of the interface or the cations one side and anions towards or at the other of the interface.
- 15 3. A PV device according to Claim 1 or 2, wherein the ion pairs are provided on, tethered to, or as side chains to the or one of the conjugated polymer(s) and/or molecular semiconductors.
- 20 4. A PV device according to Claim 1, 2 or 3, wherein one or both of the donor and acceptor conjugated polymers are copolymers.
5. A PV device according to Claim 4, wherein the copolymers comprise an ionic unit and a non-ionic unit.
- 25 6. A PV device according to Claim 5, wherein the ionic unit provides a minor proportion of the copolymer.
- 30 7. A PV device according to Claim 4 or 5, wherein the ionic unit comprises less than 40, say less than 30, e.g. less than 20 and preferably 10% or less of the copolymer.
8. A PV device according to Claim 7, wherein the ionic unit comprises between 0.001 and 9.999% of the copolymer.

9. A PV device according to any preceding Claim wherein the ions are redox inert ions.

5

10. A PV device according to any preceding Claim, comprising a polymer of the form:



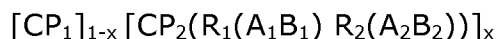
10

Where CP_1 and CP_2 are conjugated polymers;

R_1 is an alkyl group of C_2 - C_{18}

A_1B_1 are together an ion pair.

11. A PV device according to any preceding Claim, comprising a polymer of the form:



20

Where CP_1 and CP_2 are the same or different conjugated polymers;

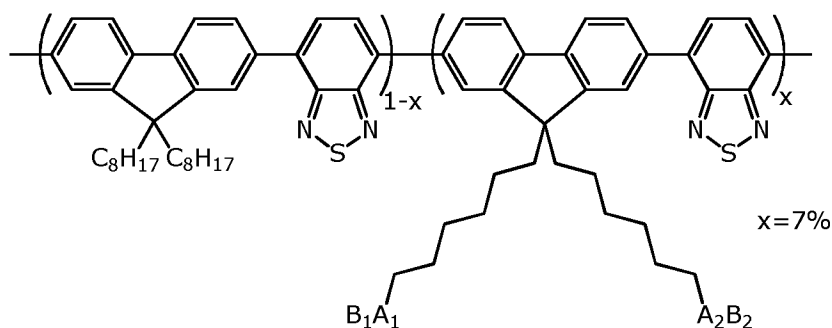
R_1 and R_2 are the same or different alkyl or substituted groups of C_2 - C_{20}

A_1B_1 are together an ion pair

A_2B_2 are together an ion pair

25

12. A PV device according to any preceding Claim, comprising:



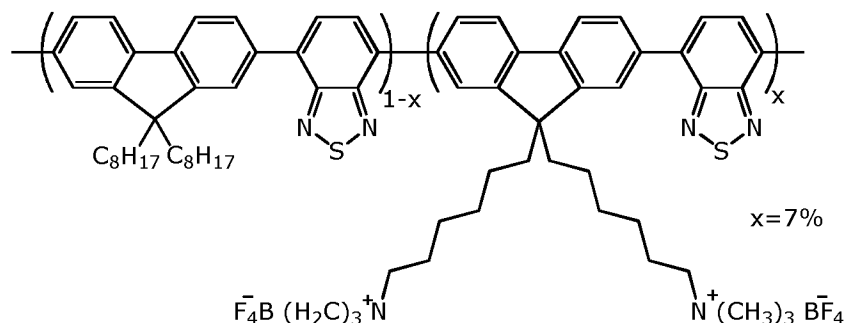
30

Where A_1B_1 and A_2B_2 are together an ion pair.

13. A PV device according to Claim 11 or 12, wherein A_1B_1 and A_2B_2 are the same.

5

14. A PV device according to any preceding Claim, comprising:



- 10 15. A PV device according to Claim 1, wherein the interface between donor and acceptor regions is formed from or comprises a tri-block oligomer comprising donor and acceptor blocks.

- 15 16. A PV device according to Claim 1, wherein the interface between donor and acceptor regions is formed from or comprises donor and acceptor polymers having respective complementary ion pairs.

17. A photoresponsive device including a semiconducting polymer comprising redox inert ions.

20

18. A device according to Claim 17, wherein the semiconducting polymer is a copolymer.

19. A device according to Claim 17, wherein the redox inert ions are located at, adjacent or towards the interface between donor and acceptor regions.

25

20. A device as hereinbefore described and with reference to the accompanying Figures.

30

21. A method of providing ions at the interface of donor and acceptor regions in a PV device, the method comprising blending an n-block oligomer having donor and acceptor blocks with homopolymers of the respective donor and acceptor.

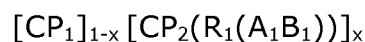
22. A method of providing ions at the interface of donor and acceptor regions in a PV device, the method comprising providing donor and acceptor polymers having respective complementary ion pairs.

23. A method of facilitating electron-hole separation by locating ions at or towards an interface between donor and acceptor regions of a photovoltaic or photoresponsive cell to screen the electrostatic attraction between the electron and associated hole.

24. A method according to Claim 23, further comprising generating a neutral exciton in a donor region to align with the ions.

25. A method as hereinbefore described.

26. A polymer for a PV device of the form:

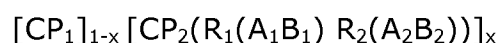


Where CP_1 and CP_2 are the same or different conjugated polymers;

R_1 is an alkyl group of C_2 - C_{20}

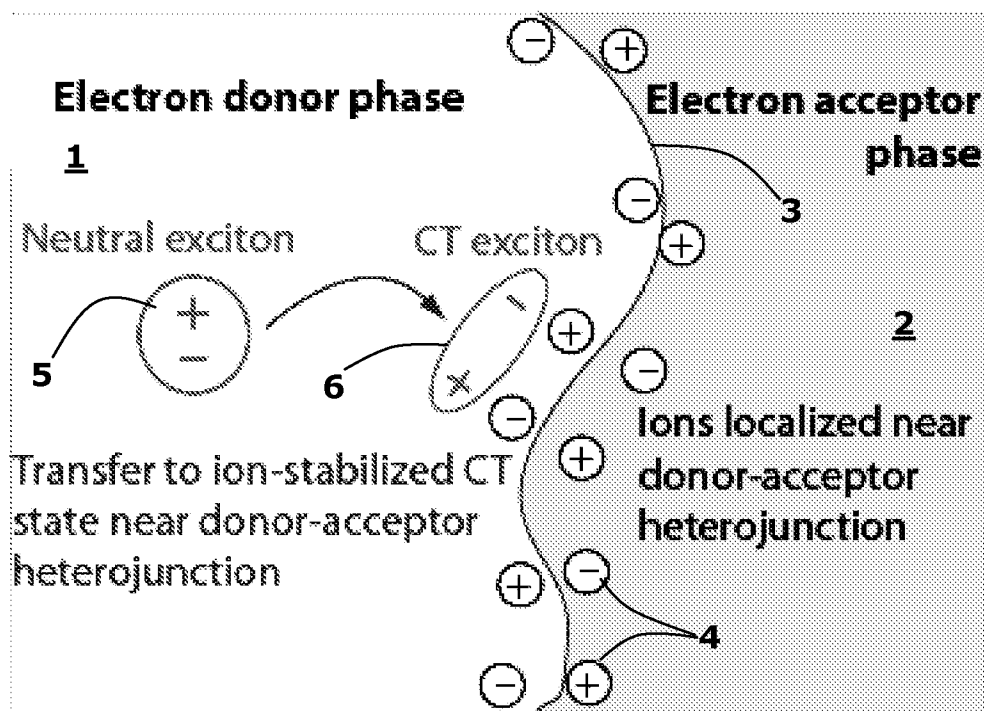
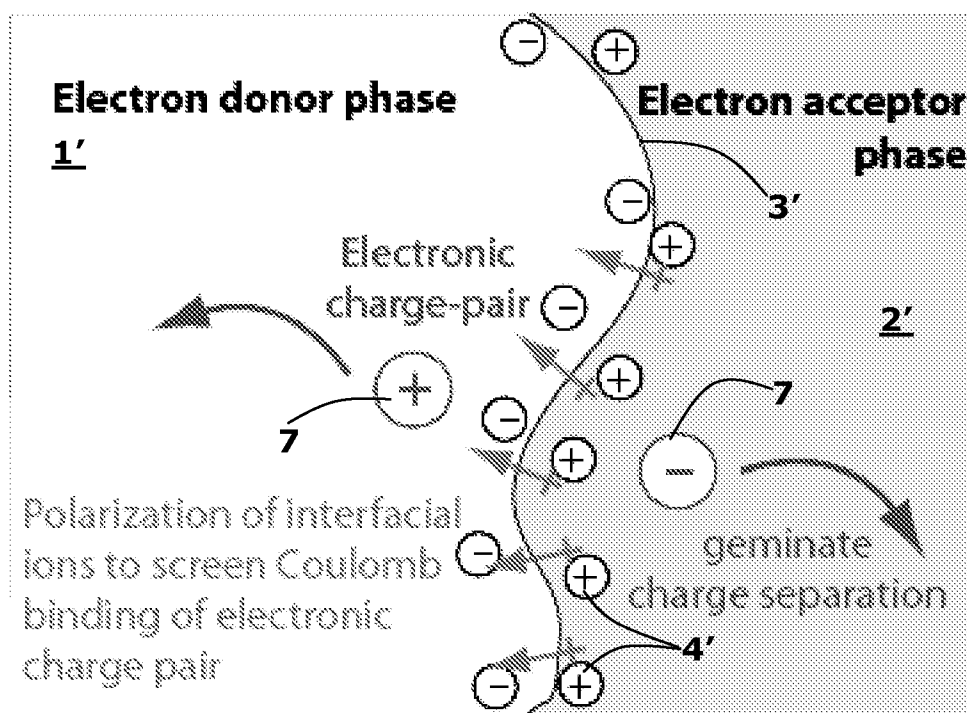
A_1B_1 are together an ion pair.

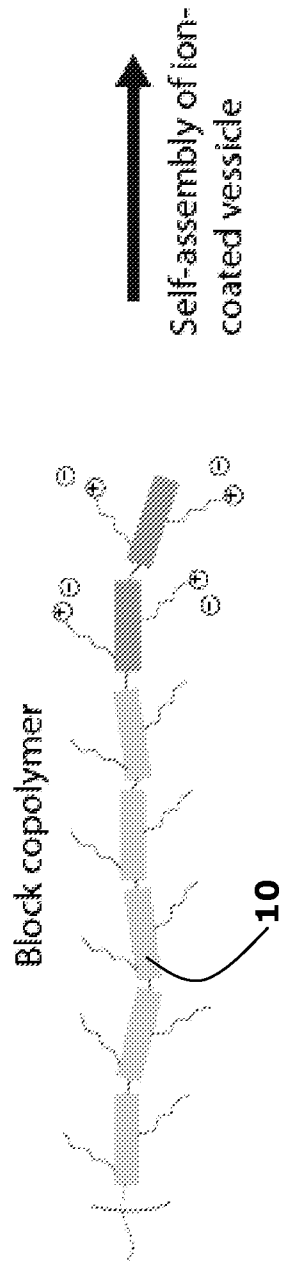
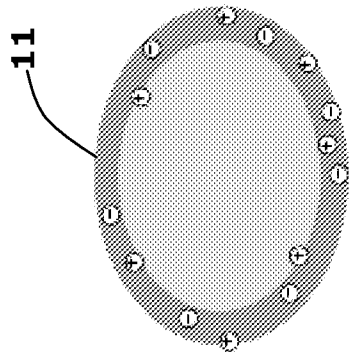
27. A polymer for a PV device of the form:



5

Where CP_1 and CP_2 are the same or different conjugated polymers;
 R_1 and R_2 are the same or different alkyl or substituted alkyl groups
of C_2 - C_{20}
 A_1B_1 are together an ion pair
 A_2B_2 are together an ion pair

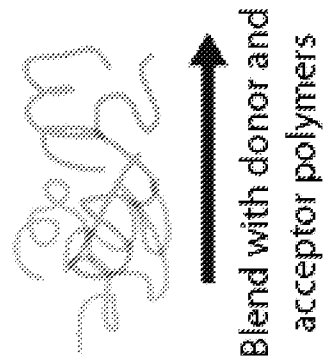
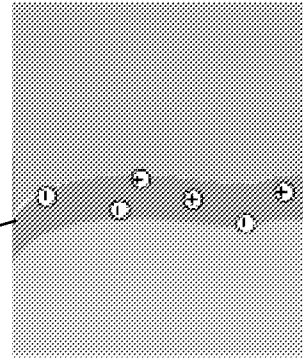
**Figure 1****Figure 2**



Self-assembly of ion-coated vesicle

Figure 3

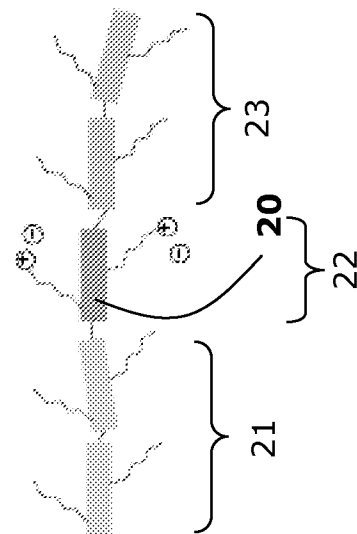
3,3'



Blend with donor and acceptor polymers

Figure 4

Tri-block donor-ion-acceptor surfactant



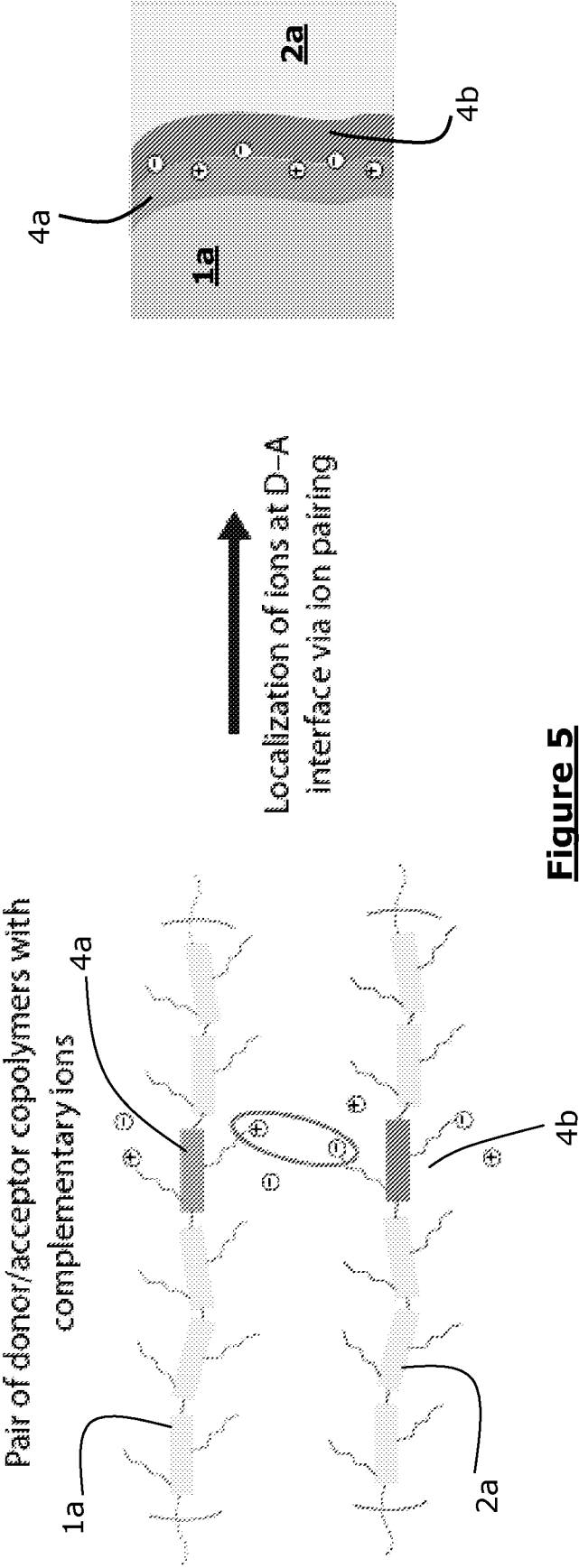
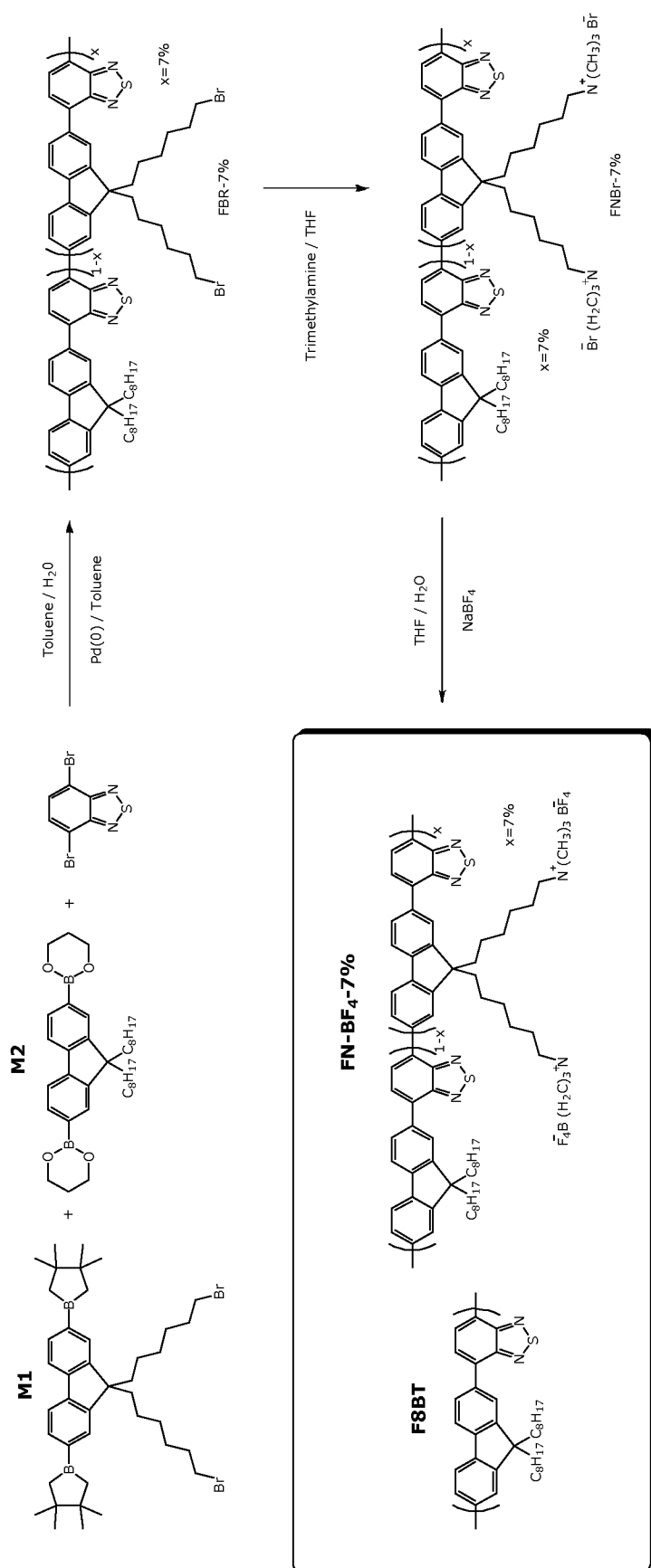
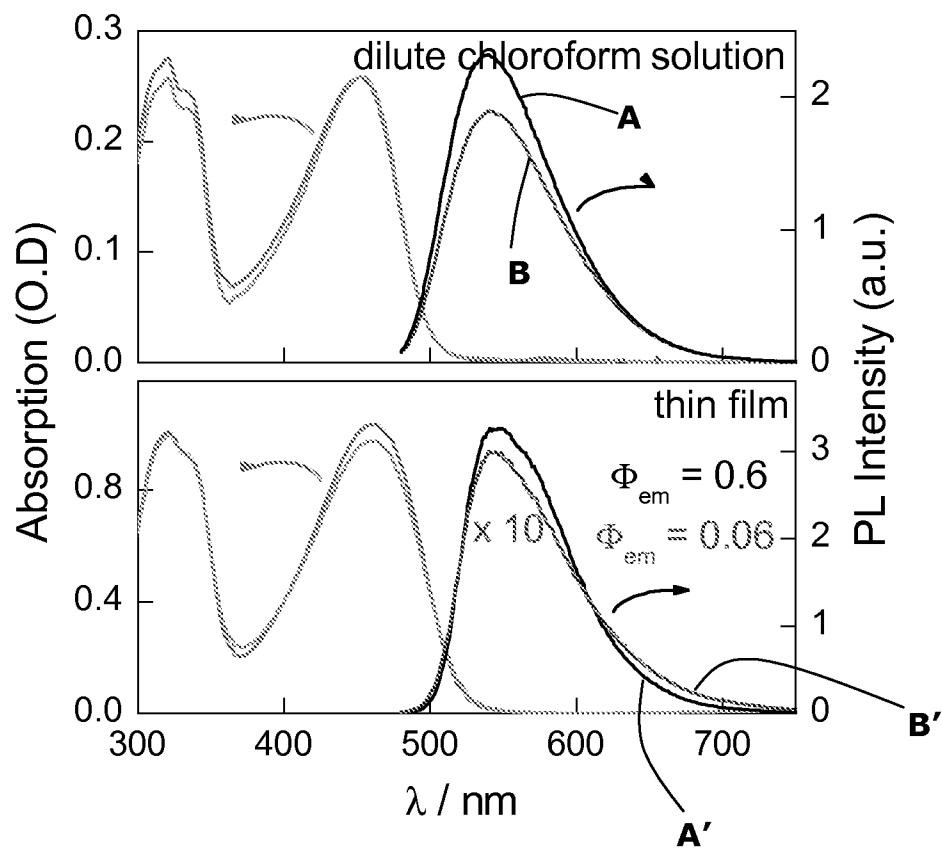
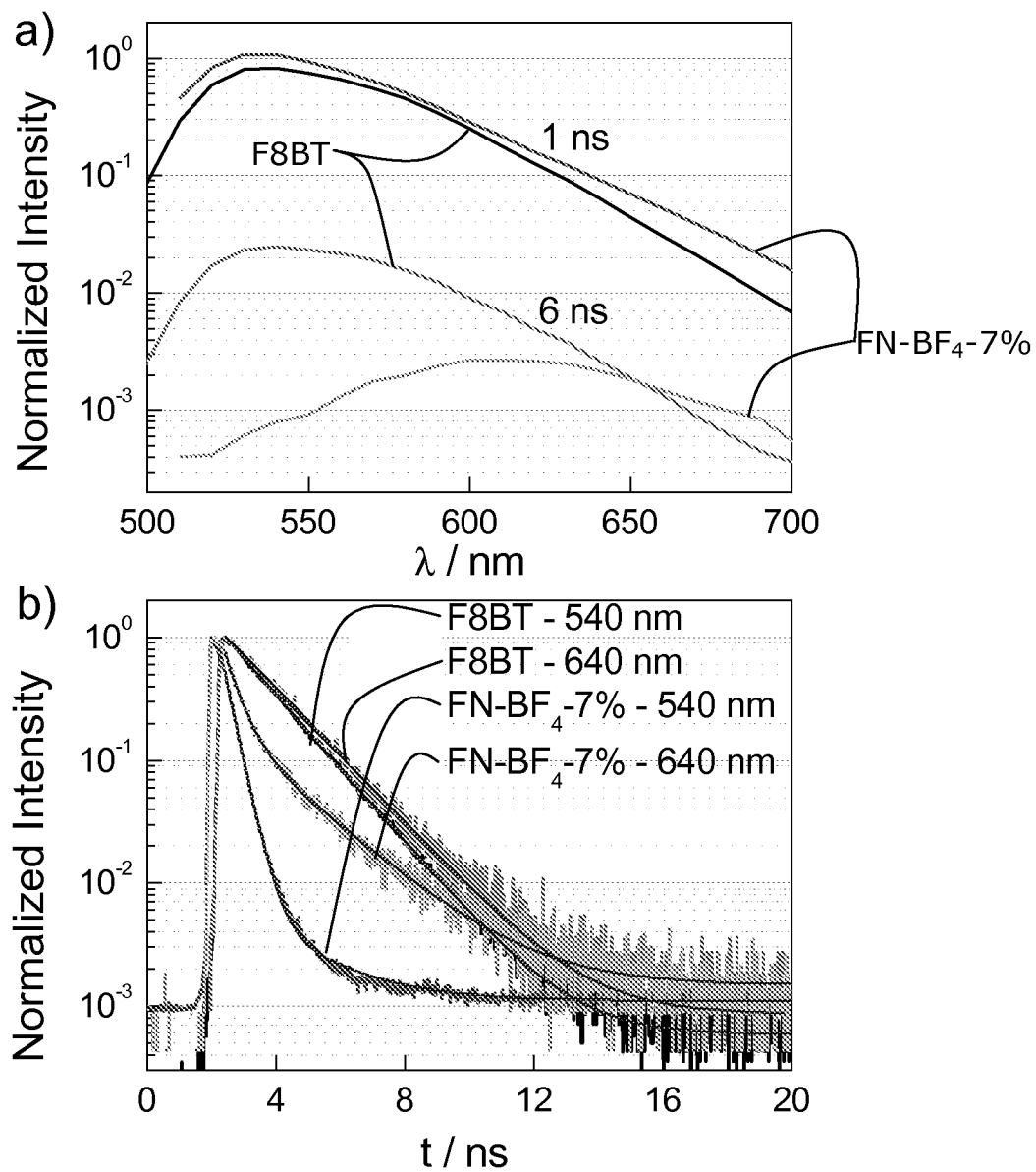
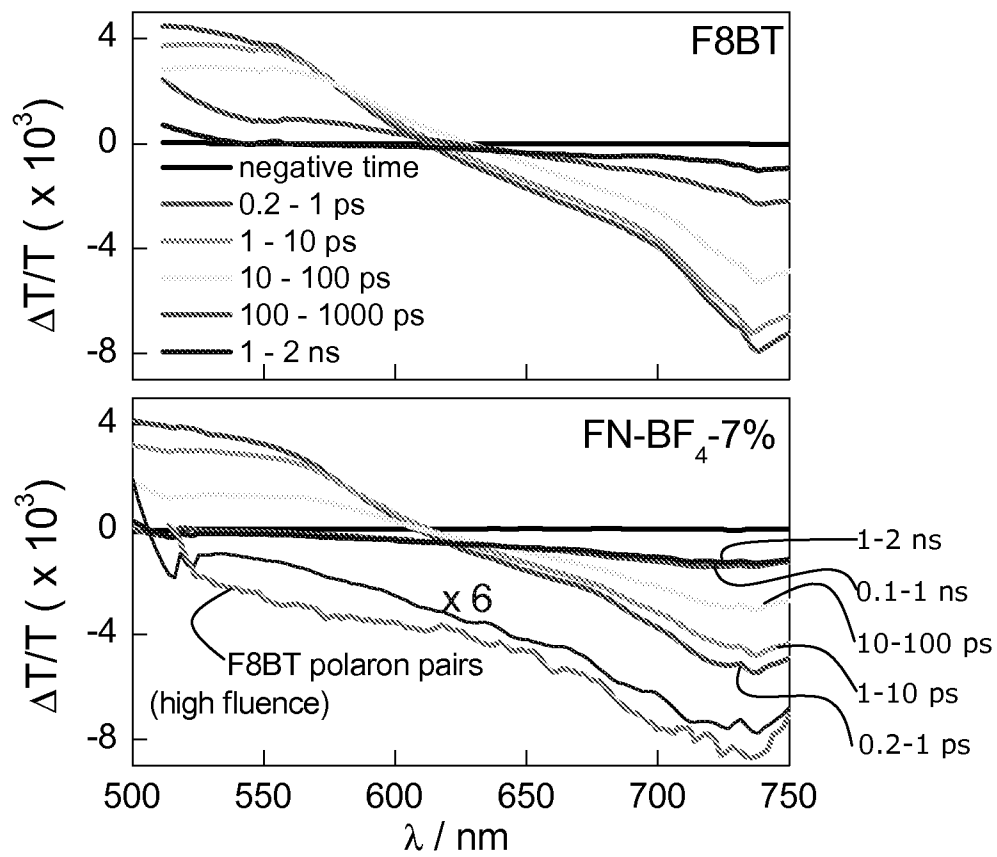


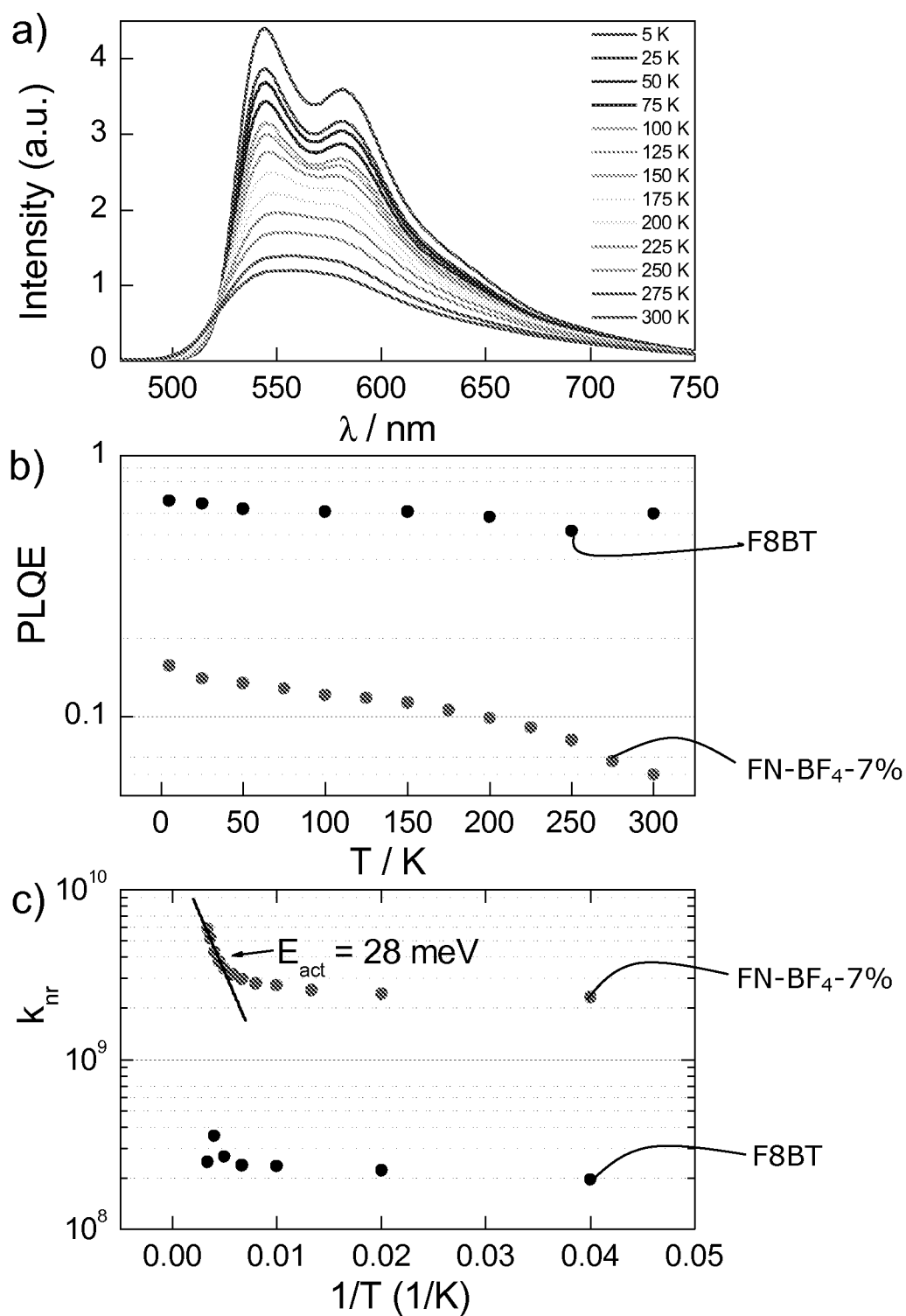
Figure 5

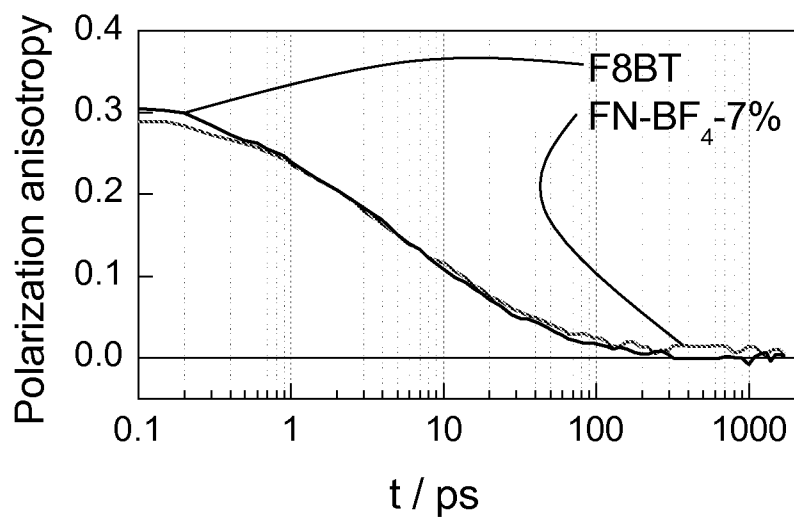
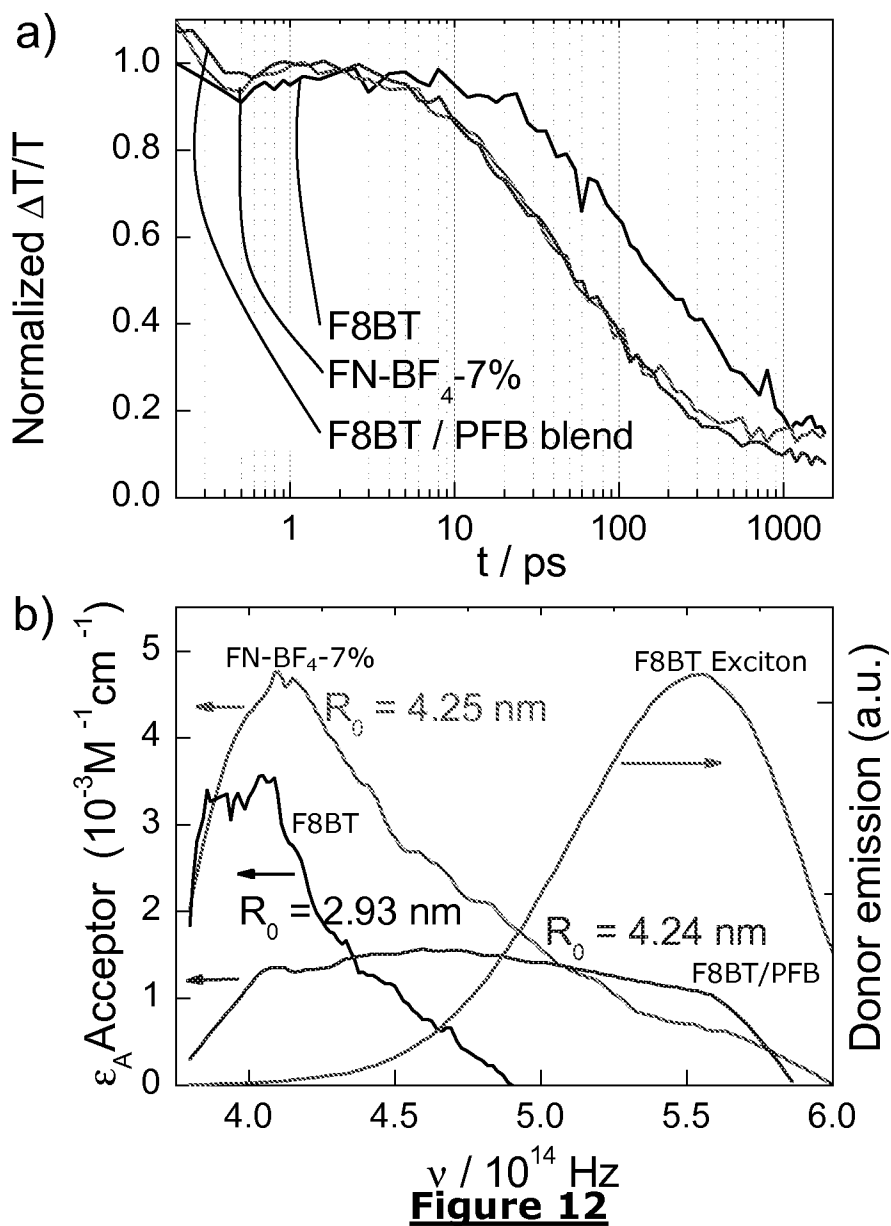
**Figure 6**

**Figure 7**

**Figure 8**

**Figure 9**

**Figure 10**

**Figure 11****Figure 12**

INTERNATIONAL SEARCH REPORT

International application No

PCT/GB2010/050726

A. CLASSIFICATION OF SUBJECT MATTER
INV. H01L51/42

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)

H01L

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 practical, search terms used)

EPO-Internal, INSPEC, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WANG P ET AL: "NOVEL ROOM TEMPERATURE IONIC LIQUIDS OF HEXAALKYL SUBSTITUTED GUANIDINIUM SALTS FOR DYE-SENSITIZED SOLAR CELLS" APPLIED PHYSICS A: MATERIALS SCIENCE & PROCESSING, SPRINGER INTERNATIONAL, DE LNKD- DOI:10.1007/S00339-003-2505-X, vol. 79, 1 January 2004 (2004-01-01), pages 73-77, XP002290891 ISSN: 0947-8396 the whole document ----- -/--	1,9

☒ 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 document 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

21 July 2010

Date of mailing of the international search report

08/10/2010

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
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Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Königstein, C

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2010/050726

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	BACH U ET AL: "SOLID-STATE DYE-SENSITIZED MESOPOROUS TiO2 SOLAR CELLS WITH HIGH PHOTON-TO-ELECTRON CONVERSION EFFICIENCIES" NATURE, NATURE PUBLISHING GROUP, LONDON, GB LNKD- DOI:10.1038/26936, vol. 395, 8 October 1998 (1998-10-08), pages 583-585, XP000783901 ISSN: 0028-0836 the whole document -----	1,2,9
X	US 2009/050199 A1 (BARTHOLOMEW GLENN P [US] ET AL) 26 February 2009 (2009-02-26) paragraph [0054] - paragraph [0060]; . figure 2 -----	1,23
X	SMESTAD G P ET AL: "A technique to compare polythiophene solid-state dye sensitized TiO2 solar cells to liquid junction devices" SOLAR ENERGY MATERIALS AND SOLAR CELLS, ELSEVIER SCIENCE PUBLISHERS, AMSTERDAM, NL LNKD- DOI:10.1016/S0927-0248(02)00252-0, vol. 76, no. 1, 15 February 2003 (2003-02-15), pages 85-105, XP004400821 ISSN: 0927-0248 the whole document -----	1,3
X	EP 1 289 028 A1 (SONY INT EUROP GMBH [DE] SONY DEUTSCHLAND GMBH [DE]) 5 March 2003 (2003-03-05) the whole document -----	1,2,9
X	GB 2 424 512 A (RISO NAT LAB [DK]) 27 September 2006 (2006-09-27) page 9, line 25 - page 11, line 10; figure 1 -----	1,3-5

INTERNATIONAL SEARCH REPORT

International application No.
PCT/GB2010/050726

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: 20, 25
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1-9, 23, 24

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box II.2

Claims Nos.: 20, 25

A meaningful search is not possible on the basis of claims 20,25, because these claims are making reference to Figures and/or the description (Rule 6.2 (a) PCT).

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guideline C-VI, 8.2), should the problems which led to the Article 17(2)PCT declaration be overcome.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-9, 23, 24

Photovoltaic device having cation and anion pairs located towards or at either side of the interface.

2. claims: 10-14, 26, 27

Copolymer and photovoltaic devices comprising the copolymers, wherein the copolymer is block copolymer, one block having conjugated units bearing one or two alkyl side chains terminated with an ion pair.

3. claim: 15

Photovoltaic device wherein the interface between donor and acceptor regions is formed from or comprises a tri-block oligomer comprising donor an acceptor blocks.

4. claims: 16, 22

Photovoltaic device and method of forming a photovoltaic device, wherein the interface between donor and acceptor regions is formed from or comprises donor and acceptor polymers having respective complementary ion pairs.

5. claims: 17-19

Photoresponsive device including a semiconducting polymer comprising redox inert ions.

6. claim: 21

Method of blending an n-block oligomer having donor and acceptor blocks with homopolymers of the respective donor and acceptor.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/GB2010/050726

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 2009050199	A1	26-02-2009	NONE	
EP 1289028	A1	05-03-2003	AU 2002300573 B2	14-12-2006
			DE 60132450 T2	17-04-2008
			EP 1837930 A1	26-09-2007
			JP 4023596 B2	19-12-2007
			JP 2003179244 A	27-06-2003
			KR 20030020854 A	10-03-2003
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