

Controlling Visible Light-Driven Photoconductivity In Self-Assembled Perylene Bisimide Structures

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Electronic Supplementary Information

Experimental details:

Solution phase voltammetry: Samples were prepared at a high pH (approximately pH 9-10) by adding 1 molar equivalent of aqueous NaOH solution (0.1 M) and then making the solution up to 10 mL by adding distilled water. A background electrolyte with a final concentration of 0.1 M of sodium chloride (NaCl) was added after the gelator had fully dissolved. The final concentration of PBI-A was 47 mM. Samples were sparged with argon for 20 minutes prior to voltammetry. Squarewave voltammetry (SWV), sweeping from negative to positive, was used to measure redox potentials of the PBI-A. Frequency = 25 Hz, amplitude = 1 mV, step size = 1 mV. WE = glassy carbon, CE = Pt mesh, RE = Ag/AgCl.

Viscosity measurements: Dynamic viscosity measurements were performed on an Anton Paar 101 rheometer. Measurements were performed using a 75 mm cone and plate geometry from 1 to 100 s⁻¹ on 2 mL of a 25 mg/mL solution prepared as described earlier. Measurements were carried out at 25 °C.

Small-Angle Neutron Scattering (SANS): The SANS measurements were carried out on the fixed-geometry, time-of-flight LOQ diffractometer (ISIS Spallation Neutron Source, Oxfordshire, UK). A white beam of radiation with neutron wavelengths spanning 2.2 to 10 Å was used to access a Q [$Q = 4\pi\sin(\theta/2)/\lambda$] range of 0.008 to 0.25 Å⁻¹ (at 25 Hz), with a fixed sample-detector distance of 4.1 m. The samples were loaded in a 2 mm path length, UV-spectrophotometer grade, quartz cuvettes (Hellma 110) and mounted in an aluminium holder on top of an enclosed, computer-controlled, sample chamber with temperature controlled to 25 ± 0.5 °C by a temperature-controlled circulating bath pumping fluid through the base of the sample chamber. The incident neutron beam was collimated to be 8 mm in diameter. Experimental measuring times were approximately 60 min. Deuterated solvents were used throughout.

All scattering data were normalized for linearity and efficiency of the detector response, the incident wavelength distribution, and the sample transmission using the Mantid software framework (www.mantidproject.org). The scattering from a quartz cell filled with D₂O was subtracted from the micelle solution data as a background correction (which also removes the inherent instrumental background arising from vacuum windows, etc). These data were put onto an absolute intensity scale by reference to the scattering from a partially deuterated polystyrene blend of known molecular weight.^{S1} The instrument-independent data were then fitted in the SasView software package (<https://www.sasview.org>) to a Kratky–Porod flexible cylinder model.^{S2, S3}

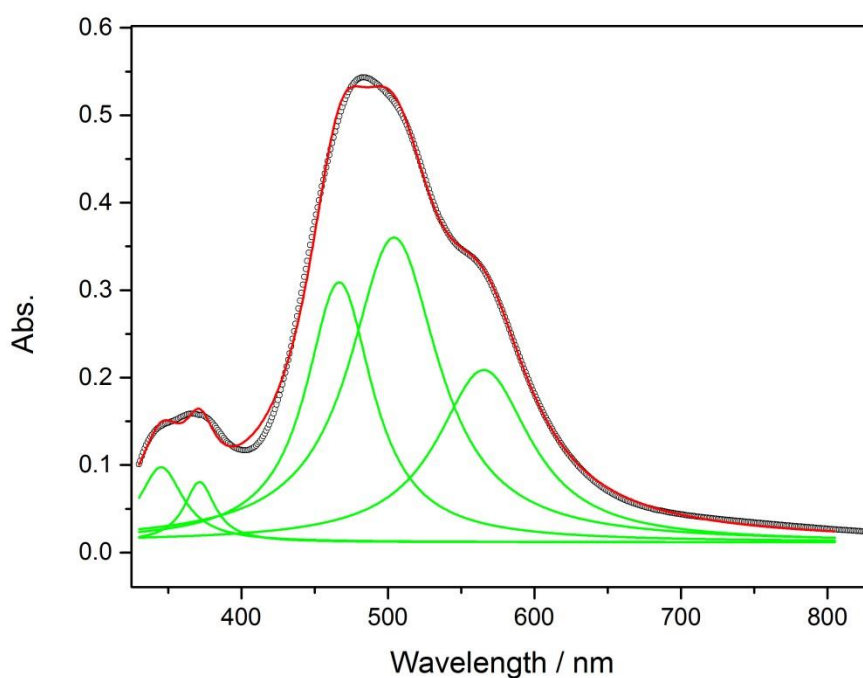


Figure S1: *UV/Vis spectrum of PBI-A film drop-cast onto a glass microscope slide and allowed to dry in air. The raw data is shown as open circles (black), the individual Lorentzian peaks (green) and overall fit line (red) are also shown.*

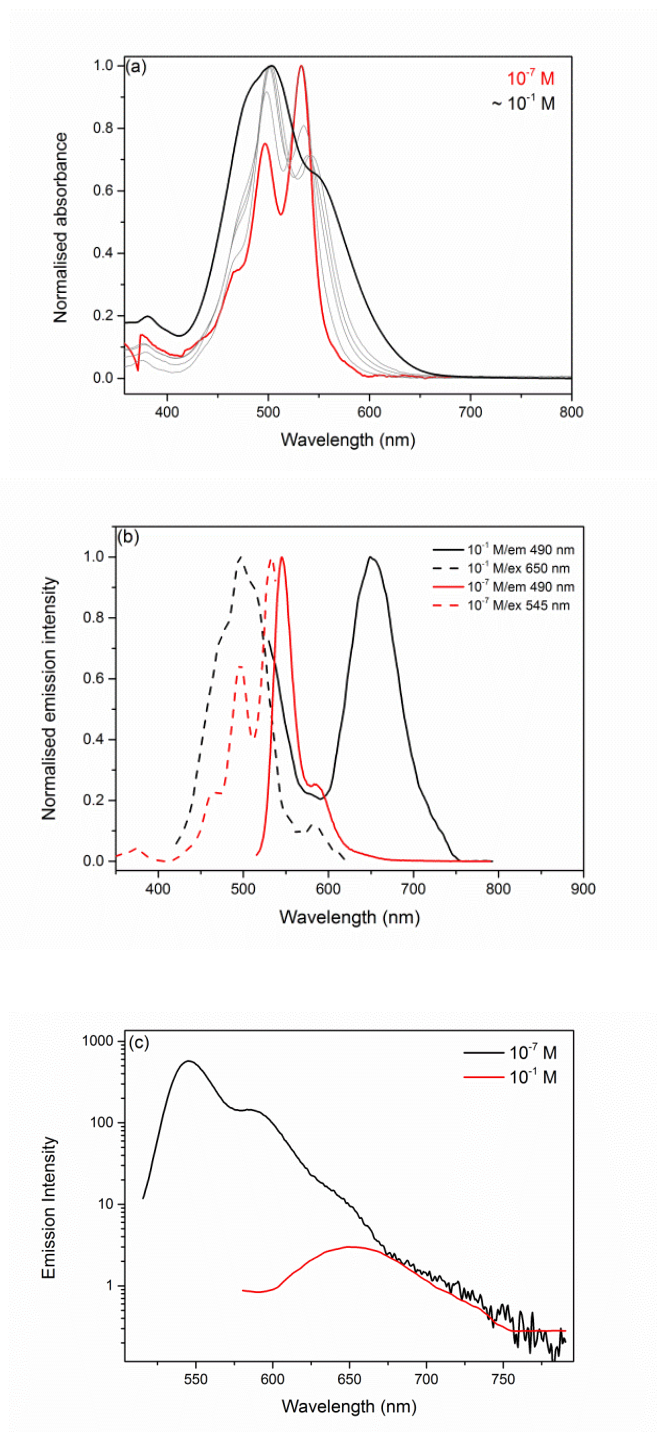


Figure S2 (a): Normalised UV/Vis spectroscopy of PBI-A solutions at 10^{-7} M (red) and ca. 10^{-1} M (black) in aerated aqueous solutions. Grey lines show the spectra at intermediate concentrations. (b): Normalised fluorescence spectroscopy of PBI-A solutions at 10^{-7} M (red) and ca. 10^{-1} M (black) in aerated aqueous solutions. Solid lines - emission spectra ($\lambda_{em} = 490$

nm); dashed lines - excitation spectra ($\lambda_{ex} = 545$ or 650 nm). (c) Raw emission data (not normalised) showing the difference in emission intensities.

Concentration dependent UV/Vis spectroscopy was performed over a range of concentrations from 10^{-7} to *ca.* 10^{-1} M (Figure 2 (a)). At 10^{-7} M, PBI-A adopts a monomer like configuration with a Huang-Rhys (HR) factor^{S4} of 1.25. At 10^{-6} M this had already dropped to 1.1, and by 10^{-5} M had dropped to 0.81, suggesting a significant amount of stacking already occurs at these concentrations.^{S5} Moving from 10^{-3} M to *ca.* 10^{-1} M this factor continues to drop from 0.70 to 0.65, suggesting that increasing levels of aggregation are still occurring even at these very high concentrations. The increased stacking behaviour is reflected in the fluorescence emission and excitation data shown in Figure 2 (b). From 10^{-7} to 10^{-3} M the PBI-A emission is observed with fine structure maxima at 546 and 583 nm, upon excitation at 490 nm; however as the concentration is increased the emission is quenched upon stacking. At *ca.* 10^{-1} M the PBI-A monomer emission appears completely quenched and a new band grows in at 600 – 700 nm, with a maximum at 652 nm (1.9 eV), though with a much weaker intensity than the monomer band (Figure S2 (c)). This is the region where excimer emission has previously been seen at > mM concentrations in aggregates of amino acid appended PBIs.^{S6} An excitation spectrum taken at 650 nm confirmed that the state responsible for emission is a stacked PBI, which is reflected in the corresponding *ca.* 10^{-1} M UV/Vis spectrum in Figure 2 (a).

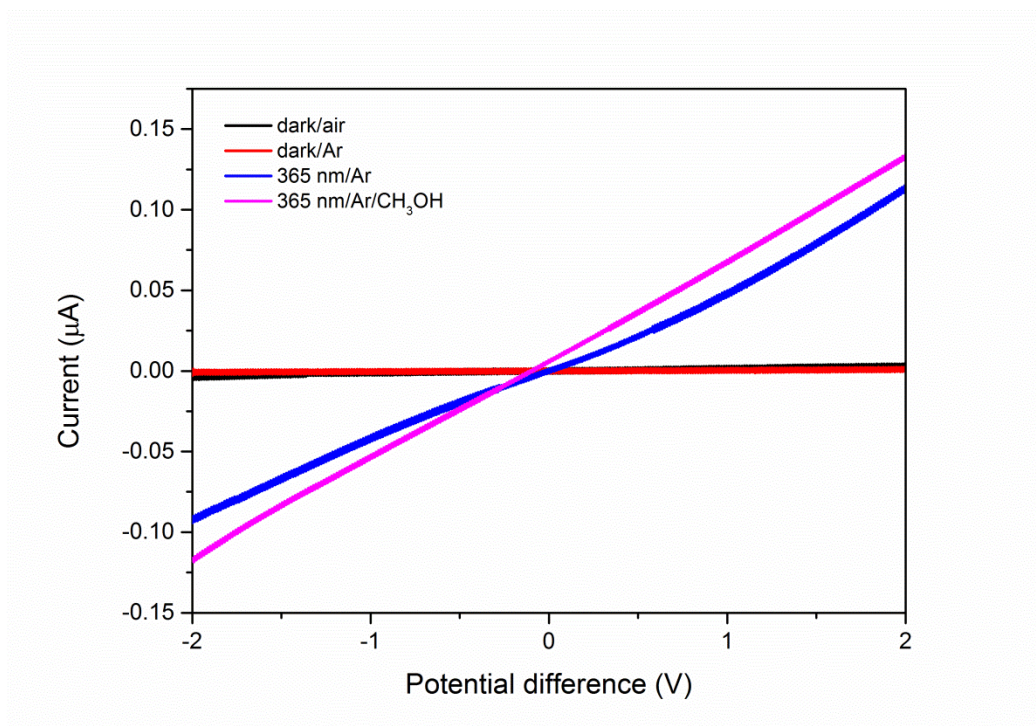


Figure S3: *I-V curves for a dried solution of PBI-A under controlled atmospheres under illumination at 365 nm only.*

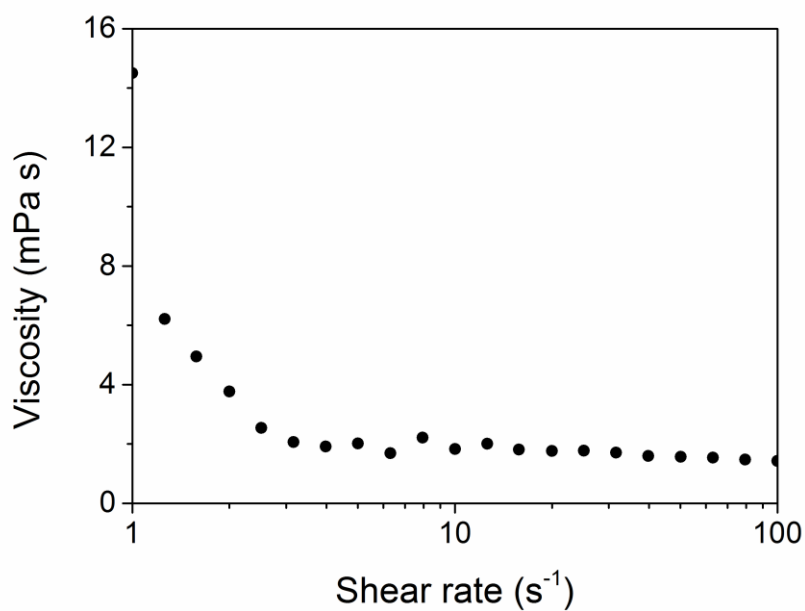


Figure S4: *Dynamic viscosity data of PBI-A solution at 25 mg/mL showing shear thinning consistent with the presence of worm-like micelles in solution.*

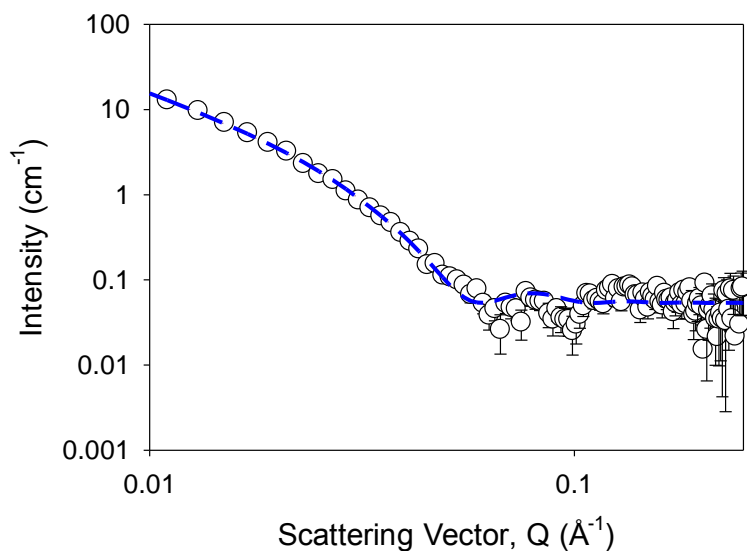


Figure S5: SANS intensity profile for a solution of PBI-A at a concentration of 25 mg/mL in D_2O at pH 9. The dashed line represents the fit to the data generated by the flexible cylinder model, giving a radius of 6.4 ± 0.1 nm, and a Kuhn length of 10.1 ± 1.3 nm.

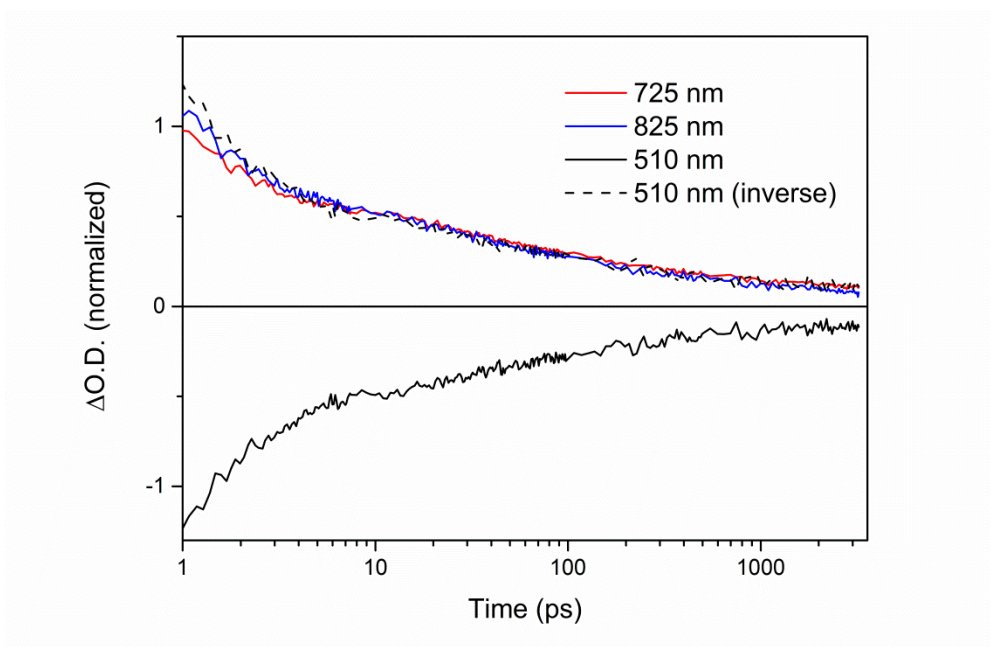


Figure S6: Kinetics of decays after excitation of PBI-A (47 mM, H_2O) under 490 nm excitation.

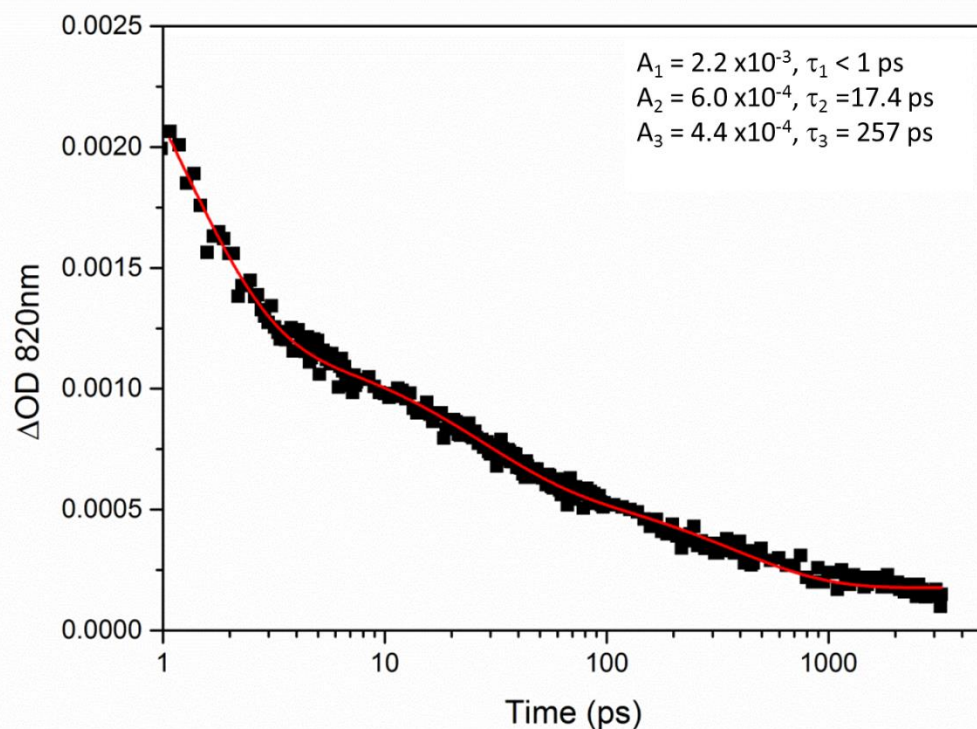


Figure S7: Kinetics of decay for an aqueous solution of PBI-A at 820 nm excited at 490 nm.

Decay curve fit to a tri-exponential decay is shown.

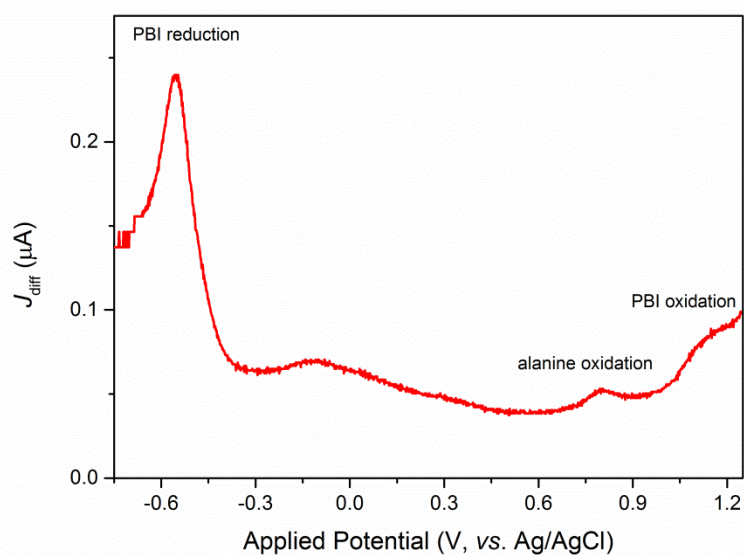


Figure S8: Squarewave voltammetry (SWV) of PBI-A (47 mM) in argon-purged pH 9 aqueous solution, 0.1 M NaCl supporting electrolyte, sweeping from negative to positive.

Frequency = 25 Hz, amplitude = 1 mV, step size = 1 mV. WE = glassy carbon, CE = Pt mesh, RE = Ag/AgCl. The peak at ca. - 0.1 V is due to residual O₂.

	PBI-A		Alanine		PBI
	Neutral	Deprotonated	Neutral	Deprotonated	--
Reduction	-0.68/ -0.52	-0.88/ -0.72	--	--	--
Oxidation	1.22/ 1.38	1.36/ 1.52	1.62/ 1.78	0.31/ 0.47	1.20/ 1.36

Table S1: B3LYP+D3/def2-TZVP predicted redox potentials for the different species versus the Ag/AgCl electrode (saturated NaCl). Values before and after the slash differ in the experimental value of the absolute value of the standard hydrogen electrode potential used, 4.44 and 4.28 V respectively, where the values in the table are calculated as $E_{\text{Ag/AgCl}} = E_{\text{vacuum}} - 4.44/4.28 - 0.197$.

	PBI-A			Na ₂ PBI-A	
	Neutral	Neutral	Deprotonated	Neutral	Neutral.4H ₂ O
ϵ_r	80	1	80	1	1
ΔE	2.0 (1.9)	4.8	1.9 (2.2)	4.3	4.2

Table S2: B3LYP+D3/DZP predictions of the energy required to make a pair of charge-separated states. Def2-TZVP results, where available, presented between parentheses.

Note that the large ion pair energy in Table S2 for Na₂PBI-A and Na₂PBI-A.4H₂O is not due to the replacement of the carboxylic protons by sodium ions. This is clearly demonstrated by the fact that a calculation of the ion pair energy for neutral PBI-A in a low dielectric

permittivity environment ($\epsilon_r = 1$) results in a similarly large ion pair energy as for $\text{Na}_2\text{PBI-A}$ and $\text{Na}_2\text{PBI-A}\cdot 4\text{H}_2\text{O}$.

	$E_{OX\ ALANINE}$ ($\text{V}_{\text{Ag}/\text{AgCl}}$)	$E_{RED\ PBI}$ ($\text{V}_{\text{Ag}/\text{AgCl}}$)	C (eV)	S (eV)	E_{i-p} (eV)	E^* (eV)	ΔG_{ET} (eV)
PBI-A, pH 9	0.80	-0.56	0.03	0	1.3	2.3	-1.0
PBI-A film	ca. 0.8	ca. -0.56	0.68	1.3	ca. 2.0	ca. 2.3	ca. -0.3

Table S3: Calculated Gibbs energy of photoinduced electron transfer from the intramolecular alanine donor functionality to the PBI core, with the terms relating to equations S1 and S2.

$$\Delta G_{ET} = E_{OX} - E_{RED} - E^* - \frac{e^2}{4\pi r_{DA}\epsilon_0\epsilon_s} + \frac{e^2}{8\pi\epsilon_0} \left(\frac{1}{r_D} + \frac{1}{r_A} \right) \left(\frac{1}{\epsilon_s} - \frac{1}{\epsilon_p} \right) \quad \text{Eq. S1}$$

$$\Delta G_{ET} = E_{OX} - E_{RED} - E^* - C + S \quad \text{Eq. S2}$$

To calculate the Gibbs energy of photoinduced electron transfer Equation S1 is employed in the manner described in the main text. E^* is the estimated excited state energy, ϵ_s and ϵ_p the dielectric constant of the solvents used for the spectroscopy and for the electrochemical measurements. The donor-acceptor is the distance (r_{DA}) between the chiral carbon atom of the amino acid and centre of the PBI core, ca. 7 Å by the DFT calculations described above. The transient measurements in Figure 2 are recorded in the same polar solvent used for the cyclic voltammetry to obtain E_{OX} and E_{RED} (pH 9 aqueous solution) and the final term of Equation 1, S, can therefore be disregarded in this case. In Table S3 the singlet excited state energy is used for E^* and is calculated from the average of the energies of its absorption maximum at

2.34 eV (530 nm) and emission maximum 2.27 eV (546 nm) of the material in its monomeric state at low concentration, Figure S2. We note that at the higher concentrations in solution a low energy emission maximum at 652 nm (1.77 eV, Figure S2) was observed. Charge separation from an “excimer” type state (in this case excimer refers to excited multimer as opposed to excited dimer) has been previously reported for an aggregated PBI structure and it is feasible that it may also be occurring here.^{S7} The energy of the excimer-like state can be estimated in the manner previously described.^{S7} In this case the upper exciton band of the aggregate PBI-A (pH 9 solution at 47 mM) is at 500 nm (2.48 eV) and the lower disallowed absorption would be expected to be at *ca.* 2.1 eV, giving rise to an estimated energy of the excimer state of *ca.* 1.9 eV. This does not change the key conclusion of Table S3, namely that in a high dielectric environment there is a large driving force for charge separation.

As noted in the main text the calculated Gibbs free energy for charge transfer in the film should be treated with extreme caution as the site of hole localisation is more complicated than in solution. This value is only included to provide a qualitative indication for the dielectric environment in controlling charge separation. For the dried film the final term of the equation (C) must be considered as the local dielectric of the sample (a dried organic film, $\epsilon \sim 3$) is markedly different from that of the solvent in which the oxidation potentials were recorded ($\epsilon \sim 80$). In this case the ionic radii of the donor and acceptor groups should be included. The lack of accurate ionic radii for such species is a known major limitation of the calculation,^{S5, S8, S9} further limiting the absolute accuracy of values obtained. Here we use an acceptor radius of 7.6 Å based on a previously measured value for a PBI core.^{S10} DFT calculations indicate localisation of the positive charge on the carboxylate group of deprotonated and sodium exchanged PBI-A (see below), a species with an approximate radius of 2.4 Å. Clearly this donor radius is an approximation.

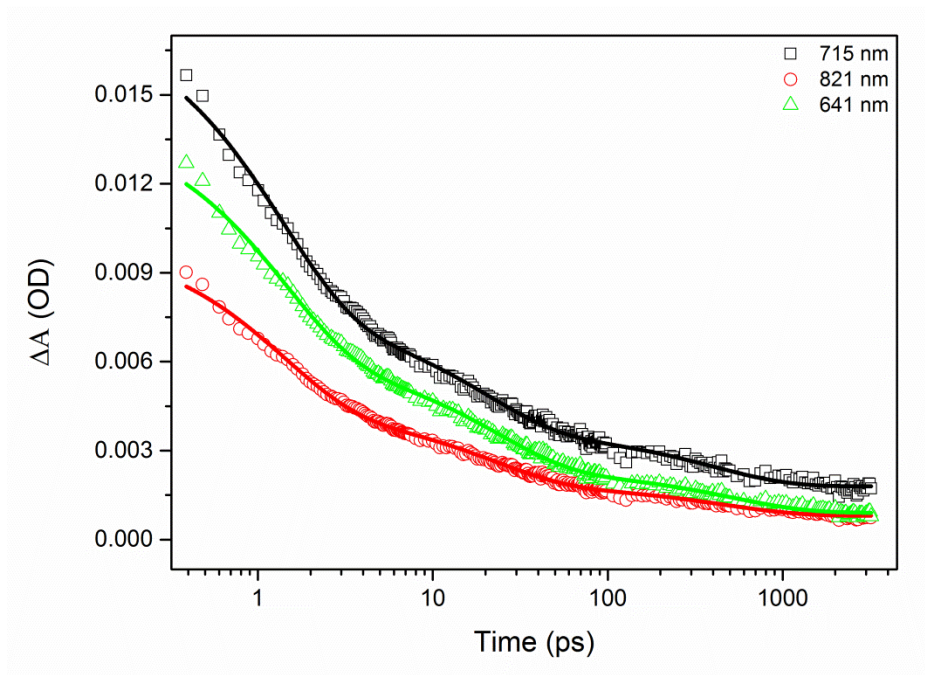


Figure S9: Kinetics of decays after excitation of a PBI-A dried film (47 mM, H₂O, Ar atmosphere) under 365 nm excitation across the visible/NIR region fit to a tri-exponential decay.

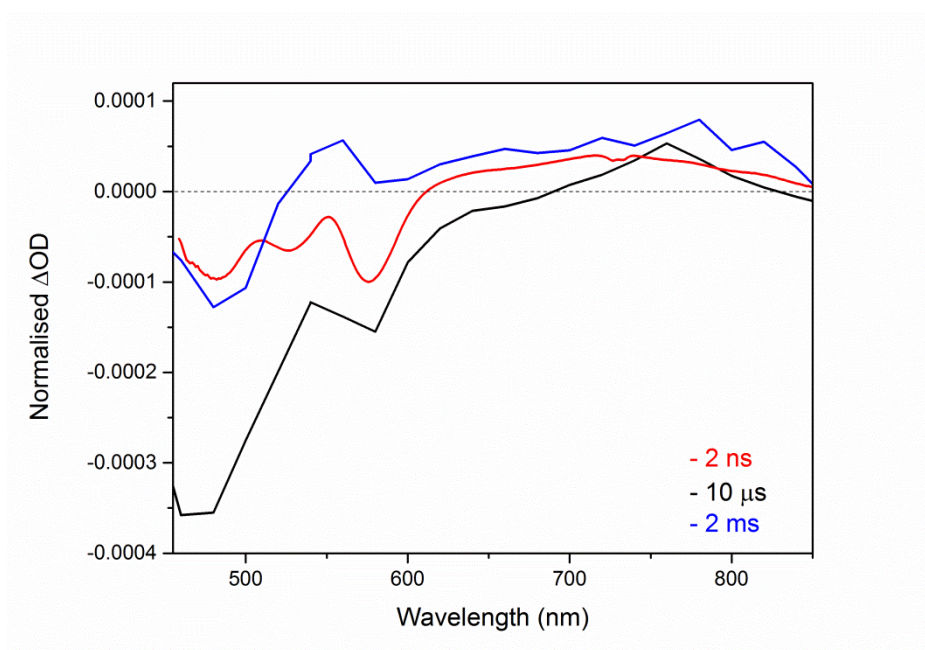


Figure S10: Comparison between μs and fs TA spectra of a PBI-A film in argon under 355 nm (μs -ms data) or 365 nm (fs-ns data) laser pump.

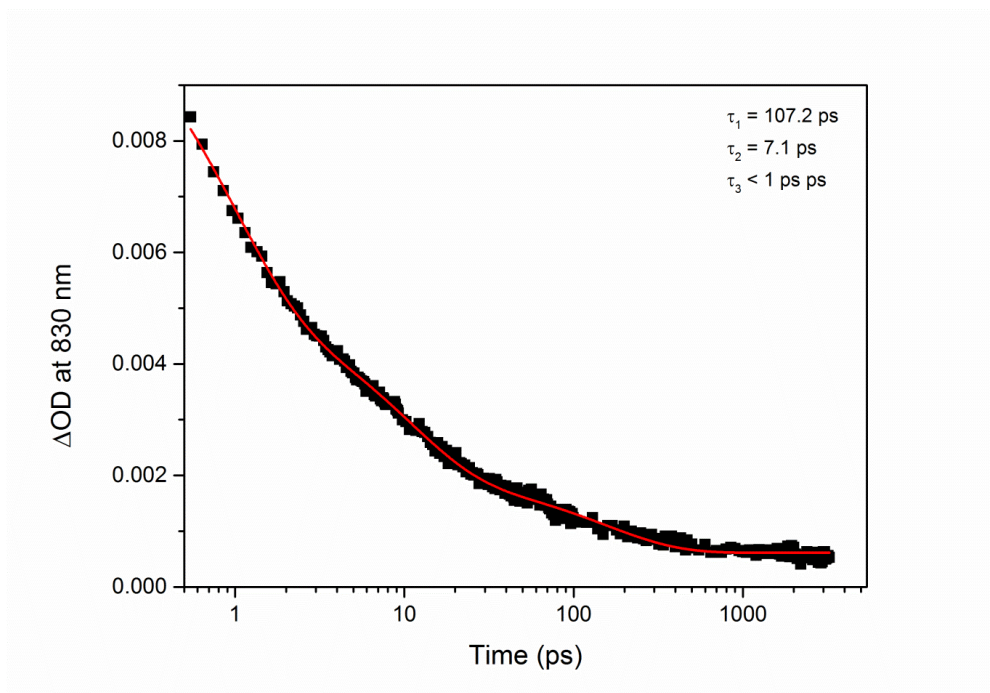


Figure S11: Kinetics of decay for a dried film of PBI-A at 830 nm excited at 490 nm. Decay curve fit to a triexponential decay.

References

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- S10. A. S. Lukas, Y. Zhao, S. E. Miller and M. R. Wasielewski, *J. Phys. Chem. B*, 2002, **106**, 1299-1306.

DFT optimised xyz structures of relevant molecules

PBI-A optimised with B3LYP+D/def2-TZVP and COSMO 80

58

Energy = -1865.3032018313/ -1865.3036692443 (with outlying charge correction)

C -0.9045926 -2.6858377 -1.5791925

C -2.2652400 -2.9816198 -1.5592235

C -3.2029575 -1.9683571 -1.5795477

C -2.7817937 -0.6227700 -1.6153778

C -3.7389027 0.4133543 -1.6423445

C -3.3215581 1.7293869 -1.6723904

C -1.9645891 2.0425811 -1.6658654

C -0.9863096 1.0538485 -1.6355956

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C -0.4426746 -1.3738509 -1.6126409

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H	7.4896383	0.6390455	-1.3801852
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H	-7.0004372	-2.7352091	1.4169228
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**PBI-A with excess electron (charge -1) optimised with B3LYP+D/def2-TZVP and
COSMO 80**

58

Energy = -1865.4444874925/ -1865.4490212934 (with outlying charge correction)

C	-0.9042785	-2.7020067	-1.5995017
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C	1.9702077	-2.0583616	-1.6344960
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C	3.7402363	-0.4169981	-1.6180064
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H 1.6894042 -3.1007191 -1.6448814
H 4.0519589 -2.5360842 -1.6427761
C 5.1623281 -0.1194774 -1.6105900
C 4.6155632 2.3003992 -1.5710308
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H 0.2056148 3.5247546 -1.5962600
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C -6.9501690 -1.5705422 -1.5870615
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N 5.5204217 1.2354613 -1.5805517
O 6.0390110 -0.9882311 -1.6300070
O 5.0540301 3.4544091 -1.5370079
C 6.9505752 1.5707556 -1.5876717
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C	7.4299626	2.0587630	-2.9490980
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H	-6.9831844	-2.8120038	1.3857535
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PBI-A with excess hole (charge +1) optimised with B3LYP+D/def2-TZVP and COSMO

80

58

Energy = -1865.0912931279/ -1865.0885163751 (with outlying charge correction)

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C -2.2561254 -2.9857239 -1.5972989

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C -2.7663207 -0.6182234 -1.6243782

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C -1.3805126 -0.3083929 -1.6334622

C -0.4339619 -1.3673085 -1.6316634

C 0.9751566 -1.0522833 -1.6403999

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C 3.3140307 -1.7393359 -1.6515353

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C -5.1749727 0.1055849 -1.6313000
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H -1.6891537 3.0954698 -1.6571101
H 1.6894261 -3.0952280 -1.6580234
H 4.0544037 -2.5262192 -1.6612030
C 5.1752618 -0.1054683 -1.6305297
C 4.6330222 2.2938249 -1.5684173
H 2.5925778 4.0128148 -1.5802189
H 0.2085193 3.5198825 -1.6157473
N -5.5393384 -1.2394878 -1.5820995
C -6.9770038 -1.5750112 -1.5801994
O -6.0136635 0.9861294 -1.6700437
O -5.0280876 -3.4441707 -1.5191375
N 5.5397112 1.2396387 -1.5833195
O 6.0138777 -0.9862076 -1.6666297
O 5.0285742 3.4443882 -1.5215930
C 6.9773778 1.5750115 -1.5809212
C 7.3350702 2.4853312 -0.4124308
C -7.4492671 -2.1060574 -2.9267592
H -8.5240387 -2.2760132 -2.8920139
H -7.2372669 -1.3689754 -3.7012909
O 6.6626674 2.1632750 0.6985277
O 8.1894974 3.3356304 -0.4600761

C	7.4501655	2.1072384	-2.9268662
H	8.5251032	2.2760782	-2.8918102
H	6.9555253	3.0443924	-3.1751945
C	-7.3344382	-2.4867861	-0.4127283
H	7.4899135	0.6364986	-1.3677525
H	7.2375519	1.3712585	-3.7022805
H	-6.9537062	-3.0424705	-3.1761008
H	-7.4897446	-0.6368177	-1.3661421
O	-6.6646506	-2.1633904	0.6994434
O	-8.1865445	-3.3392907	-0.4620809
H	-6.9538531	-2.7403717	1.4268000
H	6.9524582	2.7389962	1.4266485

Doubly deprotonated PBI-A (charge -2) optimised with B3LYP+D/def2-TZVP and COSMO 80

56

Energy = -1864.3755645504/ -1864.3852937575 (with outlying charge correction)

C -0.9072449 -2.6851153 -1.5863068

C -2.2693153 -2.9795905 -1.5773610

C -3.2070216 -1.9669634 -1.6033102

C -2.7812543 -0.6237798 -1.6312528

C -3.7409623 0.4084686 -1.6618592

C -3.3246771 1.7246049 -1.6839830

C -1.9674082 2.0402608 -1.6693327

C -0.9869084 1.0539242 -1.6386130

C -1.3918355 -0.3120236 -1.6287256

C -0.4423319 -1.3743051 -1.6167036

C 0.9872094 -1.0537608 -1.6385905

C 1.9677147 -2.0401097 -1.6691326

C 3.3249782 -1.7244572 -1.6838491

C 3.7412556 -0.4083185 -1.6618509

C 2.7815639 0.6239405 -1.6312832

C 3.2073583 1.9671222 -1.6034437

C 2.2696568 2.9797570 -1.5775890

C 0.9075719 2.6853010 -1.5864994

C 0.4426305 1.3744872 -1.6167360

C 1.3921439 0.3121966 -1.6287359

H -0.2131724 -3.5119270 -1.5678027

H -2.6001174 -4.0087862 -1.5525222
C -4.6448634 -2.2997294 -1.5987495
C -5.1843646 0.0975283 -1.6728659
H -4.0622176 2.5147504 -1.7106191
H -1.6938272 3.0845522 -1.6852780
H 1.6941924 -3.0844328 -1.6848755
H 4.0625195 -2.5146049 -1.7103467
C 5.1846554 -0.0974085 -1.6729504
C 4.6452205 2.2998661 -1.5988239
H 2.6004665 4.0089568 -1.5529751
H 0.2135456 3.5121743 -1.5680781
N -5.5534926 -1.2450091 -1.6418266
C -6.9929257 -1.5795010 -1.5923336
O -6.0296415 0.9841236 -1.7115149
O -5.0415601 -3.4558816 -1.5675166
N 5.5538248 1.2451264 -1.6422095
O 6.0298855 -0.9840581 -1.7114165
O 5.0419287 3.4560035 -1.5673207
C 6.9932798 1.5794825 -1.5927980
C 7.3477663 2.3499374 -0.2876556
C -7.4742463 -2.2191675 -2.8900568
H -8.5530959 -2.3561469 -2.8385280
H -7.2447958 -1.5710366 -3.7390908
O 6.6643672 2.0786269 0.7267942
O 8.3415035 3.1112182 -0.3458157

C	7.4744725	2.2201012	-2.8901222
H	8.5534304	2.3563371	-2.8388622
H	7.0111056	3.1918315	-3.0495928
C	-7.3468819	-2.3510759	-0.2876861
H	7.4940852	0.6193447	-1.4832877
H	7.2443315	1.5729431	-3.7397045
H	-7.0103351	-3.1904702	-3.0505813
H	-7.4938054	-0.6195039	-1.4819189
O	-6.6643009	-2.0789933	0.7271189
O	-8.3393406	-3.1139603	-0.3464827

Doubly deprotonated PBI-A with excess electron (charge -3) optimised with B3LYP+D/def2-TZVP and COSMO 80

56

Energy = -1864.5088374730/ -1864.5234521479 (with outlying charge correction)

C -0.9050880 -2.7019746 -1.5779790

C -2.2516019 -2.9916840 -1.5790822

C -3.2060948 -1.9705777 -1.5954861

C -2.7832567 -0.6250473 -1.6051078

C -3.7424350 0.4101097 -1.6233530

C -3.3149633 1.7414462 -1.6308476

C -1.9740582 2.0553297 -1.6182699

C -0.9768225 1.0553261 -1.6019314

C -1.3854995 -0.3109478 -1.5989599

C -0.4317268 -1.3714892 -1.5919771

C 0.9771815 -1.0551424 -1.6027907

C 1.9744088 -2.0551424 -1.6198739

C 3.3153107 -1.7412675 -1.6319686

C 3.7427949 -0.4099344 -1.6235329

C 2.7836257 0.6252328 -1.6049370

C 3.2064743 1.9707586 -1.5950396

C 2.2519931 2.9918530 -1.5778453

C 0.9054749 2.7021493 -1.5763321

C 0.4320948 1.3716734 -1.5910603

C 1.3858677 0.3111312 -1.5988751

H -0.2062361 -3.5250781 -1.5651873

H -2.5881014 -4.0198816 -1.5687484
C -4.6242938 -2.3017787 -1.6039267
C -5.1664593 0.1052502 -1.6390218
H -4.0575098 2.5279740 -1.6464346
H -1.6950060 3.0984604 -1.6254096
H 1.6953806 -3.0982794 -1.6277855
H 4.0578511 -2.5277926 -1.6479403
C 5.1668289 -0.1050883 -1.6384632
C 4.6246674 2.3019704 -1.6043638
H 2.5884964 4.0200425 -1.5671834
H 0.2066555 3.5252755 -1.5628416
N -5.5327466 -1.2425532 -1.6304269
C -6.9694957 -1.5773878 -1.6129136
O -6.0314504 0.9894594 -1.6648200
O -5.0395003 -3.4636663 -1.5971661
N 5.5331130 1.2427072 -1.6300511
O 6.0318350 -0.9893160 -1.6635838
O 5.0398739 3.4638595 -1.5989818
C 6.9698612 1.5775064 -1.6124120
C 7.3519438 2.3968284 -0.3485064
C -7.4315442 -2.1673014 -2.9413911
H -8.5104548 -2.3128699 -2.9141558
H -7.1920308 -1.4844158 -3.7602377
O 6.7219966 2.1338905 0.7032878
O 8.3200692 3.1866409 -0.4629084

C 7.4322747 2.1657459 -2.9415140
H 8.5110983 2.3118819 -2.9139920
H 6.9576797 3.1262183 -3.1334945
C -7.3519212 -2.3950795 -0.3480431
H 7.4714777 0.6210849 -1.4741537
H 7.1934713 1.4816265 -3.7595283
H -6.9573663 -3.1282842 -3.1317993
H -7.4711505 -0.6207955 -1.4760221
O -6.7228313 -2.1300736 0.7037517
O -8.3194356 -3.1857334 -0.4618362

**Doubly deprotonated PBI-A with excess hole (charge -1) optimised with
B3LYP+D/def2-TZVP and COSMO 80**

56

Energy = -1864.1602772130/ -1864.1650164669 (with outlying charge correction)

C -0.9126110 -2.6806908 -1.5467509

C -2.2723285 -2.9756293 -1.5311333

C -3.2104233 -1.9616092 -1.5543704

C -2.7898700 -0.6149835 -1.5881218

C -3.7447462 0.4240880 -1.6146977

C -3.3244822 1.7401166 -1.6444328

C -1.9680698 2.0511228 -1.6440285

C -0.9910392 1.0603104 -1.6188183

C -1.3995329 -0.3051564 -1.5962623

C -0.4500750 -1.3684399 -1.5818985

C 0.9794822 -1.0497858 -1.6061147

C 1.9580528 -2.0381701 -1.6192768

C 3.3162229 -1.7252997 -1.6398376

C 3.7336026 -0.4098551 -1.6426776

C 2.7757145 0.6241386 -1.6290040

C 3.2038202 1.9666553 -1.6274856

C 2.2687043 2.9813348 -1.6174128

C 0.9058397 2.6886685 -1.6131357

C 0.4389484 1.3783573 -1.6156149

C 1.3862324 0.3149017 -1.6167363

H -0.2180005 -3.5066440 -1.5298529

H -2.6027061 -4.0048927 -1.5023554
C -4.6382832 -2.2949113 -1.5397673
C -5.1837045 0.1252821 -1.6176974
H -4.0600672 2.5323268 -1.6669626
H -1.6912116 3.0941526 -1.6659200
H 1.6836460 -3.0822538 -1.6156599
H 4.0523044 -2.5170362 -1.6518923
C 5.1788114 -0.1011523 -1.6607780
C 4.6434643 2.2971480 -1.6340080
H 2.6010272 4.0102518 -1.6145773
H 0.2138835 3.5173422 -1.6073112
N -5.5444118 -1.2298474 -1.5690041
C -6.9719772 -1.5660749 -1.6150837
O -6.0453551 0.9899196 -1.6653265
O -5.0660030 -3.4403352 -1.4980238
N 5.5502532 1.2406187 -1.6576558
O 6.0209381 -0.9904520 -1.6812607
O 5.0403486 3.4529676 -1.6274536
C 6.9904625 1.5737411 -1.6141978
C 7.3441338 2.3689109 -0.3234256
C -7.4293569 -2.1241011 -2.9581880
H -8.4976545 -2.3402568 -2.9207064
H -7.2589130 -1.3767063 -3.7329266
O 6.6578134 2.1187678 0.6944433
O 8.3392622 3.1269674 -0.3948747

C	7.4732183	2.1885582	-2.9232773
H	8.5523064	2.3241935	-2.8736253
H	7.0114768	3.1577011	-3.1019589
C	-7.3231679	-2.4509831	-0.4513820
H	7.4898096	0.6152253	-1.4857378
H	7.2430384	1.5253996	-3.7604012
H	-6.8914108	-3.0353258	-3.2098493
H	-7.5020478	-0.6322006	-1.4165360
O	-6.8202900	-2.3494684	0.6978807
O	-8.2343590	-3.3140567	-0.4702898

Na₂PBI-A optimised with B3LYP+D/DZP

8

Energy = -2187.8953895640

C -0.9642029 -2.6776707 -1.5534640

C -2.3367063 -2.9462926 -1.5668585

C -3.2590434 -1.9131727 -1.5453404

C -2.8004103 -0.5748099 -1.5219806

C -3.7456740 0.4752027 -1.5095773

C -3.3098125 1.7893303 -1.4914522

C -1.9420662 2.0821439 -1.4916464

C -0.9716257 1.0775966 -1.5106570

C -1.4008507 -0.2876459 -1.5185930

C -0.4675253 -1.3725411 -1.5256930

C 0.9720337 -1.0774618 -1.5082194

C 1.9424797 -2.0819522 -1.4867515

C 3.3102252 -1.7891266 -1.4865143

C 3.7460928 -0.4750321 -1.5068170

C 2.8008115 0.5749405 -1.5213389

C 3.2594486 1.9132665 -1.5464837

C 2.3371159 2.9463504 -1.5703526

C 0.9646146 2.6777333 -1.5575142

C 0.4679380 1.3726490 -1.5277409

C 1.4012573 0.2877741 -1.5182379

H -0.2796064 -3.5232831 -1.5694338

H -2.6998954 -3.9727384 -1.5962576

C -4.7085262 -2.2249943 -1.5440075
C -5.2021240 0.1919902 -1.5225124
H -4.0539456 2.5853072 -1.4796801
H -1.6460841 3.1292316 -1.4773084
H 1.6464802 -3.1290087 -1.4705542
H 4.0544038 -2.5850443 -1.4731758
C 5.2025405 -0.1918428 -1.5203741
C 4.7089329 2.2251712 -1.5446857
H 2.7004377 3.9726974 -1.6013098
H 0.2800196 3.5233072 -1.5755494
N -5.5975666 -1.1635166 -1.5311242
C -7.0626104 -1.4338906 -1.5187930
O -6.0260986 1.0870474 -1.5341917
O -5.0901291 -3.3996483 -1.5630170
N 5.5979874 1.1636333 -1.5307622
O 6.0265336 -1.0869055 -1.5311745
O 5.0904207 3.3998244 -1.5642214
C 7.0631688 1.4339503 -1.5195012
C 7.3746367 2.5295134 -0.4688390
C -7.5665746 -1.7611941 -2.9170802
H -8.6440871 -1.9593496 -2.8685912
H -7.3792101 -0.9244392 -3.6066702
O 6.7219346 2.4775989 0.6046531
O 8.1646204 3.4441056 -0.8157500
C 7.5664682 1.7583630 -2.9187069

H	8.6440518	1.9563597	-2.8712696
H	7.0800673	2.6654337	-3.3026250
C	-7.3742817	-2.5272100	-0.4655682
H	7.5126798	0.4983350	-1.1688203
H	7.3784889	0.9202714	-3.6065133
H	-7.0802691	-2.6689445	-3.2995323
H	-7.5120392	-0.4975434	-1.1698871
O	-6.7189146	-2.4750159	0.6063463
O	-8.1665994	-3.4407265	-0.8095856
Na	-6.4012210	-4.6151774	-0.0515344
Na	6.4030106	4.6199502	-0.0549083

Na₂PBI-A with excess electron (charge -1) optimised with B3LYP+D/DZP

58

Energy = -2187.9937082270

C -0.9614700 -2.6939498 -1.5335222

C -2.3172072 -2.9589382 -1.5341994

C -3.2570111 -1.9173643 -1.5242614

C -2.8028376 -0.5750279 -1.5220170

C -3.7460081 0.4774662 -1.5248513

C -3.2977186 1.8053182 -1.5264483

C -1.9467322 2.0969944 -1.5240745

C -0.9612770 1.0784775 -1.5241948

C -1.3952699 -0.2864344 -1.5235085

C -0.4575927 -1.3687466 -1.5258542

C 0.9614397 -1.0779606 -1.5234878

C 1.9468561 -2.0965128 -1.5228815

C 3.2978435 -1.8048677 -1.5254455

C 3.7461346 -0.4770229 -1.5245152

C 2.8030117 0.5755080 -1.5225055

C 3.2572671 1.9178220 -1.5261615

C 2.3174518 2.9593803 -1.5371395

C 0.9616894 2.6944302 -1.5359021

C 0.4577639 1.3692585 -1.5268785

C 1.3954418 0.2869437 -1.5237960

H -0.2702851 -3.5344406 -1.5419234

H -2.6850114 -3.9847269 -1.5468383

C -4.6808461 -2.2240268 -1.5100686
C -5.1842104 0.2035005 -1.5368013
H -4.0465141 2.5973867 -1.5295489
H -1.6441084 3.1424026 -1.5228649
H 1.6442109 -3.1419087 -1.5210133
H 4.0466285 -2.5969461 -1.5281666
C 5.1843486 -0.2031070 -1.5362619
C 4.6811561 2.2244845 -1.5124108
H 2.6852275 3.9851693 -1.5510061
H 0.2705114 3.5349260 -1.5450880
N -5.5750310 -1.1601236 -1.5177049
C -7.0342611 -1.4297687 -1.5294964
O -6.0315953 1.0900439 -1.5715428
O -5.0912800 -3.4044890 -1.4983349
N 5.5752701 1.1604473 -1.5176923
O 6.0317197 -1.0897082 -1.5702887
O 5.0915649 3.4049442 -1.5028544
C 7.0347622 1.4295665 -1.5284690
C 7.3979456 2.4868966 -0.4569482
C -7.5048937 -1.7994198 -2.9306359
H -8.5849204 -1.9930162 -2.9121872
H -7.2896554 -0.9834759 -3.6374660
O 6.8158108 2.3895307 0.6538510
O 8.1608400 3.4282434 -0.8076432
C 7.5073206 1.7933170 -2.9304937

H	8.5873965	1.9866281	-2.9114232
H	7.0100920	2.7110324	-3.2731518
C	-7.3990126	-2.4828829	-0.4541113
H	7.4866010	0.4789675	-1.2225299
H	7.2927212	0.9744861	-3.6341612
H	-7.0069369	-2.7183699	-3.2688794
H	-7.4868731	-0.4781054	-1.2279928
O	-6.8162616	-2.3828239	0.6561580
O	-8.1629079	-3.4244617	-0.8016922
Na	-6.3221492	-4.4905906	0.0002410
Na	6.3220510	4.4985441	-0.0086632

Na₂PBI-A with excess hole (charge +1) optimised with B3LYP+D/DZP

Energy = -2187.6405184170

C -0.9659663 -2.6790318 -1.5180704

C -2.3366945 -2.9473291 -1.5124878

C -3.2586489 -1.9110055 -1.5001115

C -2.8010405 -0.5702020 -1.5040112

C -3.7408642 0.4850345 -1.5079514

C -3.3035382 1.8002987 -1.5088716

C -1.9362914 2.0888021 -1.5076017

C -0.9688620 1.0790585 -1.5091110

C -1.4010463 -0.2854302 -1.5076460

C -0.4693572 -1.3711814 -1.5107860

C 0.9691810 -1.0787453 -1.5076497

C 1.9365837 -2.0885100 -1.5047374

C 3.3038242 -1.8000369 -1.5061031

C 3.7411699 -0.4847785 -1.5067091

C 2.8013796 0.5704935 -1.5043098

C 3.2590138 1.9112966 -1.5021176

C 2.3370475 2.9476067 -1.5160418

C 0.9663155 2.6793268 -1.5214273

C 0.4696837 1.3714897 -1.5124461

C 1.4013766 0.2857420 -1.5078016

H -0.2829052 -3.5254318 -1.5286229

H -2.6971676 -3.9750249 -1.5206357

C -4.7030719 -2.2192642 -1.4743972

C -5.1953787 0.2085540 -1.5246517
H -4.0442891 2.5995597 -1.5133545
H -1.6392032 3.1352680 -1.5077852
H 1.6394650 -3.1349635 -1.5036609
H 4.0445763 -2.5993020 -1.5094305
C 5.1956773 -0.2083814 -1.5232955
C 4.7034318 2.2195564 -1.4765451
H 2.6975362 3.9752869 -1.5255760
H 0.2832553 3.5257143 -1.5332135
N -5.5892788 -1.1557949 -1.5023640
C -7.0479953 -1.4225618 -1.5634656
O -6.0273134 1.0908220 -1.5631599
O -5.1060840 -3.3881690 -1.4267948
N 5.5896098 1.1559716 -1.5024907
O 6.0276451 -1.0906850 -1.5604298
O 5.1065192 3.3885055 -1.4306602
C 7.0484494 1.4224339 -1.5633240
C 7.4078216 2.4742347 -0.5201302
C -7.4948317 -1.7984722 -2.9706101
H -8.5745913 -1.9955033 -2.9704862
H -7.2850027 -0.9750200 -3.6669972
O 6.8578305 2.4491681 0.6137075
O 8.1924192 3.4125948 -0.8202389
C 7.4962277 1.7944640 -2.9712022
H 8.5760174 1.9913511 -2.9709834

H	6.9845035	2.7025886	-3.3168624
C	-7.4083028	-2.4714507	-0.5175005
H	7.5213957	0.4812486	-1.2551979
H	7.2867011	0.9691259	-3.6654400
H	-6.9828041	-2.7074726	-3.3135000
H	-7.5212062	-0.4805334	-1.2583142
O	-6.8573960	-2.4445770	0.6158579
O	-8.1940883	-3.4094841	-0.8153589
Na	-6.4167843	-4.6723332	-0.0387070
Na	6.4165473	4.6779782	-0.0459358

Na₂PBI-A.4H₂O optimised with B3LYP+D/DZP

70

Energy = -2493.5387980120

C -1.9143344 -2.1112050 -0.7870575

C -3.2869017 -1.8433121 -0.7607162

C -3.7487894 -0.5390422 -0.7152783

C -2.8209068 0.5290500 -0.7058668

C -3.3011143 1.8581891 -0.6685989

C -2.4012854 2.9102108 -0.6632055

C -1.0241238 2.6656688 -0.6868656

C -0.5037897 1.3696857 -0.7155207

C -1.4164713 0.2672548 -0.7306438

C -0.9619267 -1.0896432 -0.7657317

C 0.4829584 -1.3593035 -0.7715133

C 1.0031073 -2.6554767 -0.7920503

C 2.3803776 -2.9005399 -0.7865798

C 3.2803637 -1.8489876 -0.7593156

C 2.8002298 -0.5194579 -0.7396015

C 3.7283921 0.5479691 -0.7092126

C 3.2663975 1.8528527 -0.6923267

C 1.8936989 2.1215456 -0.7001619

C 0.9411569 1.1000859 -0.7231510

C 1.3956955 -0.2570672 -0.7464827

H -1.5988222 -3.1520252 -0.8210871

H -4.0138340 -2.6545881 -0.7720997

C -5.2068695 -0.2795121 -0.6595772
C -4.7570813 2.1460129 -0.6273353
H -2.7903148 3.9277298 -0.6357412
H -0.3552026 3.5239117 -0.6784585
H 0.3338593 -3.5133920 -0.8094216
H 2.7691913 -3.9183620 -0.8006652
C 4.7365795 -2.1381818 -0.7460164
C 5.1869771 0.2861779 -0.6799875
H 3.9935494 2.6637024 -0.6702247
H 1.5785130 3.1629024 -0.6841545
N -5.6282175 1.0394840 -0.6337112
C -7.0775831 1.3039262 -0.4741777
O -5.1823211 3.2862597 -0.5984538
O -6.0086002 -1.2120304 -0.6551150
N 5.6082313 -1.0323221 -0.7220058
O 5.1613221 -3.2787391 -0.7669652
O 5.9888066 1.2178049 -0.6408933
C 7.0601414 -1.3032940 -0.6025932
C 7.5935687 -0.6930322 0.7180772
C -7.8764763 0.9664260 -1.7262320
H -8.9275568 1.2246028 -1.5492667
H -7.5048737 1.5391802 -2.5892621
O 6.7961827 -0.7044107 1.6914965
O 8.7724181 -0.2604848 0.7015112
C 7.8360158 -0.8975536 -1.8491447

H	8.8903321	-1.1626674	-1.7048267
H	7.7811155	0.1848018	-2.0185258
C	-7.5867056	0.6218397	0.8209888
H	7.1227498	-2.3909082	-0.4785437
H	7.4489536	-1.4244746	-2.7342414
H	-7.8267635	-0.1055171	-1.9531639
H	-7.1366243	2.3832193	-0.2901607
O	-6.7757277	0.5932346	1.7829474
O	-8.7608178	0.1774027	0.7987542
Na	-8.9129449	-1.5902740	2.0702710
Na	8.9565602	1.4423967	2.0553583
O	-7.8707215	-2.8322925	0.5432773
H	-7.2855934	-3.6026823	0.5583770
O	7.8906930	2.7516458	0.6033545
H	7.3092606	3.5227595	0.6634277
H	-7.3617795	-2.1677450	0.0256242
H	7.3692813	2.1140351	0.0647833
O	-7.7418277	-0.8228547	3.7346159
H	-7.1353644	-0.9301096	4.4784232
O	7.7997623	0.6096617	3.6948262
H	7.2235839	0.6576675	4.4681398
H	-7.2970010	-0.1674514	3.0932987
H	7.3401014	-0.0108876	3.0297726

Na₂PBI-A.4H₂O with excess electron (charge -1) optimised with B3LYP+D/DZP

70

Energy = -2493.6393943430

C -2.0100753 -2.0432358 -0.4861690

C -3.3506945 -1.7129472 -0.4846043

C -3.7666736 -0.3732618 -0.4544427

C -2.7888552 0.6535320 -0.4138980

C -3.2002206 2.0046605 -0.3628189

C -2.2342974 3.0193715 -0.3335646

C -0.8863015 2.7150446 -0.3544923

C -0.4223527 1.3772224 -0.4010953

C -1.3909293 0.3224397 -0.4270597

C -0.9953646 -1.0533125 -0.4614997

C 0.4139137 -1.3878440 -0.4662107

C 0.8782363 -2.7263063 -0.4837378

C 2.2264218 -3.0307644 -0.4857702

C 3.1921589 -2.0154677 -0.4758414

C 2.7803736 -0.6635962 -0.4634392

C 3.7578398 0.3642971 -0.4658095

C 3.3418540 1.7038949 -0.4340483

C 2.0013488 2.0335126 -0.4106266

C 0.9868178 1.0431279 -0.4218821

C 1.3824098 -0.3327015 -0.4516289

H -1.7375851 -3.0962764 -0.5077428

H -4.1080033 -2.4959536 -0.4994431

C -5.1810907 -0.0408228 -0.4443438
C -4.6203340 2.3639410 -0.3310985
H -2.5796820 4.0523321 -0.2920733
H -0.1715969 3.5353253 -0.3298951
H 0.1638200 -3.5472223 -0.4918649
H 2.5722022 -4.0644001 -0.4933402
C 4.6125611 -2.3752492 -0.4711765
C 5.1722010 0.0323829 -0.4819406
H 4.0991119 2.4869727 -0.4208406
H 1.7290851 3.0864652 -0.3836139
N -5.5448164 1.2895288 -0.3652999
C -6.9863282 1.6265713 -0.2779694
O -5.0175556 3.5222191 -0.2902146
O -6.0709556 -0.9210428 -0.5102357
N 5.5367668 -1.2999045 -0.4654863
O 5.0101110 -3.5340109 -0.4846767
O 6.0613344 0.9151456 -0.5154565
C 6.9791413 -1.6397238 -0.4060023
C 7.6442313 -0.8738361 0.7695438
C -7.6801043 1.4823650 -1.6260713
H -8.7413224 1.7384376 -1.5128997
H -7.2211263 2.1512170 -2.3701932
O 7.0028077 -0.8873385 1.8526597
O 8.7272020 -0.2784548 0.5371684
C 7.6613200 -1.4332665 -1.7518350

H	8.7221862	-1.6998101	-1.6615502
H	7.6047388	-0.3803383	-2.0567996
C	-7.6419406	0.8083904	0.8672954
H	6.9928914	-2.7042594	-0.1458470
H	7.1920209	-2.0630727	-2.5230937
H	-7.6213013	0.4458835	-1.9827550
H	-6.9973126	2.6780962	0.0308399
O	-6.9898044	0.7694958	1.9433620
O	-8.7293956	0.2278710	0.6188983
Na	-7.9050217	-1.8260139	0.7443326
Na	7.9014163	1.7649707	0.7641204
O	-6.8239383	-3.4349599	-0.5265754
H	-6.1763170	-4.0902417	-0.2321027
O	6.8156996	3.4280602	-0.4321859
H	6.1690973	4.0690458	-0.1055611
H	-6.2933057	-2.6358294	-0.7669109
H	6.2841732	2.6395029	-0.7033569
O	-7.3124673	-1.6167674	2.9018257
H	-6.4708262	-1.8295432	3.3301248
O	7.3076114	1.4588348	2.9102483
H	6.4620455	1.6465756	3.3426584
H	-7.2415424	-0.6173611	2.7127273
H	7.2451481	0.4678737	2.6786790

Na₂PBI-A.4H₂O with excess hole (charge +1) optimised with B3LYP+D/DZP

70

Energy = -2493.2831415530

C -1.8957936 -2.1349166 -0.7299947

C -3.2660076 -1.8764441 -0.6958346

C -3.7331358 -0.5691384 -0.6697906

C -2.8134706 0.5036816 -0.6721076

C -3.3021870 1.8294636 -0.6487129

C -2.4097320 2.8940738 -0.6443765

C -1.0356288 2.6591633 -0.6533008

C -0.5040038 1.3584259 -0.6733097

C -1.4083199 0.2515177 -0.6930671

C -0.9450683 -1.1008986 -0.7298913

C 0.4922700 -1.3581513 -0.7616006

C 1.0237144 -2.6574580 -0.8265446

C 2.3977926 -2.8922588 -0.8421425

C 3.2905769 -1.8292677 -0.7872817

C 2.8019551 -0.5045825 -0.7265695

C 3.7217983 0.5664540 -0.6674205

C 3.2546869 1.8727196 -0.6086076

C 1.8843131 2.1323453 -0.6140947

C 0.9334454 1.1000260 -0.6697973

C 1.3967085 -0.2519466 -0.7204839

H -1.5741764 -3.1738954 -0.7529943

H -3.9884060 -2.6914820 -0.6906185

C -5.1989064 -0.3170460 -0.6282926
C -4.7620067 2.1116184 -0.6239159
H -2.8070770 3.9085387 -0.6287015
H -0.3723389 3.5214492 -0.6445287
H 0.3601762 -3.5186923 -0.8660203
H 2.7946410 -3.9058545 -0.8913283
C 4.7505390 -2.1121930 -0.7863690
C 5.1878574 0.3130722 -0.6559638
H 3.9772314 2.6861373 -0.5595308
H 1.5626393 3.1705971 -0.5695875
N -5.6270041 1.0009057 -0.6452064
C -7.0818355 1.2628368 -0.5422522
O -5.1869495 3.2489046 -0.5968120
O -5.9893273 -1.2535629 -0.5980367
N 5.6156253 -1.0020418 -0.7461108
O 5.1756475 -3.2490069 -0.8277389
O 5.9784819 1.2471873 -0.5850522
C 7.0705329 -1.2692806 -0.6597692
C 7.6001540 -0.7204527 0.6752793
C -7.8573648 0.8476043 -1.7862531
H -8.9094932 1.1272419 -1.6516280
H -7.4647748 1.3657675 -2.6729357
O 6.8194741 -0.7185579 1.6614788
O 8.7897305 -0.3191837 0.7141857
C 7.8443794 -0.7925897 -1.8827751

H	8.8966454	-1.0787230	-1.7635208
H	7.7978293	0.2976552	-1.9904125
C	-7.6081521	0.6484809	0.7650364
H	7.1445191	-2.3617374	-0.5888498
H	7.4505227	-1.2658632	-2.7936183
H	-7.8109670	-0.2359190	-1.9478581
H	-7.1556990	2.3502912	-0.4161713
O	-6.8274842	0.6081160	1.7505921
O	-8.7944446	0.2364387	0.7848210
Na	-9.1779910	-1.5453746	2.0412725
Na	9.1856975	1.4212218	2.0223927
O	-8.0603951	-2.7606086	0.5563246
H	-7.7472496	-3.6643932	0.4104059
O	8.0913675	2.6920770	0.5673235
H	7.8035382	3.6061135	0.4339123
H	-7.4255726	-2.1943837	0.0695241
H	7.4376051	2.1495186	0.0784953
O	-8.0036423	-0.7870843	3.7185169
H	-7.7979366	-0.6129520	4.6461856
O	7.9845294	0.6318955	3.6666480
H	7.7621291	0.4471379	4.5883707
H	-7.4593513	-0.1536864	3.1758268
H	7.4439992	0.0104195	3.1065814

PBI optimised with B3LYP+D/def2-TZVP and COSMO 80

40

Energy = -1330.9501348450/ -1330.9507231491 (with outlying charge correction)

C -0.9050741 -2.6859284 -1.5986272

C -2.2653982 -2.9834442 -1.5997999

C -3.2044833 -1.9726351 -1.5986620

C -2.7862224 -0.6212283 -1.5965514

C -3.7388916 0.4245506 -1.5945642

C -3.3181031 1.7384938 -1.5928860

C -1.9602744 2.0471474 -1.5935726

C -0.9857232 1.0543847 -1.5954586

C -1.3953279 -0.3110452 -1.5962999

C -0.4445782 -1.3732127 -1.5968894

C 0.9861028 -1.0542829 -1.5956813

C 1.9606614 -2.0470426 -1.5939950

C 3.3184895 -1.7383839 -1.5933933

C 3.7392763 -0.4244414 -1.5949633

C 2.7866063 0.6213335 -1.5967491

C 3.2048675 1.9727440 -1.5986994

C 2.2657865 2.9835537 -1.5997203

C 0.9054586 2.6860406 -1.5985496

C 0.4449563 1.3733228 -1.5967825

C 1.3957130 0.3111514 -1.5963793

H -0.2102085 -3.5117499 -1.5988973

H -2.5944652 -4.0137499 -1.6014442

C -4.6398408 -2.3047829 -1.5993551
C -5.1794025 0.1155215 -1.5945796
H -4.0536699 2.5314106 -1.5913178
H -1.6823705 3.0900258 -1.5929389
H 1.6827675 -3.0899300 -1.5934796
H 4.0540553 -2.5313015 -1.5920302
C 5.1797845 -0.1154088 -1.5949929
C 4.6402268 2.3048904 -1.5991626
H 2.5948526 4.0138601 -1.6011918
H 0.2105985 3.5118761 -1.5988445
N -5.5061949 -1.2276326 -1.5976867
O -6.0633687 0.9615794 -1.5918789
O -5.0806941 -3.4462123 -1.6013986
N 5.5065788 1.2277412 -1.5976764
O 6.0637501 -0.9614702 -1.5926180
O 5.0810773 3.4463199 -1.6008241
H -6.4955822 -1.4482235 -1.5979596
H 6.4959642 1.4483391 -1.5975812

PBI with excess hole (charge +1) optimised with B3LYP+D/def2-TZVP and COSMO 80

40

Energy = -1330.7388773519/ -1330.7361805901 (with outlying charge correction)

C -0.9021691 -2.6943318 -1.5996966

C -2.2547953 -2.9876623 -1.6001637

C -3.1903218 -1.9642469 -1.5983382

C -2.7706074 -0.6177255 -1.5967838

C -3.7225497 0.4229969 -1.5945167

C -3.3103474 1.7468407 -1.5937635

C -1.9612745 2.0560016 -1.5954333

C -0.9744704 1.0524524 -1.5970189

C -1.3833130 -0.3083539 -1.5973522

C -0.4351751 -1.3666466 -1.5980999

C 0.9748491 -1.0523634 -1.5971224

C 1.9616703 -2.0559052 -1.5956418

C 3.3107472 -1.7467313 -1.5941548

C 3.7229393 -0.4228900 -1.5948755

C 2.7709889 0.6178304 -1.5967958

C 3.1907041 1.9643611 -1.5982945

C 2.2551733 2.9877704 -1.5997217

C 0.9025364 2.6944435 -1.5990893

C 0.4355450 1.3667562 -1.5978602

C 1.3836963 0.3084606 -1.5972756

H -0.2064232 -3.5187874 -1.6001113

H -2.5896850 -4.0153065 -1.6016669

C -4.6372679 -2.2989747 -1.5974072
C -5.1746562 0.1113849 -1.5935939
H -4.0500373 2.5348973 -1.5922292
H -1.6820112 3.0980159 -1.5960419
H 1.6824296 -3.0979460 -1.5958628
H 4.0504653 -2.5347577 -1.5925905
C 5.1750400 -0.1112816 -1.5940238
C 4.6376524 2.2990858 -1.5976805
H 2.5900264 4.0154308 -1.6008292
H 0.2068092 3.5189320 -1.5989895
N -5.5050038 -1.2273500 -1.5953868
O -6.0383633 0.9694921 -1.5910497
O -5.0546979 -3.4426800 -1.5985803
N 5.5053844 1.2274564 -1.5955361
O 6.0387502 -0.9693871 -1.5917779
O 5.0550822 3.4427896 -1.5992603
H -6.4950050 -1.4481346 -1.5950522
H 6.4953849 1.4482437 -1.5944135

Alanine optimised with B3LYP+D/def2-TZVP and COSMO 80

13

Energy = -323.7337293839/ -323.7341807858 (with outlying charge correction)

H	2.0531568	-0.1101670	1.1337018
N	1.6876970	-0.2600811	0.1987629
H	1.9466420	0.5560243	-0.3482289
C	0.2318993	-0.3654815	0.2662019
H	-0.0225124	-1.2882496	0.7924760
C	-0.4679767	0.8106520	0.9754041
H	-0.0945177	0.8844638	1.9979613
H	-0.2502835	1.7481326	0.4582004
H	-1.5496789	0.6697954	1.0109003
C	-0.3265286	-0.4787826	-1.1386099
O	0.2180106	-0.0668331	-2.1378455
O	-1.5398306	-1.0516019	-1.1499778
H	-1.8860673	-1.0478513	-2.0589464

Alanine with excess hole (charge +1) optimised with B3LYP+D/def2-TZVP and COSMO 80

13

Energy = -323.5067060255/ -323.5044247959 (with outlying charge correction)

H	2.1448106	-0.1148420	1.1064019
N	1.5887939	-0.0633433	0.2552553
H	2.0482307	0.2345763	-0.6082450

C	0.2055257	-0.3273330	0.2729821
H	0.0313383	-1.2452541	0.8447062
C	-0.5344346	0.8274681	1.0381408
H	-0.1391797	0.9054338	2.0483067
H	-0.4006838	1.7665360	0.5056297
H	-1.5870693	0.5533383	1.0733767
C	-0.3044498	-0.4567822	-1.1573828
O	0.3459568	-0.1354625	-2.1205418
O	-1.5358388	-0.9409053	-1.1716538
H	-1.8629899	-1.0034100	-2.0869760

Deprotonated alanine optimised with B3LYP+D/def2-TZVP and COSMO 80

12

Energy = -323.2683355198/ -323.2738994336 (with outlying charge correction)

H	2.0272492	0.0412706	1.0873908
N	1.6441110	-0.3199855	0.2187725
H	1.8936616	0.3396349	-0.5132823
C	0.1768446	-0.3647893	0.2957953
H	-0.1163219	-1.2787183	0.8192450
C	-0.4340225	0.8357087	1.0355605
H	-0.0412941	0.8968136	2.0542392
H	-0.1837066	1.7647642	0.5157789
H	-1.5216503	0.7497300	1.0924839
C	-0.4401595	-0.4316651	-1.1206273
O	0.1875368	0.1310424	-2.0535717
O	-1.5545886	-1.0058664	-1.2196654

Deprotonated alanine with excess hole (charge +1) optimised with B3LYP+D/def2-TZVP and COSMO 80

12

Energy = -323.0920475955/ -323.0921695304 (with outlying charge correction)

H	2.2272097	-0.8526114	0.1993705
N	1.6511731	-0.0615156	0.4428566
H	2.0031469	0.8336694	0.1357156
C	0.3177524	-0.2316067	0.5886737

H	0.0254669	-1.2147983	0.9404287
C	-0.4938685	0.9443820	1.0378285
H	-0.2842085	1.1636447	2.0913047
H	-0.2495976	1.8370634	0.4567401
H	-1.5584427	0.7391868	0.9401627
C	-0.5753709	-0.5681230	-1.3536067
O	0.1940583	-0.1313284	-2.1557339
O	-1.6196597	-1.1000234	-1.1116211