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Amino acid appended perylene bisimides: self-assembly, immobilization on nanocrystalline TiO₂, and electrochromic properties.

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Electronic Supplementary Information

Materials and methods: The alanine-appended PBI (*N*, *N'*-di(L-alanine)-perylene-3,4:9,10tetracarboxylic acid bisimide, hereafter PBI-A) was synthesised as described previosuly.^{S1} Anatase TiO₂ electrodes were prepared by depositing commercial TiO₂ colloidal precursor (Dyesol 90-T) paste onto fluorine-doped tin oxide (F:SnO₂, FTO, Sigma-Aldrich, thickness = 2.3 mm, resistivity *ca*. 7 Ω /sq.). The slides were sonicated in ethanol for 20 minutes before deposition. The paste was deposited on the films and spread with a glass rod. The thickness was controlled using Scotch Magic tape (3M) and was measured *via* profilometry to be approximately 8 µm. The films were heated to dryness at 100 °C, followed by annealing in air at 450 °C for 30 minutes in a tube furnace. The slides were cut so that the geometric surface area of the TiO₂ films was approximately 1 cm², covering roughly half of a *ca*. 1 x 2 cm slide. Acetonitrile (MeCN, spectroscopic grade, VWR), methanol (MeOH, spectroscopic grade, Sigma-Aldrich, ferrocene (Fc, > 98 %, Sigma-Aldrich), potassium chloride (> 99 %, Sigma-Aldrich), silver nitrate (Johnson Matthey), tetrabutylammonium hexafluorophosphate (> 99 %, electrochemical grade, Sigma-Aldrich) and lithium perchlorate (LiClO₄, > 95 %, Sigma-Aldrich) were used as received.

PBI-A was soaked onto TiO₂ electrodes using various solutions. For clarity, films soaked in H₂O (0.1 M NaOH to help dissolution, pH = 6.1) at 10⁻⁴ or 10⁻⁵ M were labelled type A and type C, respectively; while films soaked from 10⁻⁴ M MeOH were labelled type B. The TiO₂-coated half of the slide was immersed fully in the soaking solution inside a glass sample vial, the lid screwed on, and the solution left to soak in the dark. When the desired soaking time had elapsed, the slide was removed, rinsed thoroughly with clean solvent, and gently dried under a stream of N₂.

All electrochemical measurements were performed using a CHInstruments 660 potentiostat with a FTO/TiO_2 or $FTO/TiO_2/PBI-A$ working electrode, a Pt coil counter electrode and a Ag/AgNO₃ reference electrode (filling solution: 0.1 M LiClO₄ + 0.01 M AgNO₃ in MeCN), which was calibrated daily using a solution of Fc in 0.1 M MeCN/LiClO₄ and a glassy carbon working electrode (d = 3 mm,

CHInstruments). ATR-FTIR spectra were recorded using a Perkin-Elmer Spectrum 100 (16 scans, 4 cm⁻¹ resolution). UV/Vis spectroscopy was performed using a Jasco V750 spectrometer with slit widths of 1 mm and quartz cuvetters of various pathelengths (I = 10, 2 or 0.1 mm), or soaked FTO/TiO₂/PBI-A film (recorded in air). Fluorescence spectra were measured using a Perkin-Elmer LS55 spectrometer and 10 mm pathlength quartz cuvettes using slits of 1 and 1 nm. Solutions, 10^{-4} M in either H₂O or MeOH, were not deoxygenated. Spectra of immobilised PBI-A could not be obtined on TiO₂ due to electron injection, analogous to in a DSSC; therefore samples were soaked onto SiO₂ TLC plates under the same conditions as for TiO₂. Fluorescence spectra of these SiO₂/PBI-A films were recorded in air. TiO₂ film thicknesses were measured using a Bruker DektakXT stylus profilometer. Field emission scanning electron microscopy (FESEM) images were recorded with a Zeiss Supra microscope at an accelerating voltage of 5 keV and a working distance of 1.5 mm. Films were sputter coated with Au:Pd at 0.15 mbar before use.

UV/Vis spectroscopy:

Sample	H-R factor
10 ⁻⁴ M MeOH soak/10 mins	1.40
10 ⁻⁴ M MeOH soak/20 mins	1.43
10 ⁻⁴ M MeOH soak/30 mins	1.31
10 ⁻⁴ M MeOH soak/12 hr	1.01
10 ⁻⁴ M MeOH soln	1.41
10^{-4} M H ₂ O soln	0.71
10 ⁻⁴ M H ₂ O soak/12 hr	0.82

Table S1: Huang-Rhys factors for soaking solutions and coated TiO₂ films.

FTIR spectroscopy: ATR-FTIR spectroscopy of solid PBI-A and PBI-A/TiO₂ are shown for comparison in Fig. S1. For solid PBI-A, the imide C=O symmetric and asymmetric stretches are visible at 1692 and 1652 cm⁻¹, respectively, with other modes at 1588 and 1573 cm⁻¹ (C=C symmetric stretching) and 1365 cm⁻¹ (imide C-N stretch). The C=O symmetric stretch for the alanine carboxylic acid group is present at 1745 cm⁻¹. Upon immobilisation onto TiO₂ (12 hr soak in a 10⁻⁴ M/H₂O solution) this mode vanishes completely, indicating the complete conversion to the carboxylate form. Given that soaking solutions of PBI-A are made up in NaOH, both terminal alanine carboxylic acid groups are expected to be present as sodium carboxylate salts. Due to steric considerations, it is highly unlikely that both carboxylate groups at each end of the molecule are covalently bound to the TiO₂, so we propose that binding occurs through one carboxylate group with the PBI core pointing away from the TiO₂, probably at an angle, and given that the UV/Vis spectra in Fig. 1(a) show a high degree of stacking on the surface, the majority of the surface PBI is likely π-stacked onto a few monomer units that are covalently attached to the TiO₂.

The binding of carboxylate groups to TiO_2 has been studied by us and others previously.⁵² The asymmetric and symmetric $v_{as}(CO_2^{-})$ and $v_s(CO_2^{-})$ modes of the alanine carboxylic acid group in solid PBI-A were observed at 1636 and 1401 cm⁻¹, respectively, while these modes appeared at 1649 and 1403

cm⁻¹ for PBI-A on TiO₂. The peak separation v_{as-s} , characterized by $v_{as}(CO_2^{-})$ and $v_s(CO_2^{-})$, can be used to assess the binding mode of a carboxylate group to a TiO₂ surface according to the empirical rule that band separation follows v_{as-s} (monodentate) > v_{as-s} (isolated) > v_{as-s} (bidentate).^{S3} The band splitting for PBI-A on TiO₂ was 246 cm⁻¹, larger than the 235 cm⁻¹ for the free complex, which implies monodentate surface co-ordination. This kind of monodentate co-ordination has been observed for [Ni(cyclam-CO₂H)]²⁺ adsorbed on TiO₂ previously.^{S4} FTIR spectroscopy of a film soaked from an equimolar MeOH solution revealed essentially the same spectrum, indicating that the binding mode to the surface is the same in the case of MeOH.



Fig. S1: ATR-FTIR spectra of solid PBI-A (black) and a TiO₂ film soaked from type A solution (red).





Fig. S2: Fluorescence spectra of aerated 10⁻⁴ M PBI-A solutions. Black: H₂O, λ_{exc} = 500 nm; red: MeOH, λ_{exc} = 520 nm. The spectra have been normalized for intensity.



Fig. S3: Fluorescence spectra of 10^{-4} M PBI-A soaked SiO₂. The spectra have been normalized for intensity, and were recorded in air. λ_{exc} = 460 nm for both samples.

Cyclic voltammetry:



Fig. S4: CV (first cycle only) of a type A soaked TiO_2 film in aqueous 0.1 M KCl electrolyte. The PBI-A was seen to desorb after one cycle.

Field-emission scanning electron microscopy:



Fig. S5: TiO_2 films soaked from PBI-A/H₂O solutions for 12 hours (red film, 10^{-4} M, left) or 30 mins (pink film, 10^{-5} M, centre). The colourless film on the right is unmodified TiO_2 .



Fig. S6: FESEM image type C soaked PBI-A on TiO₂. The low soaking concentration resulted in an overall lighter coloured electrode than in the equivalent 10⁻⁴ M (type A) soak shown in Fig. 4, indicating a lower overall surface coverage of PBI-A, but the mesopores remain partially blocked. This gives further evidence that the properties of surface adsorbed PBI on TiO₂ are dictated by the degree and type of self-

assembled PBI superstructures formed in various solutions. The highly-aggregated nature of PBI-A at 10⁻⁵ M in H₂O has been shown by us previously, and *ca*. 10⁻⁷ M was required to favour monomer-like PBI-A in water.^{S5}

Preliminary electrochromism:

The preliminary electrochromic response of a type A soaked film was monitored at 715 nm as a function of applied potential, corresponding to the switching between the fully oxidised PBI, which has no absorbance at this wavelength, and the one electron reduced PBI. (λ_{max} of PBI. = 715 nm).^{S5} The optical contrast (OC) of the film was calculated according to Eqn. S1:

$$OC = \frac{T_b T_c}{T_b}$$

Where T_b and T_c are the transmittances of the bleached and coloured film, respectively, at the wavelength of max response (715 nm). The coloration efficiency (CE) of the film, defined as the change in optical density per unit of charge consumed by the electrochromic layer is given by Eqn. S2:

$$CE = log \frac{T_b T_c}{q/A}$$

Where *q* is the charge passed (in Coulombs) and *A* is the geometric surface area of the electrode (in cm²). Using Equations S1 and S2, the OC was calculated to be 32 % and CE calculated as 37 cm².C⁻¹; in contrast, literature values for a PBI polymerised on FTO gave OC of 29 % and CE 295 cm².C⁻¹ at a comparable wavelength.^{S6} These figures suggest our device performance is relatively modest, and the lower CE of our system relative to the literature PBI example suggest the presence of a parasitic side reaction in our case. We attribute this to the observable visual and electrochemical decomposition of the FTO substrate (*vide infra*).



Fig. S7, top: Electrochromic response for a blank TiO_2 film as a function of applied potential. Below: The grow-in of absorbance at 900 nm corresponds to the conduction band edge of TiO_2 .



Fig. S8, top: Electrochromic response of a type A soaked film as a function of applied potential. Below: Same data expanded.

Analysis of sample post-electrochromism:



Fig. S9: CVs (25 mV.s⁻¹) of a type A soaked PBI-A/TiO₂ electrode showing the PBI electrochemistry pre (black) and post (red) 500 electrochromic cycles. Loss of reversibility is clear post-reaction. Corresponds to Fig. 4 in main body of paper.



Fig. S10: UV/Vis spectra of a type A electrode showing the surface adsorbed PBI-A before cycling (black), post one cycle (red), and post 500 electrochromic cycles (blue). Loss of reversibility is clear post-reaction, as the PBI-A remains in the one-electron reduced form. The starting material could not be reformed even after application of an oxidizing potential. The λ_{max} and Franck-Condon progression of the S₀-S₁ transition at *ca*. 500 nm indicate that the PBI-A remains adsorbed and remains in the same self-assembled structure throughout the electrochromic cycling process. Loss of activity is therefore mainly attributed to substrate decomposition.^{52, S7, S8} Corresponds to Fig. 4 in main body of paper.

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