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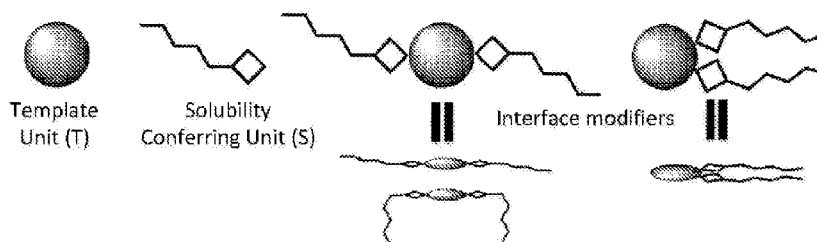
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(54) Title: ACTIVE LAYER MORPHOLOGY CONTROL IN ORGANIC THIN FILMS

FIGURE 1



(57) Abstract: There are provided interface modifiers for template morphology development in organic thin films. The interface modifiers may surface accumulate and self-organise, inducing advantageous morphological changes in organic thin films. The interface modifiers find use in organic electronic devices.

ACTIVE LAYER MORPHOLOGY CONTROL IN ORGANIC THIN FILMS

FIELD

[0001] Interfacial materials for template morphology development in organic thin films are disclosed. These interfacial materials can surface accumulate and self-organise inducing morphological changes in organic thin films. Such interfacial materials find particular, although not exclusive, use in organic electronic devices.

BACKGROUND

[0002] Device performance of bulk heterojunction (BHJ) organic photovoltaics (OPVs) is strongly linked to charge carrier generation and transport, which are closely related to the morphology of the active layer. The exciton diffusion limit in organic semiconductors of 5–15 nm sets an upper limit for the donor domain sizes. The donor and acceptor blend should form a bicontinuous interpenetrating network to allow efficient charge transport to the electrodes. Charge transport can be improved by ordered or crystalline domains that provide high charge carrier mobilities. The active layer morphology can be influenced by methods including thermal annealing, solvent annealing, use of co-solvents, solvent additives, or solid additives. These methods, however, lack in the ability to induce a preferential orientation of molecules in the domains that may be beneficial for the efficient extraction of charge carriers from the bulk heterojunction. For example, self-assembly by π – π stacking may lead to a columnar mesophase of polycyclic aromatic hydrocarbons (PAHs), which exhibit anisotropic semiconducting properties with charge and exciton mobilities being the highest along the main axis of the columns.

[0003] Hexa-peri-hexabenzocoronenes (HBCs) are an illustrative example of PAHs that have a high tendency to self-assemble into columnar structures and display high charge carrier mobility along their main columnar axis. Substrate–HBC interactions are the main driving force for controlled directional growth of HBC molecules. The directional growth of HBC columns can also be controlled by using a monolayer of HBCs as a nucleation site.

[0004] Solution processible organic materials with good film forming ability can offer significant advantages over vacuum deposition in the reduction in complexity of steps and the ability to fabricate large area devices.

[0005] The performance of organic electronic devices is directly related to the properties, both molecular and bulk, of the organic electroactive components. While

desired molecular properties can generally be achieved with smart molecular structure design, bulk materials properties are much more difficult to target in a specific manner. This is due to the fact that bulk properties are a combination of molecular properties as well as intermolecular interactions from the molecular level to nano-metre scale and beyond. As such, it would be desirable to provide methods to control the alignment and molecular association in organic electroactive materials.

[0006] However, the control of molecular alignment is usually complex and substrate specific. It would therefore be desirable to provide a general method to influence morphology development in a controlled manner.

SUMMARY

[0007] There is provided an organic thin film comprising an active layer, a blocking layer, and an interlayer located between the active layer and the blocking layer, said interlayer comprising an amphiphilic interface modifier.

[0008] The amphiphilic interface modifier may, advantageously, provide a templating interlayer at the interface of the blocking layer and the active layer and may provide control of the morphology of the active layer. The interface modifier, when present as a layer on top of the blocking layer, may template the crystallisation of subsequently formed active layers. Advantageously, the interface modifier may change the domain size of molecules in the active layer, and/or change the crystal packing of molecules in the active layer, and/or change the orientation of molecules in the active layer. Such changes may be advantageous in the application of the thin film in organic electronic devices.

[0009] The amphiphilic interface modifier may be self-assembled in the interlayer via hydrophilic-hydrophobic interactions.

[00010] The interlayer comprising the amphiphilic interface modifier may be disposed congruently above the blocking layer.

[00011] As used herein the term 'blocking layer' refers to a layer with high injection barrier for electrons or holes. Blocking layers may contribute to a confinement of electrons and holes, for example, a hole blocking layer may be designed to block holes and allow free passage of electrons, that is transport electrons, and an electron blocking layer may be designed to block electrons and allow free passage of holes, that is transport holes. The term 'blocking layer' as used herein refers to both electron blocking layers and hole blocking layers.

[00012] The amount of amphiphilic interface modifier may be between 0.01 and 10% by weight based on the total weight of the blocking layer and the interface modifier, or between 0.05 and 5% by weight based on the total weight of the blocking layer and the interface modifier, or between 0.05 and 1% by weight based on the total weight of the blocking layer and the interface modifier.

[00013] The interface modifier may be at least partially soluble in a blocking layer formulation. By blocking layer formulation it is meant a solution or mixture of the blocking layer in a suitable solvent. The interface modifier may be substantially soluble in the blocking layer formulation. In this regard the term 'substantially' means that the interface modifier is at least 90% by weight soluble in the blocking layer formulation, or at least 95% by weight soluble in the blocking layer formulation, or 100% by weight soluble in the blocking layer formulation.

[00014] The interface modifier may comprise one or more template units, said template units comprising one or more substituents chemically bonded thereto, wherein the said one or more substituents confers solubility to the interface modifier in an organic solvent.

[00015] The solubility conferring substituents may impart solubility to the interface modifier in solvents orthogonal to those typically used for deposition of an active layer.

[00016] The amphiphilic interface modifier may comprise a hydrophobic template unit and one or more hydrophilic substituents.

[00017] The template unit may be a linear or branched, fused or unfused polycyclic aromatic or polyheteroaromatic.

[00018] The polyheteroaromatic may contain one or more of nitrogen, oxygen, sulphur, phosphorous, boron, silicon or germanium atoms.

[00019] The linear or branched, fused or unfused polycyclic aromatic or polyheteroaromatic may be selected from acenes, rylenes, diketopyrrolopyroles, BODIPY dyes, porphyrins, confused porphyrins, porphyrazines, phthalothocyanines, their metal containing analogues and mixtures thereof.

[00020] The template unit may comprise a coronene unit. The template unit may comprise a hexabenzocoronene unit.

[00021] The template unit may comprise one or more of the following: P3HT (poly(3-hexylthiophene)), PCDTBT (poly[N-9"-hepta-decanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',r,3'- benzothiadiazole)], MEH-PPV (poly[2-methoxy-5-(2'-ethyl-

hexyloxy)-p-phenylene vinylene)), MDMOPPV (poly[2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylene vinylene), phthalocyanine, pentacene, poly(2,7-(9-(2'-ethyl-hexyl)-9-hexyl-fluorene)-alt-5,5-(4',7'-di-2-thienyl-2',r,3'-benzothiadiazole)) (PFDTBT), poly(p-phenylene-ethynylene)-alt-poly(p-phenylene-vinylene) (PPE-PPV), poly((2,7-(9-(2'-ethylhexyl)-9-hexyl-fluorene)-alt-5,5-(4',7'-di-2-thienyl-2', 1', 3'-benzothiadiazole))-co-(2,7-(9-(2'-ethylhexyl)-9-hexyl-fluorene)-alt-2,5-thiophene)) (APFO-5), poly(4,8-bis-alkyloxybenzo(1,2-b:4,5-b')dithiophene-2,6-diyl-alt-(alkylthieno(3,4-b)thiophene-2-(2-ethyl-1-hexanone)-2,6-diyl)) (PBDTTT-C), poly(4,8-bis-alkyloxybenzo(1,2-b:4,5-b')dithiophene-2,6-diyl-alt-(thieno(3,4-b)thiophene-2-carboxylate)-2,6-diyl) (PBDTTT-E), 2-((7-(5-(di-*p*-tolylamino)thiophen-2-yl)benzo[c][1,2,5]thiadiazol-4-yl)methylene)malononitrile (DTDCTB), 3,6-bis(5-(benzofuran-2-yl)thiophen-2-yl)-2,5-bis(2-ethylhexyl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (DPP-(TBFu)₂), perylene, PTCBI (3,4,9,10-perylenetetracarboxylic-bis-benzimidazole), DPP (dihydropyrrolo[3,4-*c*]pyrrole), copper hexadecafluorophthalocyanine (F16-CuPc), 2,3,5,6-tetrafluoro-7, 7,8,8 - tetracyanoquinodimethane (F4TCNQ), 3,4,9,10- perylenetetra-carboxylic dianhydride (PTCDA), fluoro- substituted PTCDA, cyano-substituted PTCDA, naphthalene-tetracarboxylic-dianhydride (NTCDA), fluoro- substituted NTCDA, cyano-substituted NTCDA, and 3,4,9,10-perylene tetracarboxylic bisbenzimidazole (PTCBI), or a repeat unit or oligomeric unit derived therefrom.

[00022] The one or more solubility conferring substituents may be independently selected from branched or unbranched, linear or cyclic, substituted or unsubstituted ethers, polyethers, amines, amides, carbamates, acids and alcohols.

[00023] The solubility conferring substituents may be independently substituted with one or more further substituents comprising a linear, branched or cyclic hydrocarbon optionally comprising one or more heteroatoms.

[00024] The solubility conferring substituents may be a branched or unbranched, substituted or unsubstituted, polyether group comprising between 4 and 30 carbon atoms.

[00025] The amphiphilic interface modifier may comprise a linear or branched, fused or unfused polycyclic aromatic or polyheteroaromatic substituted with one or more branched or unbranched, substituted or unsubstituted, polyether groups comprising between 4 and 30 carbon atoms.

[00026] The amphiphilic interface modifier may comprise a polyheteroaromatic containing one or more of nitrogen, oxygen, sulphur, phosphorous, boron, silicon or germanium atoms wherein the polyheteroaromatic is substituted with one or more branched or unbranched, substituted or unsubstituted, polyether groups comprising between 4 and 30 carbon atoms.

[00027] The amphiphilic interface modifier may comprise a linear or branched, fused or unfused polycyclic aromatic or polyheteroaromatic selected from acenes, rylenes, diketopyrrolopyroles, BODIPY dyes, porphyrins, confused porphyrins, porphyrazines, phthalothocyanines, their metal containing analogues and mixtures thereof substituted with one or more branched or unbranched, substituted or unsubstituted, polyether groups comprising between 4 and 30 carbon atoms.

[00028] The amphiphilic interface modifier may comprise a coronene unit substituted with one or more branched or unbranched, substituted or unsubstituted, polyether groups comprising between 4 and 30 carbon atoms.

[00029] The amphiphilic interface modifier may comprise a hexabenzocoronene unit substituted with one or more branched or unbranched, substituted or unsubstituted, polyether groups comprising between 4 and 30 carbon atoms.

[00030] The template unit may be substituted by the solubility conferring substituents so as to direct orientation of the interface modifier in a preferred orientation at an interface. In this way, the crystal orientation in the organic thin film may be controlled by the placement of the solubility conferring groups on the interface modifier.

[00031] The template unit may be self-assembled through π - π stacking. The template unit may be self-assembled through π - π stacking of a linear or branched, fused or unfused polycyclic aromatic or polyheteroaromatic selected from acenes, rylenes, diketopyrrolopyroles, BODIPY dyes, porphyrins, confused porphyrins, porphyrazines, phthalothocyanines, their metal containing analogues and mixtures thereof substituted with one or more branched or unbranched, substituted or unsubstituted, polyether groups comprising between 4 and 30 carbon atoms.

[00032] The template unit may have a free energy such that it migrates to and accumulates at the blocking layer–air interface during preparation of the organic thin film, for example during deposition or drying or annealing of the blocking layer or transport layer.

[00033] The solubility conferring substituents may increase the conductivity of the blocking layer or transport layer.

[00034] The template unit may be chosen to match a unit in the active layer. The template unit may comprise a unit or subunit that is the same as a unit or subunit in the active layer. For example, if the active layer comprises a hexabenzocoronene unit then the template unit may also comprise a hexabenzocoronene unit.

[00035] The active layer may comprise a donor or an acceptor or a donor:acceptor blend.

[00036] The active layer may comprise a linear or branched, fused or unfused, substituted or unsubstituted, polycyclic aromatic or polyheteroaromatic.

[00037] The polyheteroaromatic may contain one or more of nitrogen, oxygen, sulphur, phosphorous, boron, silicon or germanium atoms.

[00038] The linear or branched, fused or unfused polycyclic aromatic or polyheteroaromatic may be selected from acenes, rylene, diketopyrrolopyroles, BODIPY dyes, porphyrins, confused porphyrins, porphyrazines, phthalothocyanines, their metal containing analogues and mixtures thereof.

[00039] The active layer may comprise a coronene. The active layer may comprise a hexabenzocoronene unit. The active layer may comprise a hexabenzocoronene unit substituted with one or more fluorenyl units.

[00040] The active layer may comprise but is not limited to one or more of the following: P3HT (poly(3-hexylthiophene)), PCDTBT (poly[N-9"-hepta-decanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',r,3'- benzothiadiazole)], MEH-PPV (poly[2-methoxy-5-(2'-ethyl-hexyloxy)-p-phenylene vinylene]), MDMOPPV (poly[2-methoxy-5-(3,7-dimethyloctyloxy)-l-4-phenylene vinylene]), phthalocyanine, pentacene, poly(2,7-(9-(2'-ethyl-hexyl)-9-hexyl-fluorene)-alt-5,5-(4',7'-di-2-thienyl-2',r,3'- benzothiadiazole)) (PFDTBT), poly(p-phenylene-ethynylene)-alt-poly(p-phenylene-vinylene) (PPE-PPV), poly((2,7-(9-(2'-ethylhexyl)-9-hexyl-fluorene)-alt-5,5-(4',7'-di-2-thienyl-2', 1', 3'-benzothiadiazole))-co-(2,7-(9-(2'-ethylhexyl)-9-hexyl-fluorene)-alt-2,5-thiophene)) (APFO-5), poly(4,8-bis-alkyloxybenzo(l,2-b:4,5-b')dithiophene-2,6-diyl-alt-(alkylthieno(3,4-b)thiophene-2-(2-ethyl-l-hexanone)-2,6-diyl)) (PBDTTT-C), poly(4,8-bis-alkyloxybenzo(l,2-b:4,5-b')dithiophene-2,6-diyl-alt-(thieno(3,4-b)thiophene-2-carboxylate)-2,6-diyl) (PBDTTT-E), 2-((7-(5-(di-p-tolylamino)thiophen-2-yl)benzo[c][1,2,5]thiadiazol-4-yl)methylene)malononitrile (DTDCTB), 3,6-bis(5-(benzofuran-2-yl)thiophen-2-yl)-2,5-bis(2-ethylhexyl)pyrrolo[3,4-c]pyrrole-1,4(2*H*,5*H*)-

dione (DPP-(TBFu)₂), perylene, PTCBI (3,4,9,10-perylenetetracarboxylic-bis-benzimidazole), DPP (dihydropyrrolo[3,4-c]pyrrole), copper hexadecafluorophthalocyanine (F16-CuPc), 2,3,5,6-tetrafluoro-7, 7,8,8 - tetracyanoquinodimethane (F4TCNQ), 3,4,9,10- perylenetetra-carboxylic dianhydride (PTCDA), fluoro- substituted PTCDA, cyano-substituted PTCDA, naphthalene-tetracarboxylic-dianhydride (NTCDA), fluoro- substituted NTCDA, cyano-substituted NTCDA, and 3,4,9,10-perylene tetracarboxylic bisbenzimidazole (PTCBI), or a repeat unit or oligomeric unit derived therefrom.

[00041] The blocking layer may comprise polyethylenedioxythiophene doped with polystyrenesulfonate (PEDOT:PSS), MoO₃, V₂O₅, NiO, CrO₃, ZnO or TiO₂.

[00042] The organic thin film may comprise an active layer comprising a hexabenzocoronene unit, a blocking layer comprising PEDOT:PSS, and an interlayer located between the active layer and the blocking layer, said interlayer comprising an amphiphilic interface modifier. The amphiphilic interface modifier may comprise a hexabenzocoronene template unit substituted with branched or unbranched, linear or cyclic, substituted or unsubstituted ethers, polyethers, amines, amides, carbamates, acids and alcohols.

[00043] There is also provided a method of preparing an organic thin film comprising the steps of:

- (a) forming a blocking layer on a substrate;
- (b) forming a layer of amphiphilic interface modifier on the blocking layer;
- and
- (c) forming an active layer on the layer of amphiphilic interface modifier.

[00044] The substrate may be a transparent conducting oxide. The substrate may be an indium tin oxide glass. The blocking layer may be formed by spin coating. The method may further comprise the step of annealing the blocking layer prior to forming the layer of amphiphilic interface modifier. The layer of amphiphilic interface modifier may be formed by spin coating. The method may further comprise the step of annealing the layer of amphiphilic interface modifier prior to forming the active.

[00045] The interface modifier may be provided dissolved in a suitable solvent. The layer of interface modifier may be spin coated from a solution of the interface modifier in a suitable solvent. The material for the active layer may be provided dissolved in a suitable solvent. The active layer may be spin coated from a solution of the active material. The active material may be provided in a solvent that is

orthogonal to the solvent used for the interface modifier. This may allow the active layer to be deposited without comprising the already formed layer of interfacial modifier.

[00046] There is also provided a method of preparing an organic thin film comprising the steps of:

- (a) blending a blocking material with an amphiphilic interface modifier;
- (b) forming a layer of the blend on a substrate; and
- (c) forming an active layer on the layer of the blend.

[00047] The substrate may be a transparent conducting oxide. The substrate may be an indium tin oxide glass. The layer of the blend of blocking material and amphiphilic interface modifier may be formed by spin coating. The method may further comprise the step of annealing the layer of the blend of blocking material and amphiphilic interface modifier prior to forming the active layer.

[00048] The blend may be provided dissolved in a suitable solvent. The layer of the blend may be spin coated from a solution of the blend in a suitable solvent. The active material may be provided dissolved in a suitable solvent. The layer of active material may be spin coated from a solution of the active material. The active material may be provided in a solvent that is orthogonal to the solvent used for the blend. This may allow the active layer to be deposited without comprising the already formed layer of the blend.

[00049] The method may also involve the step of, after forming the layer of the blend on the substrate, but before forming a layer of active material, treating the thin film so that the interface modifier migrates to the surface of the blend layer, and/or surface accumulates on the blend layer, and/or self assembles on the blend layer. Such treatment may include depositing, drying and/or annealing.

[00050] The method involving blending a blocking material with an amphiphilic interface modifier is advantageous as it avoids the additional step of separately depositing the interlayer. This is particularly useful in roll-to-roll production of optoelectronic devices.

[00051] In any of the hereinbefore disclosed methods the amount of amphiphilic interface modifier may be between 0.01 and 10% by weight based on the total weight of the blocking layer and interface modifier, or between 0.05 and 5% by weight based on the total weight of the blocking layer and interface modifier, or between 0.05 and 1% by weight based on the total weight of the blocking layer and interface modifier.

[00052] The interface modifier may be at least partially soluble in the blocking layer formulation. By formulation it is meant a solution or mixture of the blocking layer in a suitable solvent. The interface modifier may be substantially soluble in the blocking layer formulation. In this regard the term 'substantially' means that the interface modifier is at least 90% by weight soluble in the blocking layer formulation, or at least 95% by weight soluble in the blocking layer formulation, or 100% by weight soluble in the blocking layer formulation.

[00053] In any of the hereinbefore disclosed methods the interface modifier may comprise one or more template units, said template units comprising one or more substituents chemically bonded thereto, wherein said one or more substituents confers solubility to the interface modifier in an organic solvent.

[00054] In any of the hereinbefore disclosed methods the interface modifier may comprise a hydrophobic template unit and one or more hydrophilic substituents.

[00055] The solubility conferring substituents may impart solubility to the interface modifier in solvents orthogonal to those typically used for deposition of an active layer.

[00056] The template unit may be a linear or branched, fused or unfused polycyclic aromatic or polyheteroaromatic.

[00057] The polyheteroaromatic may contain one or more of nitrogen, oxygen, sulphur, phosphorous, boron, silicon or germanium atoms.

[00058] The linear or branched, fused or unfused polycyclic aromatic or polyheteroaromatic may be selected from acenes, rylene, diketopyrrolopyroles, BODIPY dyes, porphyrins, confused porphyrins, porphyrazines, phthalothocyanines, their metal containing analogues and mixtures thereof.

[00059] The template unit may comprise a coronene unit. The template unit may comprise a hexabenzocoronene unit.

[00060] The template unit may comprise but is not limited to one or more of the following: P3HT (poly(3-hexylthiophene)), PCDTBT (poly[N-9"-hepta-decanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',r,3'- benzothiadiazole)], MEH-PPV (poly[2-methoxy-5-(2'-ethyl-hexyloxy)-p-phenylene vinylene]), MDMOPPV (poly[2-methoxy-5-(3,7-dimethyloctyloxy)-l-4-phenylene vinylene]), phthalocyanine, pentacene, poly(2,7-(9-(2'-ethyl-hexyl)-9-hexyl-fluorene)-alt-5,5-(4',7'-di-2-thienyl-2',r,3'- benzothiadiazole)) (PFDTBT), poly(p-phenylene-ethynylene)-alt-poly(p-phenylene-vinylene) (PPE-PPV), poly((2,7-(9-(2'-ethylhexyl)-9-hexyl-fluorene)-alt-5,5-(4',7'-di-2-

thienyl-2', 1', 3'-benzothiadiazole))-co-(2,7-(9-(2'-ethylhexyl)-9-hexyl-fluorene)-alt-2,5-thiophene)) (APFO-5), poly(4,8-bis-alkyloxybenzo(1,2-b:4,5-b')dithiophene-2,6-diyl-alt-(alkylthieno(3,4-b)thiophene-2-(2-ethyl-1-hexanone)-2,6-diyl)) (PBDTTT-C), poly(4,8-bis-alkyloxybenzo(1,2-b:4,5-b')dithiophene-2,6-diyl-alt-(thieno(3,4-b)thiophene-2-carboxylate)-2,6-diyl) (PBDTTT-E), 2-((7-(5-(di-*p*-tolylamino)thiophen-2-yl)benzo[*c*][1,2,5]thiadiazol-4-yl)methylene)malononitrile (DTDCTB), 3,6-bis(5-(benzofuran-2-yl)thiophen-2-yl)-2,5-bis(2-ethylhexyl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (DPP-(TBFu)₂), perylene, PTCBI (3,4,9,10-perylenetetracarboxylic-bis-benzimidazole) or DPP (dihydropyrrolo[3,4-*c*]pyrrole), copper hexadecafluorophthalocyanine (F16-CuPc), 2,3,5,6-tetrafluoro-7, 7,8,8 - tetracyanoquinodimethane (F4TCNQ), 3,4,9,10- perylenetetra-carboxylic dianhydride (PTCDA), fluoro- substituted PTCDA, cyano-substituted PTCDA, naphthalene-tetracarboxylic-dianhydride (NTCDA), fluoro- substituted NTCDA, cyano-substituted NTCDA, and 3,4,9,10-perylene tetracarboxylic bisbenzimidazole (PTCBI), or a repeat unit or oligomeric unit derived therefrom.

[00061] The one or more solubility conferring substituents may be independently selected from branched or unbranched, linear or cyclic, substituted or unsubstituted ethers, polyethers, amines, amides, carbamates, acids and alcohols.

[00062] The solubility conferring substituents may be independently substituted with one or more further substituents comprising a linear, branched or cyclic hydrocarbon optionally comprising one or more heteroatoms.

[00063] The solubility conferring substituents may be a branched or unbranched, substituted or unsubstituted, polyether group comprising between 4 and 30 carbon atoms.

[00064] In any of the hereinbefore disclosed methods the template unit may be substituted by the solubility conferring substituents so as to direct orientation of the interface modifier in a preferred orientation at an interface. In this way, the crystal orientation in the organic thin film may be controlled by the placement of the solubility conferring groups on the interface modifier.

[00065] In any of the hereinbefore disclosed methods the template unit may self-assemble through π - π stacking.

[00066] In any of the hereinbefore disclosed methods the template unit may have a free energy such that it migrates to and accumulates at the blocking layer-air

interface during preparation of the organic thin film, for example during deposition or drying or annealing of the blocking layer or transport layer.

[00067] In any of the hereinbefore disclosed methods the solubility conferring substituents may increase the conductivity of the blocking layer or transport layer.

[00068] In any of the hereinbefore disclosed methods the template unit may be chosen to match a unit in the active layer. For example, if the active layer comprises a hexabenzocoronene unit then the template unit may also comprise a hexabenzocoronene unit. The template unit may comprise a unit or subunit of the active material in the active layer.

[00069] The active layer may comprise a linear or branched, fused or unfused polycyclic aromatic or polyheteroaromatic.

[00070] The polyheteroaromatic may contain one or more of nitrogen, oxygen, sulphur, phosphorous, boron, silicon or germanium atoms.

[00071] The linear or branched, fused or unfused polycyclic aromatic or polyheteroaromatic may be selected from acenes, rylenes, diketopyrrolopyroles, BODIPY dyes, porphyrins, confused porphyrins, porphyrazines, phthalothocyanines, their metal containing analogues and mixtures thereof.

[00072] The active layer may comprise a coronene unit. The active layer may comprise a hexabenzocoronene unit.

[00073] The active layer may comprise but is not limited to one or more of the following: P3HT (poly(3-hexylthiophene)), PCDTBT (poly[N-9"-hepta-decanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',r,3'- benzothiadiazole)], MEH-PPV (poly[2-methoxy-5-(2'-ethyl-hexyloxy)-p-phenylene vinylene]), MDMOPPV (poly[2-methoxy-5-3(3,7-dimethyloctyloxy)-l-4-phenylene vinylene]), phthalocyanine, pentacene, poly(2,7-(9-(2'-ethyl-hexyl)-9-hexyl-fluorene)-alt-5,5-(4',7'-di-2-thienyl-2',r,3'- benzothiadiazole)) (PFDTBT), poly(p-phenylene-ethynylene)-alt-poly(p-phenylene-vinylene) (PPE-PPV), poly((2,7-(9-(2'-ethylhexyl)-9-hexyl-fluorene)-alt-5,5-(4',7'-di-2-thienyl-2', 1', 3'-benzothiadiazole))-co-(2,7-(9-(2'-ethylhexyl)-9-hexyl-fluorene)-alt-2,5-thiophene)) (APFO-5), poly(4,8-bis-alkyloxybenzo(l,2-b:4,5-b')dithiophene-2,6-diyl-alt-(alkylthieno(3,4-b)thiophene-2-(2-ethyl-l-hexanone)-2,6-diyl)) (PBDTTT-C), poly(4,8-bis-alkyloxybenzo(l,2-b:4,5-b')dithiophene-2,6-diyl-alt-(thieno(3,4-b)thiophene-2-carboxylate)-2,6-diyl) (PBDTTT-E), 2-((7-(5-(di-p-tolylamino)thiophen-2-yl)benzo[c][1,2,5]thiadiazol-4-yl)methylene)malononitrile (DTDCTB), 3,6-bis(5-(benzofuran-2-yl)thiophen-2-yl)-2,5-bis(2-ethylhexyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-

dione (DPP-(TBFu)₂), perylene, PTCBI (3,4,9,10-perylenetetracarboxylic-bis-benzimidazole), DPP (dihydropyrrolo[3,4-c]pyrrole), copper hexadecafluorophthalocyanine (F16-CuPc), 2,3,5,6-tetrafluoro-7, 7,8,8 - tetracyanoquinodimethane (F4TCNQ), 3,4,9,10- perylenetetra-carboxylic dianhydride (PTCDA), fluoro- substituted PTCDA, cyano-substituted PTCDA, naphthalene-tetracarboxylic-dianhydride (NTCDA), fluoro- substituted NTCDA, cyano-substituted NTCDA, and 3,4,9,10-perylene tetracarboxylic bisbenzimidazole (PTCBI).

[00074] The blocking layer may comprise polyethylenedioxythiophene doped with polystyrenesulfonate (PEDOT:PSS), MoO₃, V₂O₅, NiO, CrO₃, ZnO, or TiO₂.

[00075] There is also provided an organic thin film formed by any one of the methods as hereinbefore disclosed.

[00076] There is also provided a use of an amphiphilic interface modifier as hereinbefore disclosed in controlling the morphology of an active layer in an optoelectronic device.

[00077] There is also provided the use of an amphiphilic interface modifier as hereinbefore disclosed in the manufacture of an optoelectronic device.

[00078] There is also provided the use of an organic thin film as hereinbefore disclosed in the manufacture of an optoelectronic device.

[00079] There is also provided an optoelectronic device comprising an amphiphilic interface modifier or an organic thin film as hereinbefore disclosed.

[00080] There is also provided an amphiphilic interface modifier comprising one or more template units as hereinbefore disclosed, said template units comprising one or more substituents chemically bonded thereto, wherein said one or more substituents confers solubility to the interface modifier in an organic solvent. The solubility conferring substituents may be any one or more of those hereinbefore disclosed.

[00081] Throughout this specification, use of the terms "comprises" or "comprising" or grammatical variations thereon shall be taken to specify the presence of stated features, integers, steps or components but does not preclude the presence or addition of one or more other features, integers, steps, components or groups thereof not specifically mentioned.

BRIEF DESCRIPTION OF THE FIGURES

[00082] The present disclosure will now be described with reference to the accompanying Figures where:

Figure 1: Diagrammatic representation of the Template Unit (T), Solubility Conferring Unit (S) and Interface Modifiers IM.

Figure 2: Diagrammatic representation of the inclusion of the interface modifier.

Figure 3: Chemical structures of organic electronic materials used in thin film preparation.

Figure 4: Intermediate structures of the compounds used in the synthesis of IM1, IM2, and IM3.

Figure 5: Atomic force microscopy (AFM) images of FHBC thin films modified by amphiphilic HBC modifiers.

Figure 6: Grazing incidence wide angle X-ray scattering (GI-WAXS) images of FHBC thin films modified by amphiphilic HBC modifiers, Examples 2-3.

Figure 7: Transmission electron microscopy (TEM) dark field images of FHBC thin films modified by amphiphilic HBC modifiers, Examples 2-3.

Figure 8: Grazing incidence wide angle X-ray scattering (GI-WAXS) images of FHBC thin films modified by amphiphilic HBC modifiers, Examples 4-6.

Figure 9: Transmission electron microscopy (TEM) dark field images of FHBC thin films modified by amphiphilic HBC modifiers, Examples 4-6.

[00083] It will now be convenient to describe the disclosure with reference to particular embodiments and examples. These embodiments and examples are illustrative only and should not be construed as limiting upon the scope of the disclosure. It will be understood that variations upon the described disclosure as would be apparent to the skilled artisan are within the scope of the disclosure. Similarly, the present disclosure is capable of finding application in areas that are not explicitly recited in this document and the fact that some applications are not specifically described should not be considered as a limitation on the overall applicability of the disclosure.

[00084] Further, before the present compounds, components, compositions, devices, and/or methods are disclosed and described, it is to be understood that unless otherwise indicated this disclosure is not limited to specific compounds, components, compositions, reactants, reaction conditions, ligands, structures, devices, or the like, and as such may vary, unless otherwise specified. It is also to be

understood that the terminology used herein is for the purpose of describing particular embodiments only and is not intended to be limiting.

DETAILED DESCRIPTION

[00085] It is noted that, as used in the specification and the appended claims, the singular forms "a," "an" and "the" include plural referents unless otherwise specified. Thus, for example, reference to "a halogen atom" as in a compound "substituted with a halogen atom" includes more than one halogen atom, such that the compound may be substituted with two or more halogen atoms, reference to "a substituent" includes one or more substituents, reference to "a ligand" includes one or more ligands, and the like.

[00086] For the sake of brevity, only certain ranges are explicitly disclosed herein. However, ranges from any lower limit may be combined with any upper limit to recite a range not explicitly recited, as well as, ranges from any lower limit may be combined with any other lower limit to recite a range not explicitly recited, in the same way, ranges from any upper limit may be combined with any other upper limit to recite a range not explicitly recited.

[00087] In organic opto-electronics, polyethylenedioxythiophene doped with polystyrenesulfonate (PEDOT:PSS) is one of the most commonly used Electron Blocking Layer, or simply Blocking Layer, due to its transparency, desirable energy level and ease of processability. PEDOT:PSS functions to smooth the transparent conducting oxide indium tin oxide (ITO) anode surface and improves hole transport to the electrode. Spin-coating is one of the most attractive techniques to deposit an active layer on top of the PEDOT:PSS layer because it offers a simple means of controlling the active layer thickness. However, this technique lacks control over the molecular orientation and morphology of the film. Thermal annealing is often used to change the morphology of thin films and has been proven to be successful in many cases. However, its exact mechanism is not known and, therefore, it is likely not an appropriate method for achieving control over the morphology of the film. Moreover, it suffers from the inherent use of elevated temperatures and the possible disadvantageous effects associated with it.

[00088] Amphiphilic hexabenzocoronene (HBC) derivatives containing four polyethylene glycol moieties (Figure 3) were synthesized and their surface accumulation characteristics determined and also their effect on the morphology of

an active layer containing fluorenyl-substituted HBC (FHBCs). FHBCs self-assemble via π - π intermolecular stacking in columnar structures, which further adopt a hexagonal packing via inter-columnar interaction. FHBCs can be used as donor material in bulk hetero junction (BHJ) organic photovoltaics (OPVs). In organic field effect transistors (OFETs) a field-effect mobility of $2.8 \times 10^{-3} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ was achieved for FHBCs.

[00089] The surface characteristics of PEDOT:PSS alone or in combination with interface modifiers (IMs) were studied with contact angle measurements, atomic force microscopy (AFM) and PESA. The morphology change of the active layer induced by an interlayer of IMs located between the PEDOT:PSS and active layer was analyzed by grazing incidence wide-angle X-ray scattering (GIWAX), and TEM.

[00090] The following examples demonstrate the efficacy of the presently disclosed amphiphilic interface materials in the modification of organic thin film morphology.

[00091] Example 1 (no interface modification) involves the deposition of a PEDOT:PSS blocking layer onto a transparent conducting oxide (TCO) coated glass substrate followed by deposition of the organic electronic active material FBHC.

[00092] Examples 2-4 involve the deposition by spin casting of the interface modifiers, IM1, IM2 and IM3, onto prepared substrates consisting a TCO coated glass substrate already coated with PEDOT:PSS blocking layer. The organic electronic material FHBC was then spin cast onto the prepared substrate. Examples 2-4 are abbreviated as IM1/PEDOT:PSS, IM2/PEDOT:PSS and IM3/PEDOT:PSS. This is illustrated as Method A in Figure 2.

[00093] Examples 5-7 involve the deposition by spin casting of the interface modifiers, IM1, IM2 and IM3, dissolved in a solution of the PEDOT:PSS blocking layer onto a prepared substrate consisting of a TCO. The organic electronic active material FHBC was then spin cast onto the prepared substrate. Examples 5-7 are abbreviated as IM1:PEDOT:PSS, IM2:PEDOT:PSS and IM3:PEDOT:PSS. This is illustrated as Method B in Figure 2.

Examples 1-4: Characterization of IM/PEDOT:PSS surface properties

[00094] Interface modifier molecules IM1, IM2 and IM3 are soluble in polar solvents such as 1,4-dioxane. To form only a few monolayers of interface modifier molecules, 1 mg/ml 1,4-dioxane solution of interface modifier was spin cast at a spin rate of 1500 rpm onto PEDOT:PSS coated TCO glass, followed by annealing in air at

150°C for 10 minutes. The interlayer was denoted as "IM/PEDOT:PSS" to reflect a bi-layered structure with a substantially clear interface between the two layers.

[00095] The surface morphology of the interlayer was studied by atomic force microscopy (AFM). Figure 5 shows both the height and phase images of a pristine PEDOT:PSS film and a PEDOT:PSS film coated with IM1 (IM1/PEDOT:PSS). Figure 5 (a) and (b) show the AFM height images and Figure 5 (c) and (d) the phase images. The root-mean-square roughness of these samples is 705 pm and 567 pm, respectively. The image size is 2 x 2 μ m. The height bar scale is 5 nm and phase contrast scale is 10 degree.

[00096] The height images suggest there is little change in surface morphology after modification. The root-mean-square roughness of Figure 5(a) and (b) is quite comparable, reconfirming that spin coating IM1 on PEDOT:PSS does not substantially alter its surface morphology due to the extremely small amount of surface modifiers. However, the phase images do show some differences. Comparing Figure 5(c) with (d), the phase contrast between PEDOT and PSS in the pristine PEDOT:PSS film is significantly reduced after deposition of IM1. Without wishing to be bound by theory it may be rationalized that deposition of surface modifiers such as IM1 directly onto PEDOT:PSS produces a homogenous thin layer on top of PEDOT:PSS. Accordingly the phase contrast originating from differences in material stiffness between PEDOT and PSS can no longer be probed. The other interface modifier derivatives also showed the same trend as IM1.

[00097] The IM/PEDOT:PSS samples were further studied by other techniques to understand the change of surface properties. Table 1 indicates that the contact angle of a water droplet increases from 9° to more than 15° after coating with interface modifier molecules. Since PEDOT:PSS is hydrophilic while the HBC core of the interface modifier molecules is hydrophobic, the contact angle measurement suggests there are interface modifier molecules present at the surface of PEDOT:PSS films so that its surface hydrophobicity is altered. The result is consistent with observations in AFM phase images.

[00098] Table 1 also summarizes the ionization potential derived from PESA spectra. The ionization potential of PEDOT:PSS film was 5.32 eV before modification. It dropped by more than 0.3 eV after coating with interface modifier molecules. Because PESA is a surface sensitive technique which probes only the top 5 nm thick layer of the film, the change in ionization potential due to the difference in

ionization potential between interface modifier molecules and PEDOT:PSS implies large amount of interface modifier molecules are accumulated at the surface or within 5 nm deep below the PEDOT:PSS/air interface.

[00099] The modification of PEDOT:PSS by interface modifier molecules resulted in reduction of sheet resistance of the PEDOT:PSS film, as measured by four-point probe and shown in Table 1.

Table 1. Table of values of contact angle, ionization potential (IP) and sheet resistance of pristine PEDOT:PSS films and IM/PEDOT:PSS samples.

Example	Samples	Contact angle (°)	IP (eV)	Sheet Resistance (MΩ/Sq.)
1	PEDOT:PSS	9	5.32	820
2	IM1/PEDOT:PSS	15	5.06	127
3	IM2/PEDOT:PSS	18	5.02	331
4	IM3/PEDOT:PSS	15	4.85	44

Effect of IM/PEDOT:PSS on morphology of FHBC film

[000100] The effect of the interface modifiers on the morphology of FHBC film was examined by depositing a layer of FHBC on the interface modified PEDOT:PSS surface. 10 mg/ml of FHBC in chlorobenzene was spin coated on IM/PEDOT:PSS substrates at 1500 rpm. Subsequently, the films were thermally annealed at 150°C for 30 s to remove the residue solvent in the film. Alternatively, the films were kept in a closed Petri dish filled with dichlorobenzene vapour for 24 hr, and then taken out for thermal annealing at 150°C for 30 s in air, which was known as vapour annealing. Not to be bound by any theory, it is believed vapour annealing allows the FHBC film to relax to its thermodynamically equilibrium state, thus providing more insight into the effect of surface modification.

[000101] Figure 6 illustrates 2D GIWAXS diffractograms of FHBC film on pristine PEDOT:PSS and that on (IM1, IM2 or IM3)/PEDOT:PSS before annealing, after thermal annealing, and after vapour annealing, as well as diffractograms of the respective substrates. Specifically, Figure 6 illustrates 2D GIWAXS images of the various substrates (a, e, i and m) and FHBC pure donor layer on (b-d) PEDOT:PSS, (f-h) IM1/PEDOT:PSS, (j-l) IM2/PEDOT:PSS, and (n-p) IM3/PEDOT:PSS after

different treatments such as (b, f, j and n) without annealing, (c, g, k and o) after thermal annealing at 150 °C for 30s, and (d, h, l and p) after dichlorobenzene vapour annealing for 24 hr followed by thermal annealing at 150°C for 30s.

[000102] Figure 6(b) suggests the as-cast FHBC film on PEDOT:PSS exhibits a high degree of order. Reflections up to second order are visible. The hexagonal arrangement of the reflection spots implies a hexagonal packing of FHBC columns. It is consistent with previous observations that FHBC, like any other discotic molecule, tends to form columnar structure via π - π stacking, and the columns lie parallel to the substrate in a hexagonal fashion [E. Pouzet, V. D. Cupere, C. Heintz, J. W. Andreasen, D. W. Breiby, M. M. Nielsen, P. Viville, R. Lazzaroni, G. Gbabode and Y. H. Geerts, J. Phys. Chem. C, 2009, 113, 14398-14406]. Figure 6 (c) and (d) indicate thermal or vapour annealing does not change the diffraction patterns of FHBC on pristine PEDOT:PSS substrate. In other words, the hexagonal packing of FHBC columns seems to be the most stable configuration on PEDOT:PSS substrate.

[000103] After insertion of IM1 surface modifier in between PEDOT:PSS and FHBC, the as-cast film becomes less crystalline, as suggested by the weak reflection spots in Figure 6(f). However, as soon as the film is thermally annealed, the crystallinity is recovered. In fact, the reflection spots are more intense in Figure 6(g) than (c). A vertical Bragg rod consisting of a line of reflection spots extended in q_z direction in Figure 6 (h) after vapour annealing is observed. It is clear that the crystal packing of FHBC is changed after IM1 modification of PEDOT:PSS surface.

[000104] Hexagonal crystal packing of FHBC is also observed on IM2 and IM3 coated PEDOT:PSS substrates. The Bragg rod feature is absent in Figure 6(l) and (p). The reflection spots and Bragg rod observed in the diffractograms should result from the FHBC layer instead of substrates, because these features are not found in Figure 6(a), (e), (i) and (m).

[000105] The crystalline grains in the FHBC films were visualized with TEM. The dark field images distinguish crystalline grains according to crystal orientation (Figure 7). Figure 7 illustrates TEM dark field images of FHBC film on various substrates after vapour annealing, which was exposed to dichlorobenzene vapour for 24 hours followed by thermal annealing at 150°C for 30s. The scale bar is 200 nm for these images. The inset is the SAED of the corresponding sample.

[000106] It can be seen that an interlayer of interface modifier increases the grain size, comparing with the FHBC on pristine PEDOT:PSS. This observation is

consistent with the SAED patterns (see Figure 7 insets). The intensity of the diffraction ring in Figure 7 (a) is more or less constant in all directions, while it reduces to two diffraction fringes or spots in Figure 7 (b) and (d), suggesting the presence of a large crystal under the electron beam of TEM. The diffraction ring in Figure 7 corresponds to a d-spacing of 0.35 nm, which matches with the inter-molecular stacking distance in a FHBC crystal [W. Pisula, M. Zorn, J. Y. Chang, K. Mullen and R. Zentel, *Macromol. Rapid Commun.*, 2009, 30, 1179-1202].

Examples 5-7: GIWAXS and TEM studies of FHBC/IM:PEDOT:PSS

[000107] Since interface surface modifiers are amphiphilic and soluble in polar solvents, they may be blended with PEDOT:PSS aqueous solution and deposited together with PEDOT:PSS. The elimination of one processing step may reduce the cost in large-scale production. Due to the mismatch in free energy between the HBC core of the interface modifier molecules and PEDOT:PSS, it is possible for interface modifier molecules to diffuse to the surface of PEDOT:PSS and thus influence the morphology of an organic layer deposited on top. Therefore, 30 μ l of 1 mg/ml 1,4-dioxane solution of interface modifier molecules was blended with 1 ml of PEDOT:PSS aqueous solution. The blended solution was then used to make the interlayer by spin coating at 5000 rpm followed by thermal annealing at 150°C for 10 min in air. The interlayer fabricated in this way was denoted as "IM:PEDOT:PSS" because interface modifier molecules were blended with PEDOT:PSS and no clear boundary can be drawn between these two components. Subsequently, a FHBC layer was deposited on top and thermal or vapour treated following the same procedure as described above.

[000108] The FHBC films on IM:PEDOT:PSS substrates were studied by GIWAXS. Surprisingly, the interface modifier molecules blended in PEDOT:PSS can induce dramatic morphological change in the FHBC layer, especially after vapour annealing. Figure 8 illustrates 2D GIWAXS images of the various substrates (a, e and i) and FHBC pure donor layer on (b-d) IM1:PEDOT:PSS, (f-h) IM2:PEDOT:PSS and (j-l) IM3:PEDOT:PSS after different treatments such as (b, f and j) without annealing, (c, g and k) after thermal annealing at 150°C for 30s, and (d, h and l) after dichlorobenzene vapour annealing for 24 hr followed by thermal annealing at 150°C for 30s.

[000109] Very prominent Bragg rods can be seen in Figure 8 (d), (h) and (l). These Bragg rods imply the presence of large crystalline platelets with the a-b unit cell vector in the substrate plane but of random azimuthal orientation. [D. M. Smilgies, D. R. Blasini, S. Hotta and H. Yanagi, *J. Synchrotron Radiat.*, 2005, 12, 807-811; F. Zhang, Y. Hu, T. Schuettfort, C. A. Di, X. Gao, C. R. McNeill, L. Thomsen, S. C. Mannsfeld, W. Yuan, H. Sirringhaus and D. Zhu, *J. Am. Chem. Soc.*, 2013, 135, 2338-2349; J. Youn, S. Kewalramani, J. D. Emery, Y. Shi, S. Zhang, H.-C. Chang, Y.-j. Liang, C.-M. Yeh, C.-Y. Feng, H. Huang, C. Stern, L.-H. Chen, J.-C. Ho, M.-C. Chen, M. J. Bedzyk, A. Facchetti and T. J. Marks, *Adv. Funct. Mater.*, 2013, asap DOI: 10.1002/adfm.201203439.]. Not to be bound by any theory the interface modifiers in the blend PEDOT:PSS film may diffuse to the surface and be randomly scattered. The randomly oriented HBC core thus induces the random orientation of the FHBC molecules in azimuthal direction. The TEM dark field images shown in Figure 9 reveal such a change in FHBC morphology. Figure 9 illustrates TEM dark field images of FHBC film on PEDOT:PSS or IM:PEDOT:PSS substrates after vapour annealing, that is exposure to dichlorobenzene vapour for 24 hours followed by thermal annealing at 150°C for 30s. The scale bar is 200 nm for these images. The inset is the SAED of the corresponding sample.

Surface characterization of IM:PEDOT:PSS interlayer

[000110] To probe the presence of interface modifier molecules on the surface of (IM1, IM2 or IM3):PEDOT:PSS blend films, the samples were characterized by contact angle measurement, PESA and four point probe. Table 2 shows that the (IM1, IM2 or IM3):PEDOT:PSS samples have a slightly larger contact angle, a lower ionization potential and reduced sheet resistance than pristine PEDOT:PSS thin film. These evidences all imply surface accumulation of interface modifier molecules at the PEDOT:PSS film surface and interaction between PEG chains on interface modifier molecules and PEDOT:PSS.

Table 2. Table of values of contact angle, ionization potential (IP) and sheet resistance of pristine PEDOT:PSS films and IM:PEDOT:PSS samples.

Example	Samples	Contact angle (°)	IP (eV)	Sheet Resistance (MΩ/Sq.)
1	PEDOT:PSS	9	5.32	820
5	IM1:PEDOT:PSS	14	5.22	54
6	IM2:PEDOT:PSS	14	5.24	45
7	IM3:PEDOT:PSS	13	5.32	122

EXAMPLES

Film Characterization

[000111] Atomic force microscopic (AFM) images were acquired with an Asylum Research Cypher scanning probe microscope operated in tapping mode. Contact angle measurements were performed using the sessile drop method on a goniometer (Ramé-Hart Inc.). The contact angle of each substrate was measured at four locations and their average values are shown. The work function of the substrates was estimated by photoelectron spectroscopy in air (PESA), which was conducted on a Riken Keiki AC-2 spectrometer. A power intensity of 5 nW was used during the measurement. The sheet resistance was measured with a Jandel cylindrical four point probe at room temperature. Bright-field and dark-field transmission electron microscopy (TEM) images and selected area electron diffraction (SAED) patterns were obtained with a FEI Tecnai TF30 transmission electron microscope operated at 300 keV and equipped with beam blank function. High-angle annular dark-field scanning transmission electron microscopy (HAADF STEM) was performed at a primary electron energy of 15 keV with a FEI Quanta 3D microscope equipped with a HAADF STEM detector. Electron transparent samples for TEM were prepared by the following procedure. First, a scalpel was used to cut the organic film dividing it into small segments (~ 2 × 2 mm). As poly(3,4 ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) is water-soluble, the pieces of the active layer can be floated off the substrate by a drop of water from where they can be transferred onto conventional TEM copper grids. For electron

tomography, the same TEM samples loaded with gold fiducial markers of 10 nm in diameter were used. Tilt series were acquired using the Xplore 3D software (FEI Company). Tomograms were recorded between -65 and $+65$ degrees at 2° intervals and aligned with IMOD.²⁹ Grazing incidence wide-angle X-ray scattering (GIWAXS) was recorded at the small/wide-angle X-ray scattering beamline at the Australian Synchrotron. The samples were prepared on PEDOT:PSS coated glass substrates. Eleven kiloelectron volt photon energy and a PILATUS 1 M detector were used in the setup. The sample-to detector distance was calibrated using a silver behenate standard. Data acquisition time is 3 s to minimize any alteration or damage of the sample. Each image was photostitched from three continuous images.

Compound Synthesis

[000112] All reactions were performed by using anhydrous solvent under an inert atmosphere unless stated otherwise. ^1H and ^{13}C NMR spectroscopy were carried out by using either a Varian Inova-400 (400 MHz), a Varian Inova-500 (500 MHz) or a Bruker Avance III (600 MHz) instrument. Mass spectra were recorded with a MALDITOF MS Bruker Reflex (DCTB as matrix) or a Finnigan hybrid LTQ-FT/ICR mass spectrometer (Finnigan, LTQ-FT, Bremen, Germany). Column chromatography was carried out on Merck silica gel 60 (230-400 mesh). Compound **5** was synthesized according to a modified procedure from literature [M. Kimura, K. Kajita, N. Onoda and S. Morosawa, *J. Org. Chem.*, 1990, 55, 4887-4892], compounds **2** [W. W. H. Wong, T. B. Singh, D. Vak, W. Pisula, C. Yan, X. L. Feng, E. L. Williams, K. L. Chan, Q. Mao, D. J. Jones, C.-Q. Ma, K. Müllen, P. Bäuerle and A. B. Holmes, *Adv. Funct. Mater.*, 2010, 20, 927-938.], **4** [M. J. Wiester and C. A. Mirkin, *Inorg. Chem.*, 2009, 48, 8054-8056.], **9** [Y. Terazono, P. A. Liddell, V. Garg, G. Kodis, A. Brune, M. Hambourger, A. L. Moore, T. A. Moore and D. Gust, *J. Porphyrins Phthalocyanines*, 2005, 09, 706-723.], and 1-(p-tosylsulfonyl)-3,6,9-trioxodecane [R. K. Roy, E. B. Gowd and S. Ramakrishnan, *Macromol.*, 2012, 45, 3063-3069.] have been reported in the literature. All other precursors were commercially available and were used as received. Solvents were dried by passage through a Pure Process Technologies solvent purification system or over $4\text{\AA}$ molecular sieves and then degassed.

[000113] **Interface Modifier 1:** 2,11-bis(9,9-bis(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-9H-fluoren-2-yl)hexabenz[bc,ef,hi,kl,no,qr]coronene (**IM1**): 2-(9,9-bis(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-9H-fluoren-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **6** (0.515 g, 0.882 mmol), was dissolved in toluene

(10 mL), HBC **2** (0.200 g, 0.294 mmol) and Et₄NOH (0.200 mL, 20% wt in H₂O) were added and the resulting mixture was purged with N₂(g) for 20 min. Pd₂(dba)₃ (0.054 g, 0.059 mmol) and HP(tBu)₃BF₄ (0.068 g, 0.235 mmol) were added and the resulting mixture was stirred at 90°C for 72h. The mixture was filtered over Celite and the volatiles were evaporated under reduced pressure giving 0.930 g of a red compound. This was subjected to column chromatography, impurities were eluted with EtOAc and the product was eluted with CHCl₃/MeOH (15/1) and was obtained as a yellow sticky solid (0.110 g) after evaporating of the volatiles under reduced pressure. The product was further purified by precipitation from EtOAc giving **IM1** as a yellow powder (0.080 g, 19 %). ¹H NMR (2 mM, 500 MHz, CDCl₃) δ = 8.74 (s b, 4H, Ar-HBC), 8.59 (s b, 4H, Ar-HBC), 8.39 (s b, 4H, Ar-HBC), 8.11 (s, 2H, Ar-Flu), 7.98-7.93 (m, 4H, Ar-Flu), 7.90 (d, J = 7.1, 2H, Ar-Flu), 7.68 (t b, 4H, Ar-HBC), 7.63 (d, J = 7.1, 2H, Ar-Flu), 7.53 (t, J = 7.4, 2H, Ar-Flu), 7.48 (t, J = 6.3, 2H, Ar-Flu), 3.55 – 3.51 (m, 18H, OCH₂), 3.46 – 3.39 (m, 18H, OCH₂), 3.25 (s, 12H, OCH₃), 3.24-3.18 (m, 4H, CCH₂CH₂O), 3.10-3.05 (m, 4H, CCH₂CH₂O), 2.82-2.70 (m, 8H, CCH₂). ¹³C NMR (64 mM, 125 MHz, CDCl₃) δ = 150.12, 149.45, 141.26, 140.44, 139.85, 137.27, 129.46, 128.88, 128.82, 127.68, 127.53, 125.43, 123.61, 122.92, 121.98, 120.76, 120.67, 120.28, 119.17, 119.01, 118.79, 71.95, 70.72, 70.60, 67.64, 59.05, 51.71, 40.11. FDMS: m/z = 1458.6408 [M]⁺ calculated (1458.6358), R_f = 0.60 CHCl₃/MeOH (10/1), R_f = 0.49 CHCl₃/MeOH (15/1).

[000114] 2-(9,9-bis(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-9H-fluoren-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6**): compound (**7**) (2.95 g, 5.48 mmol), bis(pinacolato)diboron (1.391 g, 5.48 mmol), and potassium acetate (1.882 g, 19.18 mmol) were mixed with anhydrous dioxane (20 mL) and purged with N₂(g) for 20 min. Pd(dppf)Cl₂ CH₂Cl₂ (0.149 g, 0.183 mmol) was added and the resulting mixture was stirred at 90°C for 18h. The reaction product was taken up in a mixture of CH₂Cl₂ (50 mL) and H₂O (30 mL). The organic layer was washed with H₂O/Brine (1/1) (3 × 40 mL). The organic layer was dried with MgSO₄. Evaporation of the volatiles under reduced pressure gave 3.442 g black oil. The crude product was purified by column chromatography (EtOAc) to give **6** as a slightly colored oil (2.03 g, 59 %). ¹H NMR (500 MHz, CDCl₃) δ = 7.83-7.79 (m, 2H, Ar), 7.07-7.66 (m, 2H, Ar), 7.43-7.41 (m, 1H, Ar), 7.35-7.30 (m, 2H, Ar), 3.52 – 3.50 (m, 4H, OCH₂), 3.47 – 3.45 (m, 4H, OCH₂), 3.39 (t, J = 4.2, 4H, OCH₂), 3.33 (s, 6H, OCH₃), 3.19 (t, J = 4.2, 4H, OCH₂), 2.77-2.65 (m, 4H, CCH₂CH₂O), 2.47-2.35 (m, 4H, CCH₂), 1.39 (s, 12H, CCH₃). ¹³C NMR (125

MHz, CDCl_3) δ = 149.55, 148.03, 143.45, 140.31, 134.18, 129.26, 127.95, 127.32, 123.26, 120.32, 119.20, 83.90, 71.95, 70.55, 70.04, 67.09, 59.07, 51.15, 39.70, 25.06. Rf = 0.36 (EtOAc).

[000115] 2-bromo-9,9-bis(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-9H-fluorene (**7**): 2-bromofluorene (3.00 g, 12.24 mmol) was dissolved in anhydrous DMF (50 mL) and NaH (1.33 g, 33.29 mmol, 60 %w/w dispersion in mineral oil) was added under a $\text{N}_2(\text{g})$ atmosphere. The resulting mixture was stirred at 24°C for 30 minutes. Subsequently, 1-(p-tosylsulfonyl)-3,6,9-trioxodecane (9.66 g, 30.35 mmol) was added and the solution was stirred for 18h. The reaction was quenched with H_2O (60 mL) and the product was extracted with CH_2Cl_2 (2 × 50 mL). The combined organic fractions were washed with H_2O (2 × 60 mL), brine (60 mL) and dried with MgSO_4 . Evaporation of the volatiles under reduced pressure gave 9.47 g red oil. The crude product was purified by column chromatography (EtOAc) to give **7** as an orange oil (5.00 g, 76 %). ^1H NMR (500 MHz, CDCl_3) δ = 7.65-7.63 (m, 1H, Ar), 7.54 (t, J = 1.8, 1H, Ar), 7.53 (s, 1H, Ar), 7.46 (dd, J = 1.8, 6.3, 1H, ArH), 7.40-7.38 (m, 1H, ArH), 7.34-7.32 (m, 2H, ArH), 3.53 – 3.51 (m, 4H, OCH_2), 3.49 – 3.46 (m, 4H, OCH_2), 3.39 (t, J = 4.9, 4H, OCH_2), 3.34 (s, 6H, OCH_3), 2.76 (m, 4H, $\text{CCH}_2\text{CH}_2\text{O}$), 2.35 (m, 4H, CCH_2). ^{13}C NMR (125 MHz, CDCl_3) δ = 151.21, 148.53, 139.43, 139.37, 130.37, 127.77, 127.46, 126.58, 123.15, 121.10, 119.88, 71.83, 70.40, 69.96, 66.89, 58.95, 51.50, 39.55. Rf = 0.38 (EtOAc).

[000116] **Interface Modifier 2:** 2,5-bis(9,9-bis(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-9H-fluoren-2-yl)hexabenzob[bc,ef,hi,kl,no,qr]coronene (**IM2**): 2-(9,9-bis(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-9H-fluoren-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.258 g, 0.441 mmol) was dissolved in toluene (10 mL) and HBC **8** (0.120 g, 0.176 mmol) was added and the resulting mixture was ultrasonicated for 2.5 h. Et_4NOH (0.100 mL, 20% wt in H_2O) was added and the resulting mixture was purged with $\text{N}_2(\text{g})$ for 20 min. $\text{Pd}(\text{PPh}_3)_4$ (0.034 g, 0.030 mmol) was added and the mixture was stirred at 100°C for 72h. The mixture was filtered over Celite and the volatiles were evaporated under reduced pressure giving 0.370 g of a red compound. The crude product was purified with column chromatography, eluent $\text{CH}_3\text{CN}/\text{MeOH}$ 10/1 giving **IM2** as a red solid (0.041 g, 16 %). ^1H NMR (400 MHz, CDCl_3) δ = 8.71 (s b, 2H, Ar-HBC), 8.57 (s b, 2H, Ar-HBC), 8.48 (d b, J = 7.4, 2H, Ar-HBC), 8.24 (s b, 6H, Ar-HBC), 8.10 (s, 2H, Ar-Flu), 8.06 (d, J = 7.7, 2H, Ar-Flu), 8.01 (d, J = 7.6, 2H, Ar-Flu), 7.94 (d, J = 6.8, 2H, Ar-Flu), 7.66 (d, J = 7.12, 2H,

Ar-Flu), 7.59-7.48 (m, 4H and 4H, Ar-HBC and Ar-Flu), 3.55 – 3.51 (m, 16H, OCH₂), 3.47 – 3.41 (m, 16H, OCH₂), 3.28-3.22 (m, 4H, CCH₂CH₂O), 3.24 (s, 12H, OCH₃), 3.12-3.10, (m, 4H, CCH₂CH₂O), 2.86-2.72 (m, 8H, CCH₂). ¹³C NMR (100 MHz, CDCl₃) δ = 150.26, 149.52, 141.27, 140.47, 140.11, 137.57, 129.73, 129.56, 129.23, 129.18, 129.12, 129.03, 127.76, 127.56, 125.72, 125.62, 123.87, 123.72, 123.68, 123.35, 122.14, 121.17, 120.92, 120.83, 120.35, 119.57, 119.47, 119.43, 119.32, 118.99, 71.97, 70.76, 70.63, 70.39, 67.71, 59.08, 51.81, 40.23. FDMS: m/z = 1458.6139 [M]⁺ calculated (1458.6358), Rf = 0.03 CH₃CN/MeOH (10/1), Rf = 0.65 CHCl₃/MeOH (10/1).

[000117] 2,5-dibromohexabenzo[bc,ef,hi,kl,no,qr]coronene (**8**): A mixture of 1,1':2',1''-Terphenyl, 4,4''-dibromo-3',4',5',6'-tetraphenyl (**9**) (0.700 g, 1.01 mmol), DDQ (1.377 g, 6.07 mmol) in anhydrous CH₂Cl₂ (20 mL) was cooled to 0°C. Triflic acid (0.537 mL, 6.07 mmol) was slowly added and the resulting mixture was stirred for 3h at 0°C. Saturated K₂CO₃ (aq) was added and the mixture was filtered over Celite and sequentially washed with H₂O and acetone. The volatiles were removed under reduced pressure giving a red solid. The crude product was purified by soxhlet extraction with MeOH for 18h followed by CH₂Cl₂ for 6h giving **8** as a red compound (0.405 g, 59%). MALDI-TOF MS: m/z = 678.108 [M+H]⁺, 679.111, 680.100, 681.089, 682.097, 683.095 peaks are in accordance with the simulated mass spectrum.

[000118] N²,N²,N¹¹,N¹¹-tetrakis(4-(2,5,8,11-tetraoxatridecan-13-yloxy)phenyl)hexabenzo[bc,ef,hi,kl,no,qr]coronene-2,11-diamine (**IM3**): Compound **1** (1.57 g, 2.7 mmol), HBC **2** (0.835 g, 1.23 mmol), and NaOtBu (0.472 g, 4.91 mmol) were placed in an oven dried schlenk tube under N₂ (g) atmosphere. The mixture was dried under vacuum at 60°C for 3h. Dry toluene (20 mL) was added and the resulting mixture was ultrasonicated for 2h at 24°C followed by purging the mixture with N₂ (g) for 20 min. Pd₂(dba)₃ (0.112 g, 0.123 mmol), and HP(tBu)₃BF₄ (0.142 g, 0.491 mmol) were added and the resulting mixture was stirred at 110°C for 48 h. The crude product was filtered over silica with Hyflo gel on top using CH₂Cl₂ followed by EtOAc, which eluted an impurity. The product was filtered of using CH₂Cl₂/MeOH 10:1. The solvent was removed and the product was precipitated from CH₃CN giving **IM3** as a red powder (1.513 g, 73 %). ¹H NMR (400 MHz, CDCl₃) δ = 8.69 (d, J = 8.1, 4H, ArHBC), 8.46 (s, 4H, ArHBC), 8.39 (d, J = 8.0, 4H, ArHBC), 7.76 (t, J = 7.8, 4H, ArHBC), 7.34 (d, J = 8.9, 8H, PhN), 7.02 (d, J = 9.0, 8H, PhN), 3.95 (t, J = 5.0, 8H, ArOCH₂), 3.81 (t, J = 4.5, 8H, ArOCH₂CH₂), 3.76-3.65 (m, 34H, OCH₂), 3.56 (t, J =

4.9, 8H, CH₂OCH₃), 3.37 (s, 12H, OCH₃). ¹³C NMR (100 MHz, CDCl₃) δ = 155.34, 146.60, 141.39, 130.73, 129.56, 129.33, 126.86, 125.83, 124.67, 121.26, 121.07, 119.47, 119.30, 115.76, 113.64, 72.01, 70.93, 70.75, 70.71, 70.60, 69.96, 67.82, 67.13, 59.10. FDMS: m/z = 1704.74336, [M+Na] calculated m/z = 1704.74212. R_f = 0.10 (EtOAc). Elemental analysis: calcd. for C₁₀₂H₁₀₈N₂O₂₀, C 72.84, H 6.47, N 1.67, O 19.02; found C 72.33, H 6.46, N 1.55, O 19.33.

[000119] N,N-bis-phenoxy-3,6,9-trioxononanethylmethylether (1): 1-[4-Bromophenoxy]-3,6,9-trioxononanethylmethylether **4** (0.624 g, 1.786 mmol) and 1-[4-aminophenoxy]-3,6,9-trioxononanethylmethylether **3** (0.510 g, 1.786 mmol) were placed in an oven dried schlenk tube and heated at 60°C under vacuum for 3h. After allowing the mixture to cool to 24°C NaOtBu (0.515 g, 5.36 mmol) was added followed by dry Toluene (10 mL) and the resulting mixture was purged with N₂ (g) for 20 min. Pd₂(dba)₃ (0.041 g, 0.0446 mmol), and dppf (0.050 g, 0.0890 mmol) were added and the resulting mixture was stirred at 110°C for 5 h. After cooling the mixture to 24°C it was filtered over Celite. Evaporation of the volatiles under reduced pressure gave 0.961 g black oil. The crude product was purified by column chromatography (EtOAc) giving **1** as a slightly colored oil (0.613 g, 59 %). ¹H NMR (600 MHz, CDCl₃) δ = 6.91 (d, J = 8.8, 4H, Ph), 6.83 (d, J = 8.8, 4H, Ph), 4.09 (t, J = 4.6, 4H, ArOCH₂), 3.83 (t, J = 5.1, 4H, ArOCH₂CH₂), 3.72 (t, J = 4.3, 4H, OCH₂), 3.69-3.64 (m, 16H, OCH₂), 3.54 (t, J = 5.0, 4H, CH₂OCH₃), 3.37 (s, 6H, OCH₃). ¹³C NMR (125 MHz, CDCl₃) δ = 150.77, 135.47, 116.88, 116.68, 113.13, 112.98, 69.34, 68.20, 68.02, 67.33, 67.26, 67.19, 65.49, 65.38, 65.26, 56.39. R_f = 0.10 (EtOAc). HRMS, ESI⁺: m/z calcd. for C₃₀H₄₇NO₁₀ + H⁺, 582.32727; found 582.32735. Elemental analysis: calcd. for C₃₀H₄₇NO₁₀, C 61.94, H 8.14, N 2.41, O 27.50; found C 61.92, H 8.33, N 2.28, O 27.35.

[000120] 1-[4-aminophenoxy]-3,6,9-trioxononanethylmethylether (3): 1-[4-nitrophenoxy]-3,6,9-trioxononanethylmethylether **5** (4.097 g, 12.99 mmol) was dissolved in 40 mL ethanol in a round bottom flask, and Pd(C) 10% (0.040 g) was added. A balloon containing H₂ (g) was mounted on top of the flask and the mixture was stirred at 24°C for 18 h. The crude product was filtered over Celite and the volatiles were removed under reduced pressure giving 3.600 g of a brown oil which slowly crystallizes up on standing. This oil was subjected to column chromatography (EtOAc) giving **3** as a colorless oil (1.161 g, 44%) and a fraction with an estimated purity of 95% product as a slightly colored oil (1.984 g, 54%), both crystalize up on

standing. ^1H NMR (500 MHz, CDCl_3) δ = 6.76 (d, J = 8.9, 2H, Ph), 6.63 (d, J = 8.8, 2H, Ph), 4.05 (t, J = 4.1, 2H, ArOCH_2), 3.81 (t, J = 5.1, 2H, $\text{ArOCH}_2\text{CH}_2$), 3.73 – 3.70 (m, 2H, OCH_2), 3.69-3.63 (m, 8H, OCH_2), 3.54 (t, 2H, J = 4.9, CH_2OCH_3), 3.41 (s br, 2H, NH_2), 3.37 (s, 3H, OCH_3). ^{13}C NMR (125 MHz, CDCl_3) δ = 151.98, 140.31, 116.37, 115.94, 72.01, 70.84, 70.70, 70.69, 70.59, 69.98, 68.23, 59.10. R_f = 0.18 (EtOAc). HRMS, ESI $^+$: m/z calcd. for $\text{C}_{15}\text{H}_{25}\text{NO}_5 + \text{H}^+$, 300.18055; found 300.18054. Elemental analysis: calcd. for $\text{C}_{15}\text{H}_{25}\text{NO}_5$, C 60.18, H 8.42, N 4.68, O 26.72; found C 60.27, H 8.58, N 4.51, O 26.50.

[000121] 1-[4-nitrophenoxy]-3,6,9-trioxononanethylmethylether (**5**): 1-bromo-3,6,9-trioxononanethyl methylether (4.504 g, 16.61 mmol), p-nitrophenol (2.311 g, 16.61 mmol), and K_2CO_3 (6.887 g, 49.83 mmol) were stirred at 90°C in 25 mL DMF for 6 h. The volatiles were removed under reduced pressure at 90°C. The crude product was dissolved in NaOH (aq) (50 mL, 0.5 M) and the product was extracted with CH_2Cl_2 (3 $\times$ 30 mL). The combined organic layers were washed with H_2O (4 $\times$ 40 mL) and dried with MgSO_4 . Evaporation of the volatiles at reduced pressure gave **5** as a slightly coloured oil (5.158 g, 98%). ^1H NMR (500 MHz, CDCl_3) δ = 8.19 (d, J = 9.4, 2H, Ph), 6.98 (d, J = 9.3, 2H, Ph), 4.22 (t, J = 4.7, 2H, ArOCH_2), 3.89 (t, J = 4.8, 2H, $\text{ArOCH}_2\text{CH}_2$), 3.73 – 3.71 (m, 2H, OCH_2), 3.69-3.63 (m, 8H, OCH_2), 3.55-3.53 (m, 2H, CH_2OCH_3), 3.37 (s, 3H, OCH_3). ^{13}C NMR (125 MHz, CDCl_3) δ = 163.91, 141.56, 125.84, 114.62, 71.94, 70.93, 70.62, 70.53, 69.38, 68.26, 59.03. R_f = 0.34 (EtOAc).

Claims

1. An organic thin film comprising an active layer, a blocking layer, and an interlayer located between the active layer and the blocking layer, said interlayer comprising an amphiphilic interface modifier.
2. The thin film of claim 1 wherein the amount of amphiphilic interface modifier is between 0.01 and 10% by weight based on the total weight of the blocking layer and the interface modifier.
3. The thin film of claim 1 or claim 2 wherein the amphiphilic interface modifier comprises one or more template units, said template units comprising one or more substituents chemically bonded thereto, wherein said one or more substituents confers solubility to the interface modifier in an organic solvent.
4. The thin film of any one of claims 1 to 3 wherein the solubility conferring substituents impart solubility to the interface modifier in solvents orthogonal to those typically used for deposition of an active layer.
5. The thin film of claim 3 to 4 wherein the template unit is hydrophobic and the one or more substituents are hydrophilic.
6. The thin film of any one of claims 1 to 5 wherein the template unit is a linear or branched, fused or unfused polycyclic aromatic or polyheteroaromatic.
7. The thin film of claim 6 wherein the polyheteroaromatic comprises one or more of nitrogen, oxygen, sulphur, phosphorous, boron, silicon or germanium atoms.
8. The thin film of claim 6 wherein the linear or branched, fused or unfused polycyclic aromatic or polyheteroaromatic is selected from acenes, rylene, diketopyrrolopyroles, BODIPY dyes, porphyrins, confused porphyrins, porphyrazines, phthalothocyanines, their metal containing analogues and mixtures thereof.
9. The thin film of any one of claims 1 to 5 wherein the template unit comprises one or more of the following: P3HT (poly(3-hexylthiophene)), PCDTBT (poly[N-9"-

hepta-decanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',r,3'-benzothiadiazole)], MEH-PPV (poly[2-methoxy-5-(2'-ethyl-hexyloxy)-p-phenylene vinylene]), MDMOPPV (poly[2-methoxy-5-3(3,7-dimethyloctyloxy)-l-4-phenylene vinylene]), phthalocyanine, pentacene, poly(2,7-(9-(2'-ethyl-hexyl)-9-hexyl-fluorene)-alt-5,5-(4',7'-di-2-thienyl-2',r,3'-benzothiadiazole)) (PFDTBT), poly(p-phenylene-ethynylene)-alt-poly(p-phenylene-vinylene) (PPE-PPV), poly((2,7-(9-(2'-ethylhexyl)-9-hexyl-fluorene)-alt-5,5-(4',7'-di-2-thienyl-2', 1', 3'-benzothiadiazole))-co-(2,7-(9-(2'-ethylhexyl)-9-hexyl-fluorene)-alt-2,5-thiophene)) (APFO-5), poly(4,8-bis-alkyloxybenzo(l,2-b:4,5-b')dithiophene-2,6-diyl-alt-(alkylthieno(3,4-b)thiophene-2-(2-ethyl-l-hexanone)-2,6-diyl)) (PBDTTT-C), poly(4,8-bis-alkyloxybenzo(l,2-b:4,5-b')dithiophene-2,6-diyl-alt-(thieno(3,4-b)thiophene-2-carboxylate)-2,6-diyl) (PBDTTT-E), 2-((7-(5-(di-*p*-tolylamino)thiophen-2-yl)benzo[c][1,2,5]thiadiazol-4-yl)methylene)malononitrile (DTDCTB), 3,6-bis(5-(benzofuran-2-yl)thiophen-2-yl)-2,5-bis(2-ethylhexyl)pyrrolo[3,4-c]pyrrole-1,4(2*H*,5*H*)-dione (DPP-(TBFu)₂), perylene, PTCBI (3,4,9,10-perylenetetracarboxylic-bis-benzimidazole), DPP (dihydropyrrolo[3,4-c]pyrrole), copper hexa- decafluorophthalocyanine (F16-CuPc), 2,3,5,6-tetrafluoro-7,7,8,8 - tetracyanoquinodimethane (F4TCNQ), 3,4,9,10- perylenetetra-carboxylic dianhydride (PTCDA), fluoro-substituted PTCDA, cyano-substituted PTCDA, naphthalene-tetracarboxylic-dianhydride (NTCDA), fluoro-substituted NTCDA, cyano-substituted NTCDA, and 3,4,9,10-perylene tetracarboxylic bisbenzimidazole (PTCBI), or a repeat unit or oligomeric unit therefrom.

10. The thin film of any one of claims 3 to 9 wherein the one or more solubility conferring substituents is independently selected from branched or unbranched, linear or cyclic, substituted or unsubstituted ethers, polyethers, amines, amides, carbamates, acids and alcohols.

11. The thin film of any one of claims 3 to 10 wherein the one or more solubility conferring substituents is independently substituted with one or more further substituents comprising a linear, branched or cyclic hydrocarbon, optionally comprising one or more heteroatoms.

12. The thin film of any one of claims 3 to 11 wherein the one or more solubility conferring substituents is a branched or unbranched, substituted or unsubstituted, polyether group comprising between 4 and 30 carbon atoms.
13. The thin film of any one of claims 1 to 12 wherein the template unit comprises a unit or subunit that is the same as a unit or subunit in the active layer.
14. The thin film of any one of claims 1 to 13 wherein the blocking layer comprises polyethylenedioxythiophene doped with polystyrenesulfonate (PEDOT:PSS), MoO_3 , V_2O_5 , NiO , CrO_3 , ZnO , or TiO_2 .
15. The thin film of any one of claims 1 to 14 wherein the active layer comprises a donor or an acceptor or a donor:acceptor blend.
16. The thin film of any one of claims 1 to 15 wherein the active layer comprises a linear or branched, fused or unfused, substituted or unsubstituted, polycyclic aromatic or polyheteroaromatic.
17. The thin film of claim 16 wherein the linear or branched, fused or unfused polycyclic aromatic or polyheteroaromatic is selected from acenes, rylenes, diketopyrrolopyroles, BODIPY dyes, porphyrins, confused porphyrins, porphyrazines, phthalothocyanines, their metal containing analogues and mixtures thereof.
18. The thin film of any one of claims 1 to 15 wherein the active layer comprises one or more of the following: P3HT (poly(3-hexylthiophene)), PCDTBT (poly[N-9"-hepta-decanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',r,3'-benzothiadiazole)]), MEH-PPV (poly[2-methoxy-5-(2'-ethyl-hexyloxy)-p-phenylene vinylene]), MDMOPPV (poly[2-methoxy-5-3(3,7-dimethyloctyloxy)-l-4-phenylene vinylene]), phthalocyanine, pentacene, poly(2,7-(9-(2'-ethyl-hexyl)-9-hexyl-fluorene)-alt-5,5-(4',7'-di-2-thienyl-2',r,3'-benzothiadiazole)) (PFDTBT), poly(p-phenylene-ethynylene)-alt-poly(p-phenylene-vinylene) (PPE-PPV), poly((2,7-(9-(2'-ethylhexyl)-9-hexyl-fluorene)-alt-5,5-(4',7'-di-2-thienyl-2', 1', 3'-benzothiadiazole))-co-(2,7-(9-(2'-ethylhexyl)-9-hexyl-fluorene)-alt-2,5-thiophene)) (APFO-5), poly(4,8-bis-alkyloxybenzo(1,2-b:4,5-b')dithiophene-2,6-diyl-alt-(alkylthieno(3,4-b)thiophene-2-(2-ethyl-l-hexanone)-2,6-

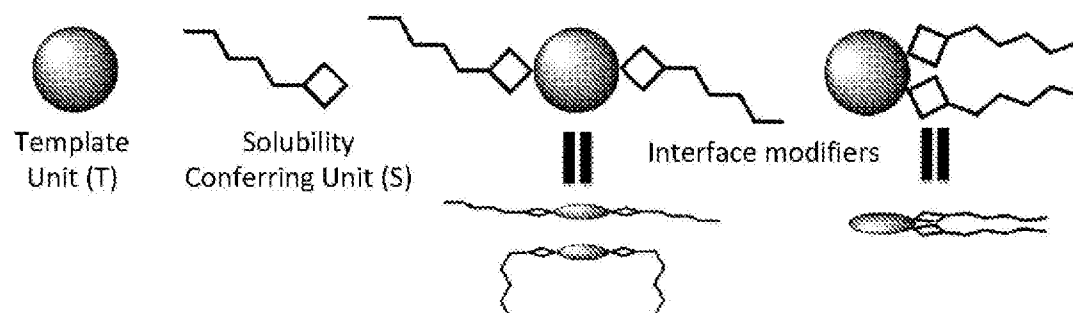
diyl)) (PBDTTT-C), poly(4,8-bis-alkyloxybenzo(l,2-b:4,5-b')dithiophene-2,6-diyl-alt-(thieno(3,4-b)thiophene-2-carboxylate)-2,6-diyl) (PBDTTT-E), 2-((7-(5-(di-*p*-tolylamino)thiophen-2-yl)benzo[*c*][1,2,5]thiadiazol-4-yl)methylene)malononitrile (DTDCTB), 3,6-bis(5-(benzofuran-2-yl)thiophen-2-yl)-2,5-bis(2-ethylhexyl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (DPP-(TBFu)₂), perylene, PTCBI (3,4,9,10-perylenetetracarboxylic-bis-benzimidazole), DPP (dihydropyrrolo[3,4-*c*]pyrrole), copper hexa- decafluorophthalocyanine (F16-CuPc), 2,3,5,6-tetrafluoro-7, 7,8,8 - tetracyanoquinodimethane (F4TCNQ), 3,4,9,10- perylenetetra-carboxylic dianhydride (PTCDA), fluoro- substituted PTCDA, cyano-substituted PTCDA, naphthalene-tetracarboxylic-dianhydride (NTCDA), fluoro- substituted NTCDA, cyano-substituted NTCDA, and 3,4,9,10-perylene tetracarboxylic bisbenzimidazole (PTCBI).

19. A method of preparing an organic thin film comprising the steps of:
 - (a) forming a blocking layer on a substrate;
 - (b) forming a layer of amphiphilic interface modifier on the blocking layer; and
 - (c) forming an active layer on the layer of amphiphilic interface modifier.
20. A method of preparing an organic thin film comprising the steps of:
 - (a) blending a blocking material with an amphiphilic interface modifier;
 - (b) forming a layer of the blend on a substrate; and
 - (c) forming an active layer on the layer of the blend.
21. The method of claim 19 or claim 20 wherein the substrate is a transparent conducting oxide.
22. An organic thin film formed by the method of any one of claims 19 to 21.
23. Use of the amphiphilic interface modifier of any one of claims 3 to 18 in controlling the morphology of an active layer in an optoelectronic device.
24. Use of the amphiphilic interface modifier of any one of claims 3 to 18 in the manufacture of an optoelectronic device.

25. Use of the organic thin film of any one of claims 1 to 18 in the manufacture of an optoelectronic device.

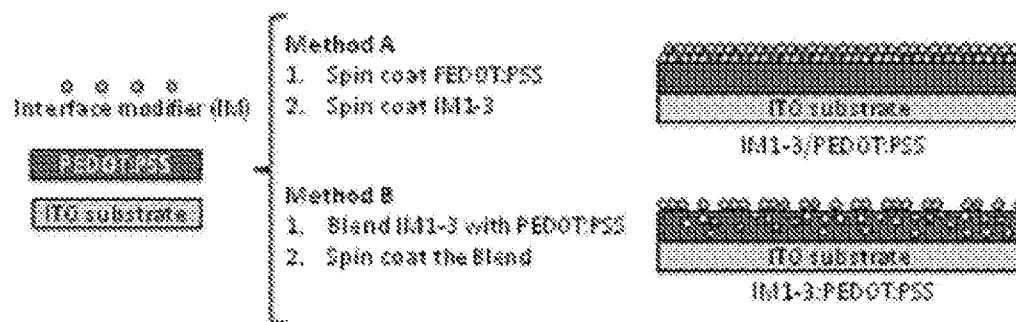
26. An optoelectronic device comprising the amphiphilic interface modifier of any one of claims 3 to 18 or the organic thin film of any one of claims 1 to 18.

FIGURE 1



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FIGURE 2



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FIGURE 3

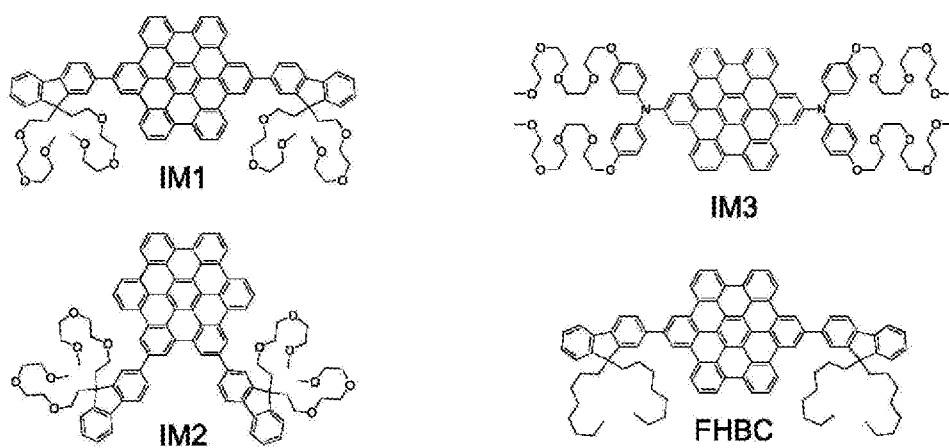
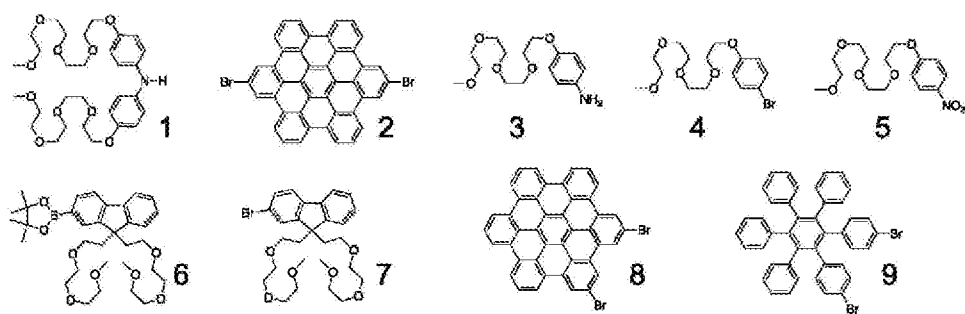
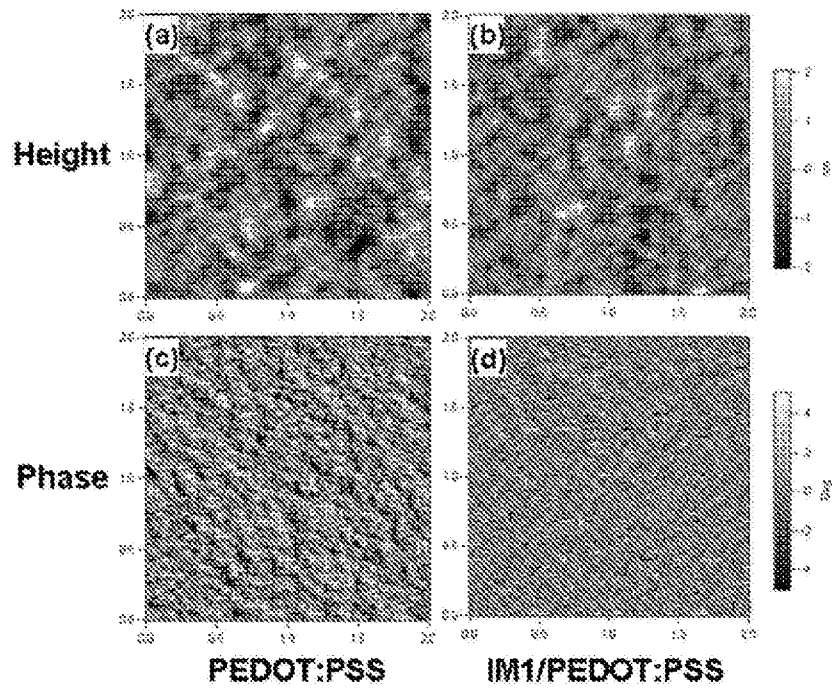


FIGURE 4



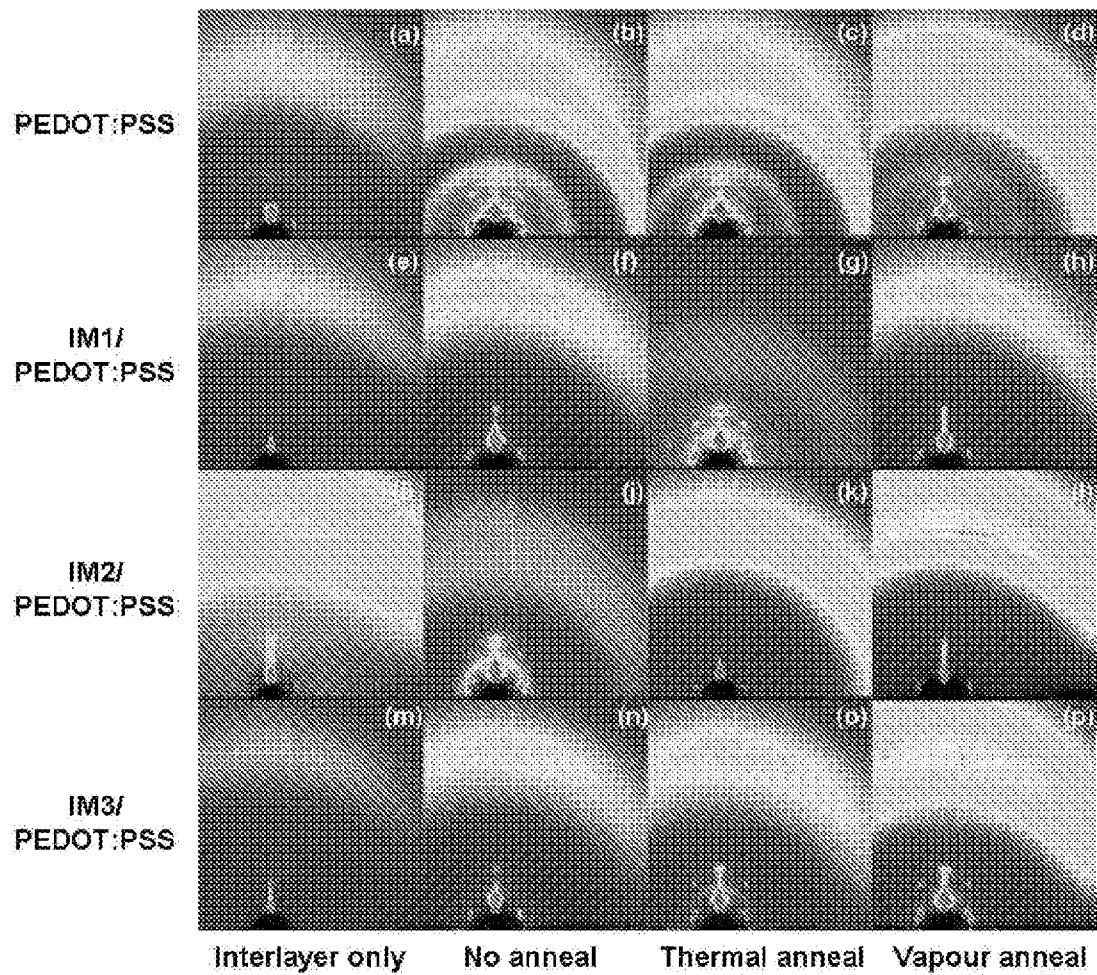
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FIGURE 5



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FIGURE 6



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FIGURE 7

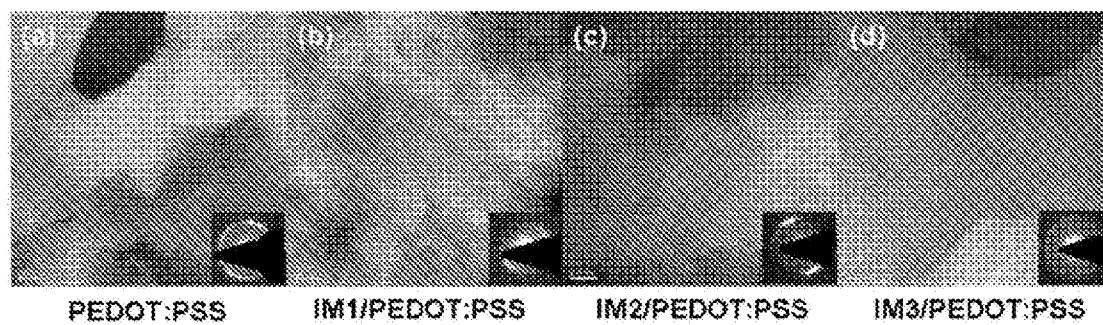


FIGURE 8

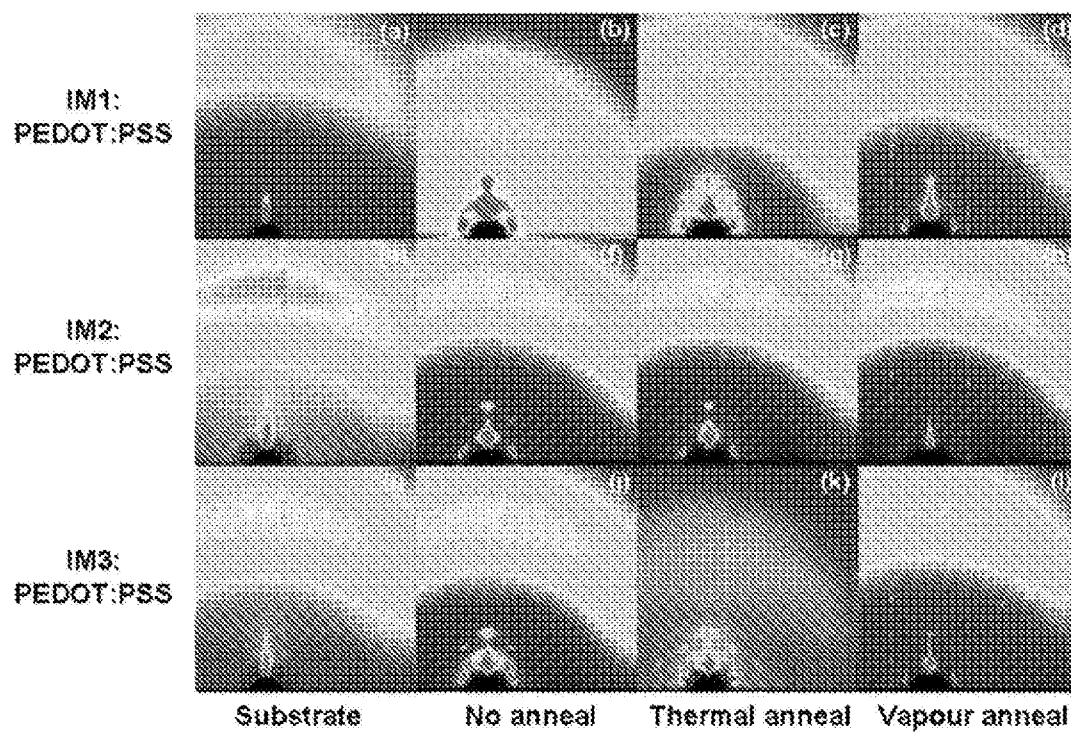
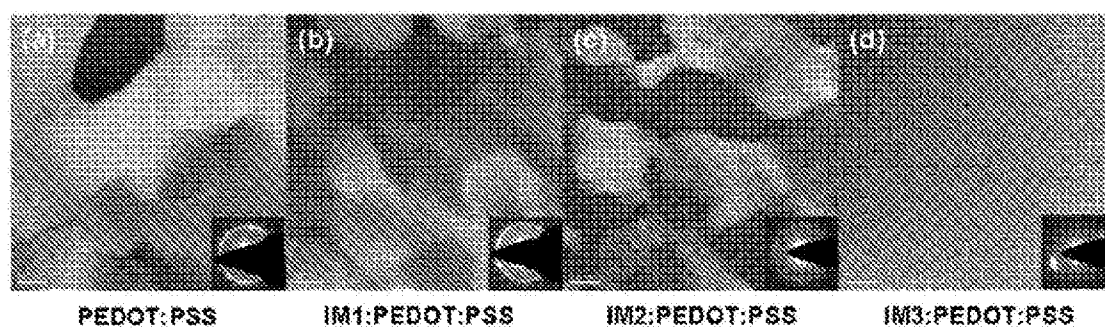


FIGURE 9



INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU2014/050059

A. CLASSIFICATION OF SUBJECT MATTER

H01L 51/05 (2006.01) H01L 51/42 (2006.01) H01L 51/50 (2006.01) H01L 31/00 (2006.01) B32B 33/00 (2006.01)

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)
IPC, CPC: H01L, B32B

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)

EPODOC, WPI, INSPEC, ZCAPLUS, CAPLUS, Espacenet, Google Patents, Google Scholar (Keywords: bulk heterojunction, BHJ, organic photovoltaics, optoelectronic, hybrid solar cells, thin films, charge/electron/energy/hole transport/transfer, interfacial modifier/interaction/alignment, and other similar terms)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	Documents are listed in the continuation of Box C	



Further documents are listed in the continuation of Box C



See patent family annex

* "A"	Special categories of cited documents: document defining the general state of the art which is not considered to be of particular relevance	"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
"E"	earlier application or patent but published on or after the international filing date	"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
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"O"	document referring to an oral disclosure, use, exhibition or other means	"&"	document member of the same patent family
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Date of the actual completion of the international search
24 July 2014

Date of mailing of the international search report
24 July 2014

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Telephone No. 0262832209

INTERNATIONAL SEARCH REPORT		International application No.
C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		PCT/AU2014/050059
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	HUANG, Y. et al., 'Employing an amphiphilic interfacial modifier to enhance the performance of a poly(3-hexyl thiophene)/TiO ₂ hybrid solar cell', J. Mater. Chem., 2011, vol. 21, pages 4450-4456 Abstract, pages 4452-4456, Figure 1	1-26
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X	WONG, W. W. H. et al., 'Solution processable fluorenyl hexa-peri-hexabenzocoronenes in organic field-effect transistors and solar cells', Adv. Funct. Mater. 2010, vol. 20, pages 927-938 Abstract, Figure 9, pages 933-936	1-26
X	US 2010/0006153 A1 (RAUSCHER et al.) 14 January 2010 Abstract, paragraphs [0030-0033], [0039-0042], [0054-0058], Figures 1, 2	1-26
X	US 2009/0205713 A1 (MITRA et al.) 20 August 2009 Paragraphs [0042, 0050, 0073, 0080], Figure 1, claims 1, 24	1-26

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INTERNATIONAL SEARCH REPORT Information on patent family members		International application No. PCT/AU2014/050059	
This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.			
Patent Document/s Cited in Search Report		Patent Family Member/s	
Publication Number	Publication Date	Publication Number	Publication Date
US 2010/0006153 A1	14 January 2010	AU 2008221066 A1 CA 2679177 A1 CN 101622730 A CN 101622730 B DE 102007009790 A1 EP 2126997 A2 EP 2126997 B1 JP 2010519745 A KR 20090125072 A MX 2009008109 A MY 150008 A TW 200845449 A WO 2008104301 A2 ZA 200905729 A	04 Sep 2008 04 Sep 2008 06 Jan 2010 13 Jun 2012 28 Aug 2008 02 Dec 2009 19 Dec 2012 03 Jun 2010 03 Dec 2009 12 Aug 2009 15 Nov 2013 16 Nov 2008 04 Sep 2008 27 Oct 2010
US 2009/0205713 A1	20 August 2009	None	
End of Annex			
Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001. Form PCT/ISA/210 (Family Annex)(July 2009)			