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Self-Organized Semiconducting Polymer-Incorporated Mesostructured Titania for Photovoltaic Applications[**]

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The quest for alternative energy sources has generated a world-wide effort to prepare materials and devices designed to harvest clean abundant energy resources such as solar radiation. Considerable interest has focused on hybrid photovoltaic systems combining an organic chromophore, conjugated polymer or dye, and an n-type inorganic semiconductor.[1–3] A suitable energy band offset between the organic and inorganic components ensures that photo-excited electron–hole pairs formed near the organic/inorganic interface will dissociate into free carriers, with the electrons preferably on one component and the holes on the other. A promising hybrid donor–acceptor pair for photovoltaics are poly(p-phenylene vinylene) (PPV)-type conjugated polymers and titanium dioxide,[4,5] owing to the high optical absorption of the polymer in the visible range and the band offset at the titania/PPV interface, which induces electron transfer from the photo-excited polymer to titanium dioxide. To provide efficient exciton dissociation into charges prior to recombination, the phase separation between the organic and inorganic species must be on the same scale as the polymer exciton diffusion length, that is, 8–20 nm.[6,7] Furthermore, carrier transport to the electrodes requires that the organic and inorganic phases form continuous networks through the entire film.[8] The challenge is, therefore, to direct a donor–acceptor organic-inorganic phase separation on a sub-20 nm length scale, and at the same time obtain continuity and orientation of each individual phase on a much longer length scale.

To achieve this goal we developed a new and general synthetic approach that employs the co-assembly of a titania precursor species, a conjugated polymer, and an amphiphilic structure-directing agent to form conjugated-polymer-incorporated mesoscopically ordered titania films. The use of non-aqueous synthetic conditions enabled, for the first time, the incorporation of the highly hydrophobic conjugated polymers within the mesostructured titania host matrix during its formation. Judicious selection of the surface-active agent type and concentration directed the deposition of a cubically ordered through-film interpenetrating titania and semiconducting polymer networks with ca. 15 nm organic–inorganic phase separation. Incorporation of the conjugated polymer into the 3D titania matrix enhances its photostability, and integration of the novel hybrid material into a photovoltaic device results in improved device performances. This study demonstrates the ability to direct the self-organization of functional components into hierarchically ordered materials with improved characteristics for electronic and opto-electronic applications.

Several approaches have been previously applied to prepare nanoscale interpenetrating conjugated-polymer/titania networks, but they typically lack at least one of the important characteristics, that is, the sub-20 nm organic-inorganic phase separation or the through-film connectivity. Mixing the semiconducting polymers with titanium oxide precursors leads to an organic-inorganic phase separation of at least 50 nm between the organic and inorganic domains,[9] which limits the potential use of these mixtures for efficient charge separation. Infiltration of conjugated polymers into preformed porous titania, with pore size <50 nm, resulted in low polymer uptake and required elevated temperature treatments that reduced the conjugation length of the infiltrated polymers, impairing the performance of the corresponding photovoltaic devices.[10]

In this Communication, a 15 nm conjugated-polymer/titania phase separation is achieved by harnessing and refining the synthetic approach commonly used for the deposition of mesostructured titania. Mesostructured metal-oxide thin films are conventionally synthesized by using the evaporation induced self-assembly (EISA) method, starting from an alcohol/ water solution of a metal-oxide precursor and an amphiphilic surfactant, initially below its critical micelle concentration (cmc).[11,12] Preferential evaporation of the alcohol during dip-coating concentrates the non-volatile surfactant and metal-oxide species, which co-assemble into highly ordered metal-oxide/ surfactant mesophases fixed by the metal-oxide polymerization. Incorporation of functional guest molecules such as semiconducting polymers into mesostructured titania during its synthesis and processing requires the solubilization of the guest in the metal-oxide precursor solution. However, conjugated polymers are not soluble in protic solvent mixtures, such as sol–gel precursor solutions. Recently, we have reported the encapsulation of semiconducting polymers in hexagonal and lamellar mesostructured silica films by replacing the ethanol solvent for EISA with tetrahydrofuran (THF).[13] The latter was shown to possess key properties for EISA, namely high

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volatility under ambient synthesis conditions, low viscosity for film processing, and high solution miscibilities for surfactants, alkoxide inorganic precursors, hydrophobic conjugated polymer guest molecules, and water. Solution processing in THF permitted highly hydrophobic, high-molecular-weight, conjugated polymers to be directly co-assembled within the mesostructured surfactant-templated silica matrix during its formation.

To prepare semiconducting polymer-incorporated mesostructured titania, a titania precursor, titanium tetra-ethoxide (TEOT), was first hydrolyzed in an acidic solution so that the TEOT:water molar ratio was slightly below the ratio necessary for full hydrolysis of TEOT, 1:4.[14,15] The water content, an important factor in mesostructured titania formation,[16] was kept minimal to prevent aggregation and sedimentation of the conjugated polymer in the precursor solution. For the same reason, the highly acidic conditions required to stall the fast titania condensation reaction[15] were avoided by adding acetylacetone (acac), a titanium chelating agent, to the initial solution (see Experimental).[15,17] The hydrolyzed titania solution in THF could then be mixed with a solution of the structure directing agent and the semiconducting PPV derivative, poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene] (MEH-PPV), also in THF, without causing aggregation and precipitation of the hydrophobic conjugated polymer. The triblock copolymer poly (ethylene- oxide)$_{106}$-poly (propylene-oxide)$_{70}$- poly(ethylene-oxide)$_{106}$, Pluronic F127, was selected as the structure-directing agent because it is known to direct the deposition of a through-film, continuous, 3D cubic titania mesophase from ethanol/water precursor solutions.[18] THF evaporation during film dip-coating accelerates titania condensation and cross linking, releasing water molecules into the solution. The water molecules progressively generated in the solution, induce the self-organization of the surfactant into micelles, and subsequently into liquid-crystal-like mesophases. In situ generation of the dilute water molecules in the THF precursor solution is sufficient to promote F127 self-organization, and at the same time, circumvents the precipitation of the hydrophobic conjugated polymer.

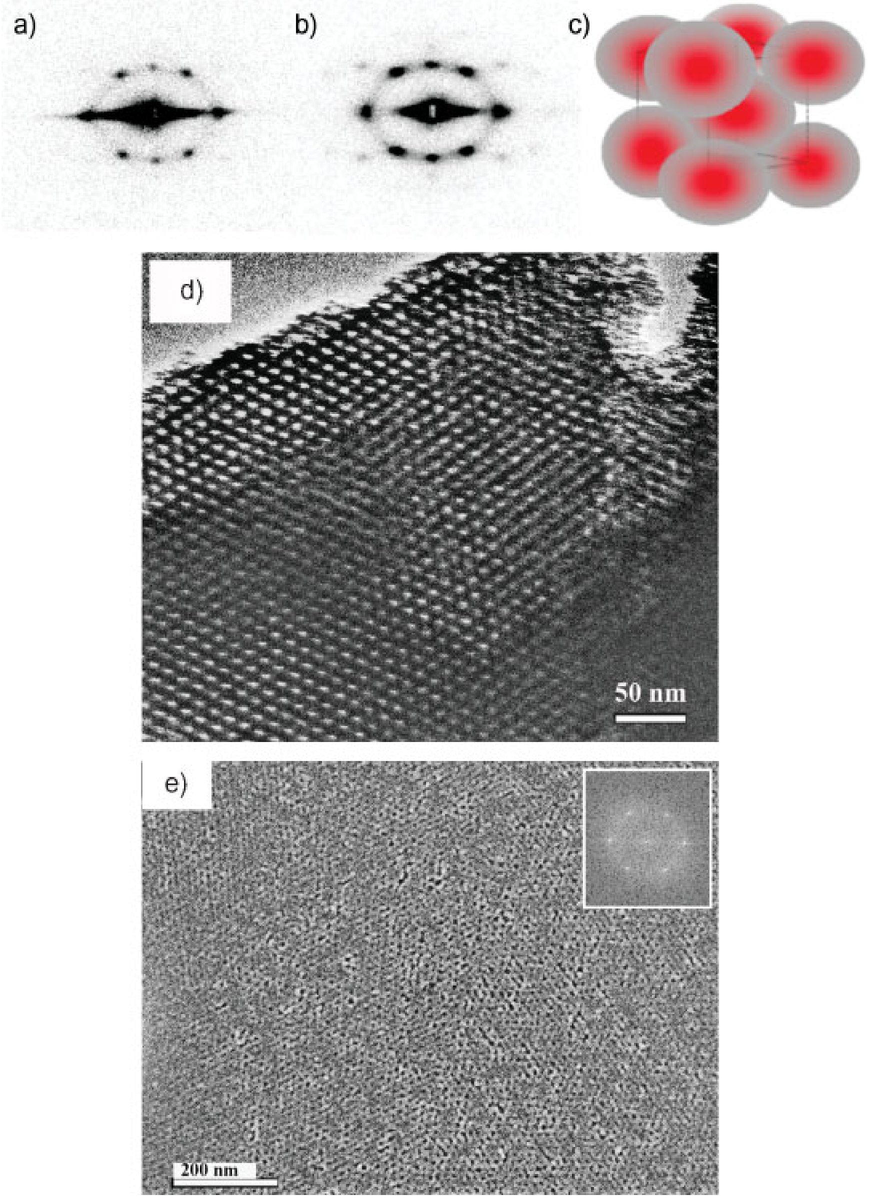

Figure 1. SAXS patterns of F127-templated titania films deposited from THF precursor solutions a)without, and b) with the addition of MEH-PPV to the precursor solution. c) A schematic illustration of the $Im\bar{3}m$ F127-templated conjugated-polymer-incorporated titania film, where the grey spheres represent the F127 surfactant, red spheres the MEH-PPV, and the titania matrix is the background. d) TEM image of F127-templated $Im\bar{3}m$ cubic titania viewed along the (111) plane; and e) a high-resolution scanning electron microscopy top view, and fast Fourier transform (inset) of a calcined (450 °C for 3 h) cubic titania/F127/MEH-PPV film.

A cubic mesostructured titania film was found for F127-directed titania films dip-coated from a THF precursor solution (with no conjugated polymer in the precursor solution). Figure 1a shows the 2D glancing-incidence small-angle X-ray spectroscopy (SAXS) pattern from a F127-directed titania film, with intense spots assigned to the (110), (101), and $(\bar{1}10)$ reflections of a distorted body-centered cubic $Im\bar{3}m$ structure, with the (110) plane parallel to the surface.[19,20] The average lattice parameter calculated by approximating the SAXS pattern to a non-distorted cubic structure is 15.1 nm, in good agreement with that reported for cubic F127-directed mesostructured titania deposited form the conventional ethanol/water precursor solution.[19] Addition of MEH-PPV to the THF F127/titania precursor solution also leads to the deposition of a cubic mesophase, as displayed in Figure 1b, with a cubic lattice parameter of 15.8 nm. We attribute the increase of the lattice parameter from 15.1 to 15.8 nm to the incorporation of conjugated polymer chains into the surfactant assemblies that template the titania network. A schematic illustration of the $Im\bar{3}m$ F127-directed conjugated polymer-incorporated titania, termed cubic titania/F127/MEH-PPV from here on, is shown in Figure 1c.

Additional evidence supporting the 3D structure of the Pluronic-directed titania films deposited from THF precursor solutions, with or without semiconducting polymers, was obtained by transmission and scanning electron microscopy measurements (TEM and SEM). A TEM image of a F127-directed titania film deposited from a THF precursor solution, Figure 1d, shows a six-fold pattern assigned to the $Im\bar{3}m$ 3D structure viewed along the (111) plane.[18] The 9–10 nm distance between in-plane nearest neighbors in the image, corresponding to the (110) plane spacing is similar to that calculated from the SAXS pattern (Fig. 1a). A high resolution scanning electron microscopy (HRSEM) top view image of a cubic titania/F127/MEH-PPV film after calcination is shown in Figure 1e. The image shows a uniform film surface with long-range ordering of a porous structure running perpendicular to the surface. The surface six-fold symmetry, apparent from the image fast Fourier transform (FFT; inset), is typical of the (111) orientation of the cubiclike lattice. The orientation discrepancy between the HRSEM and SAXS measurements could be due to different orientations of the structure at the film surface and bulk, previously reported for cubic mesostructured titania prepared using Pluronic surfactants.[21] Based on the top-view HRSEM images, we note that the conjugated-polymer-incorporated titania films reported here are endowed with the essential characteristics necessary for fabricating devices: the films are uniform and continuous over several micrometers; with top-to-bottom through-film interpenetrating organic and inorganic 3D networks and an organic–inorganic phase separation of 10–15 nm.

A crucial question related to the true nature of the self-organized films is whether the MEH-PPV is indeed incorporated into the mesochannels of the titania host. A first indication is provided by the increase of the lattice parameter upon polymer incorporation, as evident from the SAXS and electron microscopy patterns shown above. Further evidence is obtained from the photoluminescence spectra of the incorporated polymer chains. The optical properties of conjugated polymers reflect the delocalization of π-electrons along the polymer chains and are therefore sensitive to the mean conjugation length of the polymer segments, chain morphologies, chain–chain interactions, and the environment.[22] Consequently, the emission spectra of the incorporated conjugated polymers can be used as sensitive probes to provide insight on the location of the conjugated polymer in the structure.

The normalized photoluminescence (PL) spectrum of a cubic titania/F127/MEH-PPV film (solid line) resembles that of a pristine MEH-PPV film spun from a dilute THF solution (dashed line), as shown in Figure 2a. The peaks centered at 570 and 615 nm in both spectra, assigned to the (0,0) and (0,1) vibronic transitions, respectively,[23] are in good agreement with earlier reports on the PL spectra of MEH-PPV deposited from dilute THF solution.[24] The PL spectrum of the cubic titania/F127/MEH-PPV film is slightly broader than that of the pristine film, probably because of reduced energy transfer

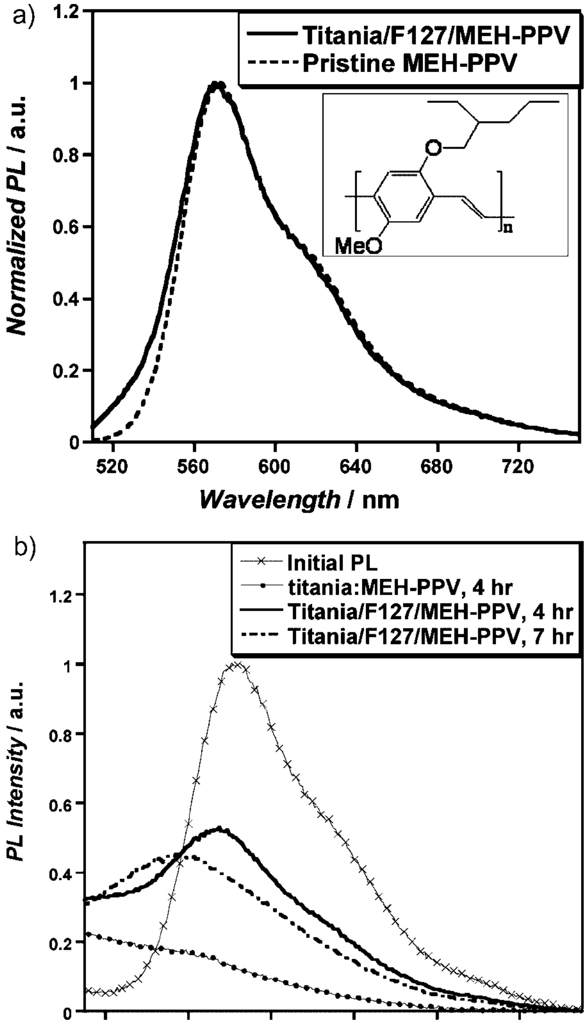

Figure 2. Photoluminescence spectra excited at 420 nm of a) a pristine MEH-PPV film and an as-prepared cubic titania/F127/MEH-PPV film, inset: chemical structure of MEH-PPV; and b) cubic titania/F127/MEH-PPV film and a titania:MEH-PPV blend before and after photo-oxidation by exposure to the UV region of the solar spectrum under ambient conditions. The initial PL intensity of both films was normalized to unity prior to photo-oxidation.

between partially isolated chains, which leads to contributions in the high-energy region.[25] Increasing the concentration of MEH-PPV in the precursor solution (not shown) and/or heat treatments of the deposited film (-x- line in Fig. 2b), led to a reorganization of the MEH-PPV chains and a slight red-shift in the PL spectrum.

To confirm that the MEH-PPV is encapsulated within the surfactant segments and not macroscopically phase-separated as large MEH-PPV domains embedded in the titania matrix, we measured the PL intensity before and after rinsing the cubic titania/F127/MEH-PPV film in xylene, a good solvent for MEH-PPV (see Supporting Information). For comparison, the same rinsing process was performed on a blend film of titania and MEH-PPV prepared by polycondensation of the titania precursor in a THF solution containing MEH-PPV, but without the presence of the surfactant. The absence of Pluronic structure-directing agent leads to disordered, mixed titania and MEH-PPV films, termed here titania:MEH-PPV. Rinsing these blend titania:MEH-PPV films in xylene dramatically decreased the PL intensity owing to removal of macrophase-separated MEH-PPV domains from the film, and quenching of the PL from remaining chains adjacent to titania. In contrast, only a very slight decrease in PL intensity was observed after rinsing the cubic titania/F127/MEH-PPV film in xylene. This strongly indicates that a substantial amount of the MEH-PPV chains are indeed encapsulated within the surfactant inside the mesostructure and consequently are not dissolved by xylene. We recognize that the presence of macrophase-separated MEH-PPV domains or single MEH-PPV chains dispersed in the titania (and not in the surfactant) can not be ruled out at this stage.

Additional evidence supporting the MEH-PPV inclusion in the surfactant domains is obtained from the improved photostability of the incorporated chains, an important property considering the expected use of MEH-PPV/titania composites in photovoltaic devices.[26,27] Figure 2b compares the PL spectra of a titania:MEH-PPV blend film (prepared with no surfactant) to that of a cubic titania/F127/MEH-PPV film after exposure to the UV region of the solar spectrum under ambient conditions. After 4 hours only, the PL from the titania:MEH-PPV blend has completely disappeared (black circles in Fig. 2b), whereas the PL from the cubic titania/F127/MEH-PPV film was reduced by 50% only (solid line in Fig. 2b). Even after 7 hours of UV exposure the F127-directed MEH-PPV still maintains its photoluminescence (dashed–dotted line in Fig. 2b). The blue-shift observed in all the PL spectra upon UV exposure is a result of a reduction in conjugation length and energy transfer efficiency by photo-oxidation. The enhanced photostability of the mesostructured film compared to the blend film demonstrates an important advantage of MEH-PPV encapsulation in an organic surfactant for titania based photo-active devices.

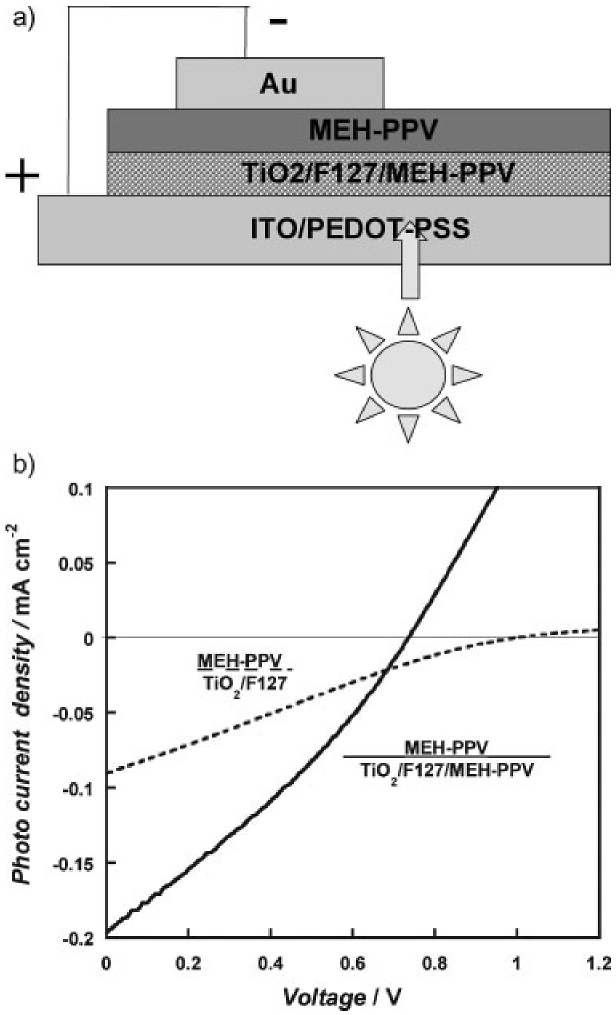

Figure 3. a) A schematic illustration of the a photovoltaic device with a transparent ITO:PEDOT-PSS electrode, a cubic titania/F127/MEH-PPV charge generating layer, a spun pristine MEH-PPV hole transporting layer, and a Au top electrode. ITO: indium tin oxide; PEDOT:PSS: poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate). b) *J–V* in light characteristics of the device shown in (a) (solid line) and a reference device with the same configuration but no MEH-PPV in the cubic titania/F127 bottom active layer (dashed line).

To demonstrate that the Pluronic-directed MEH-PPV-incorporated 3D mesostructure titania films, with a <20 nm interpenetrated continuous donor–acceptor organic-inorganic phase-separated network, are promising materials for realizing efficient solar cells we have constructed and characterized photovoltaic devices utilizing the cubic titania/F127/MEH-PPV films. The general bilayer device structure, shown in Figure 3a, is composed of an ITO/PEDOT:PSS transparent electrode to collect the electrons; a cubic titania/F127/MEH-PPV film for light absorption, charge generation and separation; a pristine MEH-PPV layer for hole transporting; and a gold electrode as the hole collector. Typical *I–V* characteristics (black solid line in Fig. 3b) exhibit open-circuit voltage (V_{oc}) of about 0.7–0.8 V, short-circuit current (J_{sc}) of 0.2 mA cm^{-2}, and a 30% fill factor, resulting in a power conversion efficiency (η) of 0.034%, which is about an order of magnitude lower than that reported for titania/PPV bilayer solar cells with a similar configuration.[4,5] The somewhat limited current in the Pluronic-directed

MEH-PPV-incorporated titania devices could be attributed to the high film thickness,[28] low electron mobility in the non-crystalline titania, and the limiting current-collection properties of top Au contacts.[5]

The contribution of the incorporated MEH-PPV chains to the photocurrent is established by fabricating devices with the same structure shown in Figure 3a, but with no MEH-PPV in the cubic titania/F127 layer. In these reference devices, the photocurrent is generated only at the interface between the cubic titania/F127 layer and the pristine MEH-PPV layer. Therefore, comparing the performance of the cubic titania/F127/MEH-PPV:pristine MEH-PPV bi-layer device (black solid line in Fig. 3b) to that of the cubic titania/F127:pristine MEH-PPV bi-layer device (dashed line in Fig. 3b) enables to identify the photocurrent generated by MEH-PPV chains that are incorporated into the mesostructured titania. The V_{oc} of the reference bilayer device (dashed line in Fig. 3b) is slightly higher than that obtained for the F127-directed MEH-PPV-incorporated titania device (solid line in Fig. 3b), but the J_{sc} is substantially lower, 0.09 mA cm^{-2}, leading to a significantly lower conversion efficiency of 0.016%. The J_{sc} value of the reference bi-layer device compared to that of the F127-directed MEH-PPV-incorporated titania device reveals that the MEH-PPV chains incorporated into the mesostructured titania generate at least 50% of the device photocurrent, clearly demonstrating the significant role of the incorporated MEH-PPV chains in the device performance.

The presence of the long F127 surfactant, EO_{106}-PO_{70}-EO_{106}, at the MEH-PPV/titania interface inside the mesostructure might pose a barrier for exciton dissociation into free carriers, apparent from the high photoluminescence intensity and perhaps the lower V_{oc} of the cubic titania/F127/MEH-PPV film. On the other hand, the surfactant can inhibit free carrier recombination into bound excitons, and improve the device photo-stability. Therefore, the effect of surfactant type, length, and location in cubic titania/surfactant/MEH-PPV films and corresponding devices is currently under further investigation. It is foreseen that judicious selection of the surfactant type and length, optimized to enhance exciton dissociation and inhibit carrier recombination, could provide a handle to dramatically enhance the performance of corresponding photovoltaic devices. Further substantial opportunities for significant improvements of the photocurrent are also expected by increasing polymer loadings, incorporation of low band-gap improved solar-light harvesting conjugated polymers, optimization of film thicknesses,[28] and perhaps shorter or functionalized surfactants.

In conclusion, we report on the self-organization of donor/acceptor, MEH-PPV/titanaia, interpenetrating 3D networks, with an organic–inorganic phase separation on the 10–15 nm length scale, and enhanced photo-stability. The films are prepared by the co-assembly of a titania precursor species, MEH-PPV and an amphiphilic structure-directing agent, Pluronic F127, from a THF-based precursor solution. The synthetic method is general and could be easily adapted to other surfactants, functional guest molecules such as conjugated polymers, and inorganic metal-oxide frameworks for a variety of applications. Photovoltaic devices utilizing the surfactant-directed MEH-PPV-incorporated cubic titania thin films showed reasonable photo-currents and open circuit voltages. Increased molecular understanding of the physicochemical processes governing charge generation, separation, and transport in this self-assembled interpenetrated organic–inorganic system, along with optimization of device structure, could lead to the desired high-performance photovoltaic devices. This study demonstrates first steps towards the prospect that a mixture of materials in solution could self-organize on a surface to form a complex high performance device.

Experimental

Materials: Titanium tetra-ethoxide (TEOT, Aldrich Germany), concentrated hydrochloric acid, HCl, 12 M in de-ionized water (Carlo Erba, Italy), acetyl acetone (GR for analysis, Merck, Germany), tetrahydrofuran (THF AR, BioLab, Israel), were used as received. A structure-directing surfactant triblock poly(ethyleneoxide)-*b*-poly(propyleneoxide)-*b*-poly(ethyleneoxide) copolymer, $EO_{106}PO_{70}$-EO_{106} (Pluronic F127, $M_n = 12600$), was a gift from BASF, USA, and used as received. The conjugated polymer used in this study, poly[2-methoxy-5-(2′-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV, $M_W = 500$ K), was purchased from ADS, Canada, and used as received. An aqueous dispersion of Poly(3,4-ethylendioxythiophene)-poly(styrenesulfonate), (PEDOT:PSS), BAYTRON F E, was used as a conductive layer in the photovoltaic devices.

Synthesis: In a typical synthesis, hydrolysis of TEOT was performed by addition of HCl (12 M, 0.35 mL) to liquid TEOT (1 mL, 4.7 mmol) and the mixture was vigorously stirred for 10 minutes until the solution was clear. The mixing caused a raise in the solution temperature and a slight color change to light yellow. Acetyl acetone (acac, 0.35 mL, 3.4 mmol) was then added and the solution turned yellow-brown. Separately, a THF solution of the structure-directing agent, F127, was prepared. After stirring, the surfactant solution was carefully added to the TEOT solution and the mixture stirred for two hours. F127 was typically 4–5 wt % of the solution, following previous reports using F127 for the preparation of a cubic titania film from water/alcohol sol–gel [18]. The final molar ratios in the precursor solution were 1 TEOT:0.9 HCl:3 H_2O:0.716 acac:0.004 F127:12 THF. In order to incorporate MEH-PPV into the mesostructured titania, a MEH-PPV solution in THF (1.5 mL, concentration 1–5 mg mL^{-1}) was carefully added to the TEOT/surfactant solution (1.5 mL) and the mixture stirred for a few minutes before film deposition. Notably, all conjugated polymer/TEOT/surfactant solutions remained clear and stable for weeks under ambient conditions.

Film Deposition: Thin films were prepared by dip coating at 2 mm s^{-1} glass, Si, polyimide, or ITO/PEDOT:PSS substrates, for optical, HRSEM, SAXS and device measurements, respectively. The relative humidity in the deposition chamber was set to 70–80% which promotes the deposition of the preferred cubic mesophases [20, 29]. The typical thickness of the mesostructured titania films, measured with an α-step instrument, was 100–200 nm. Conjugated polymer loading was estimated by dissolving freshly deposited films in 2 mL of THF under stirring for two days. The weight of the incorporated polymer was calculated by determining the concentration of the conjugated polymer in the solution of the dissolved film using optical absorption spectroscopy (Varian Cary 100 Scan UV-vis spectrophotometer) The total film-weight was calculated from the film dimensions and approximated specific gravity based on the initial quantities of the titania precursor, F127 and MEH-PPV. Polymer uptake was found to depend on the concentration of MEH-PPV in THF solution added to the precursor solution, and was estimated to be 1.5 and 6.3 wt % for films deposited from solutions with 1 and 5 mg mL^{-1} MEH-PPV, respectively.

Film Characterization: Small-angle X-ray scattering measurements (SAXS) were performed on polyimide coated samples using a small-angle diffractometer (Bruker Nanostar, KFF CU 2 K-90) with Cu Kα radiation with $\lambda = 1.542$ Å ($V = 40$ kV, $I = 20$ mA). The measurements were taken in ''glancing incidence'' scattering geometry which shows diffracted intensity exclusively out-of-the-film-plane. The patterns were recorded by a 2D position-sensitive wire detector situated 64.3 cm behind the sample. High-resolution microscopy measurements were performed using a Philips CM120 TEM with operating voltage of 120 KV, and a high resolution SEM, LEO Gemini 982 field emission gun, at accelerating voltage of 4 kV. For TEM measurements the films were scratched off the glass surface with a razor blade and placed on a copper grid. Photoluminescence measurements were conducted using a Varian Cary Eclipse fluorescence spectrometer.

Photovoltaic Devices: Thin films of PEDOT-PSS were deposited on 12×12 mm^2 ITO-coated glass substrates by spin coating at 1500 rpm, and the film heat-treated for 3 h at 110 °C. Either a cubic titania/F127/MEH-PPV film or a cubic titania/F127 film (with no MEH-PPV) was deposited on to the ITO/PEDOT:PSS films by dip-coating, and the films dried in a glove box. A thin layer of MEH-PPV from a 7 mg mL^{-1} solution in xylene was then spun on top at 1500 rpm under inert conditions, followed by a heat treatment at 90 °C in vacuum for 3 h. Device configuration was completed by thermal evaporation of a gold layer, 100 nm thick, through an eight-pixel shadow mask. The devices were characterized with an Agilent SPA while exposed to an Oriel Xenon lamp, with input power of 130 mW cm^{-2}.

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