Electronic Supplementary Information for

Guest and solvent modulated photo-driven charge separation and triplet generation in a perylene bisimide cyclophane

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1. Optical spectroscopy

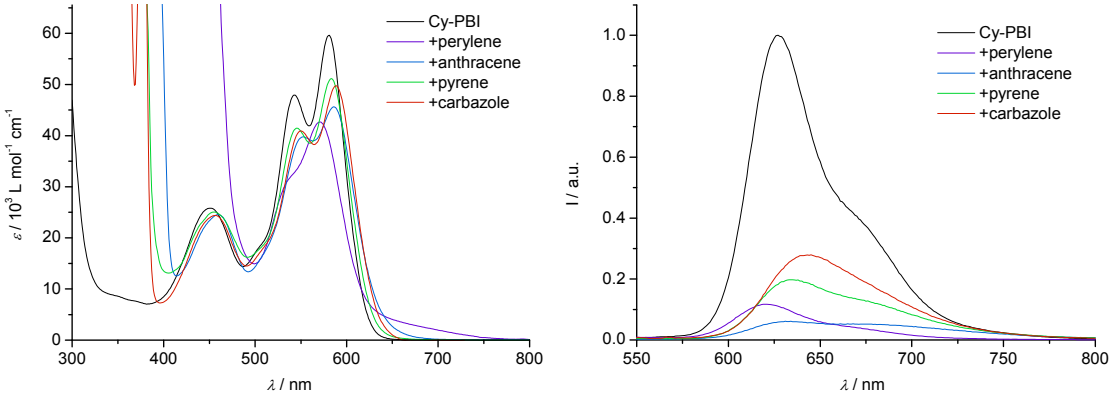

Fig. S1 UV-vis absorption (left) and fluorescence (right) spectra of **Cy-PBI** and guest@**Cy-PBI** in dichloromethane; *c*(**Cy-PBI**) = 5 x 10^{-6} M, RT.

2. Transient absorption spectroscopy

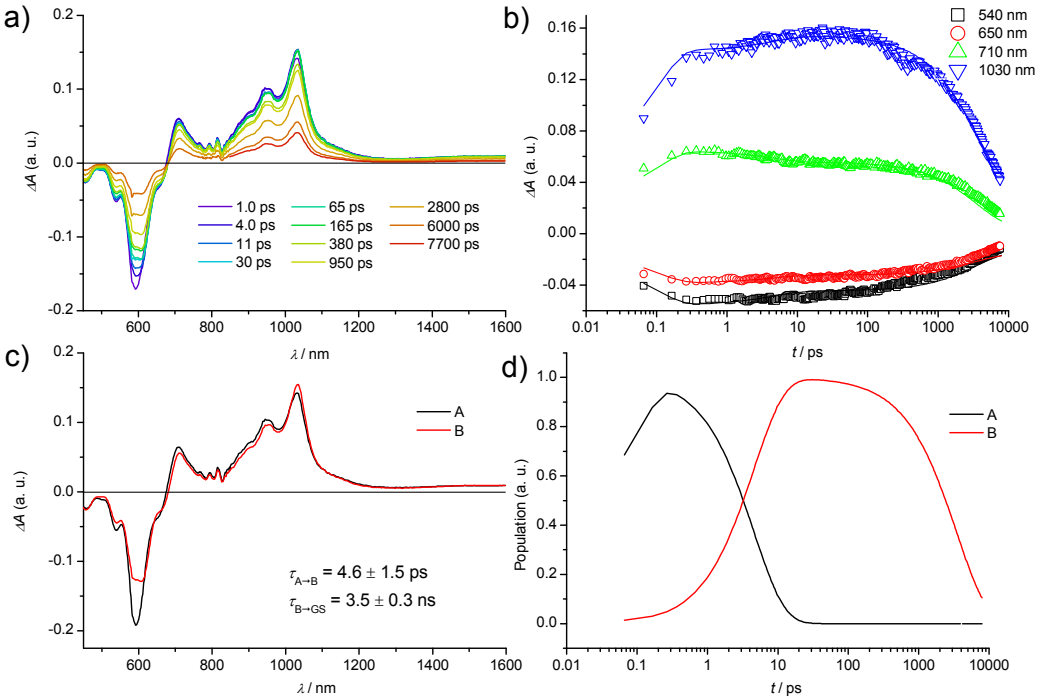

Fig. S2 a) Femtosecond transient absorption of **Ref-PBI** in dichloromethane showing excited state dynamics after photoexcitation; b) plots of selected kinetic traces superimposed with matching curves at different wavelengths; c) species-associated spectra plots; d) kinetic model plots (λ_{ex} = 580 nm, 1.0 μJ/pulse, 298 K). A and B: singlet excited state S_1 (A→B likely presents relaxation on the singlet state based on the timescale and the similarity of the spectra).

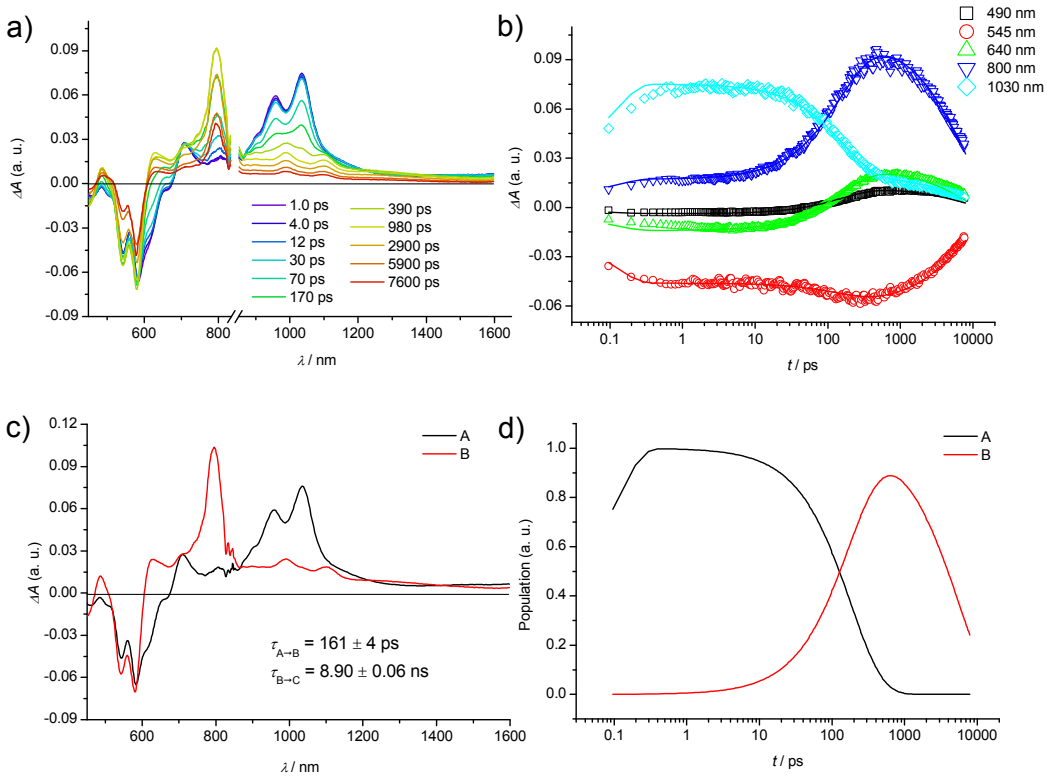

Fig. S3 a) Femtosecond transient absorption of the **Cy-PBI** in dichloromethane showing excited state dynamics after photoexcitation; b) plots of selected kinetic traces superimposed with matching curves at different wavelengths; c) species-associated spectra plots; d) kinetic model plots (λ_{ex} = 580 nm, 1.0 μJ/pulse, 298 K). A: singlet excited state S_1; B: charge separated state SB-CS.

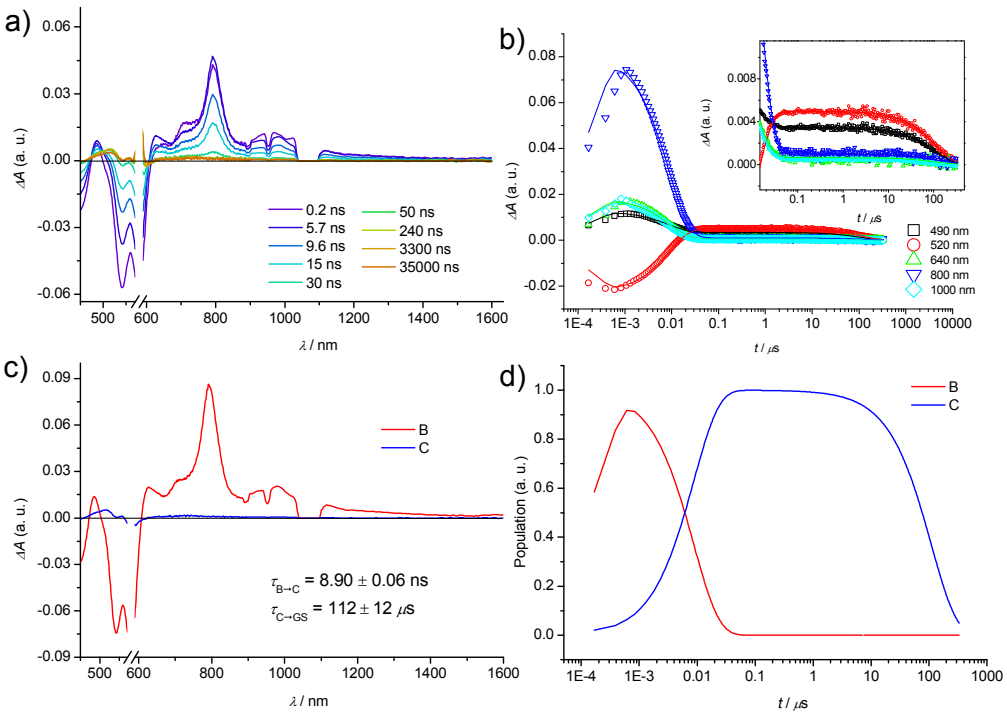

Fig. S4 a) Nanosecond transient absorption of **Cy-PBI** in dichloromethane showing excited state dynamics after photoexcitation; b) plots of selected kinetic traces superimposed with matching curves at different wavelength; c) species-associated spectra plots; d) kinetic model plots (λ_{ex} = 580 nm, 1.0 μJ/pulse, 298 K). B: charge separated state SB-CS; C: PBI triplet state.

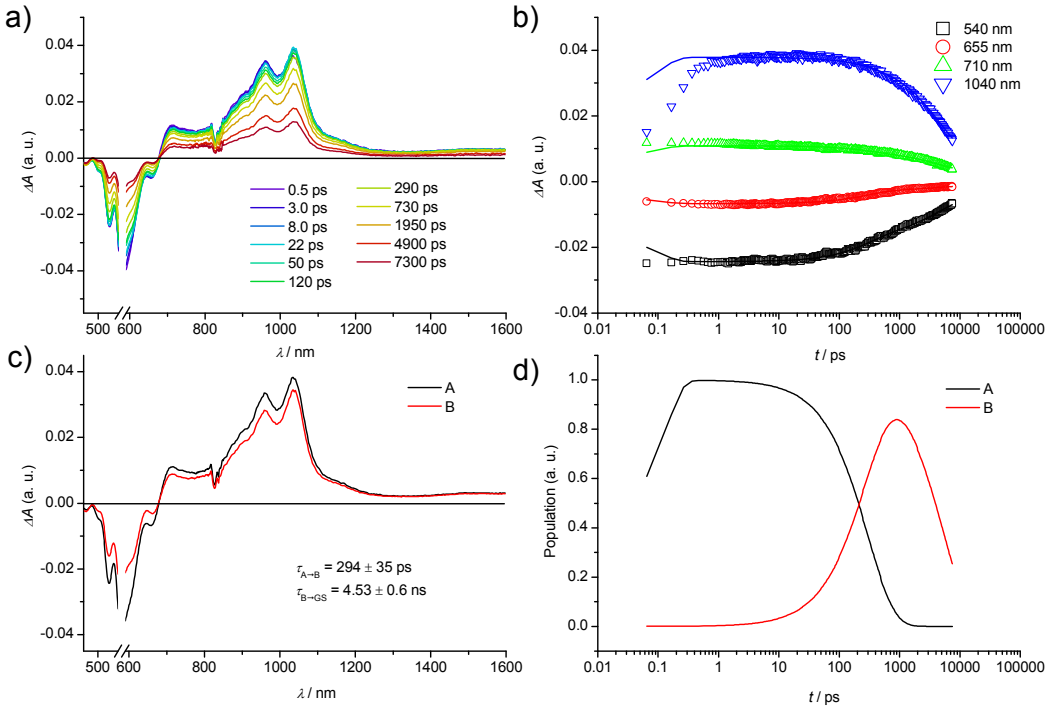

Fig. S5 a) Femtosecond transient absorption of **Cy-PBI** in toluene showing excited state dynamics after photoexcitation; b) plots of selected kinetic traces superimposed with matching curves at different wavelengths; c) species-associated spectra plots; d) kinetic model plots (λ_{ex} = 580 nm, 1.0 μJ/pulse, 298 K). A and B: singlet excited state S_1 (A→B likely presents relaxation on the singlet state based on the timescale and the similarity of the spectra).

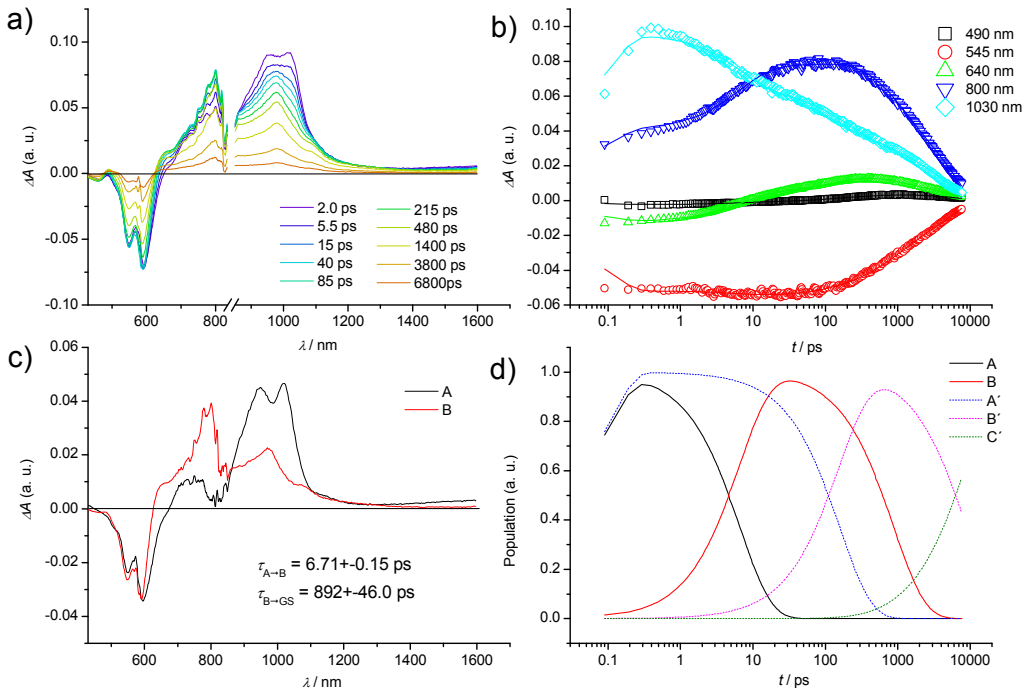

Fig. S6 a) Femtosecond transient absorption of the carbazole@**Cy-PBI** complex in dichloromethane showing excited state dynamics after photoexcitation; b) plots of selected kinetic traces superimposed with matching curves at different wavelength; c) species-associated spectra plots; d) kinetic model plots (λ_{ex} = 580 nm, 1.0 μJ/pulse, 298 K). A: singlet excited state S_1; B: charge transfer state CT; A´, B´ and C´ correspond to the free **Cy-PBI** and are not shown in c) for clarity reasons.

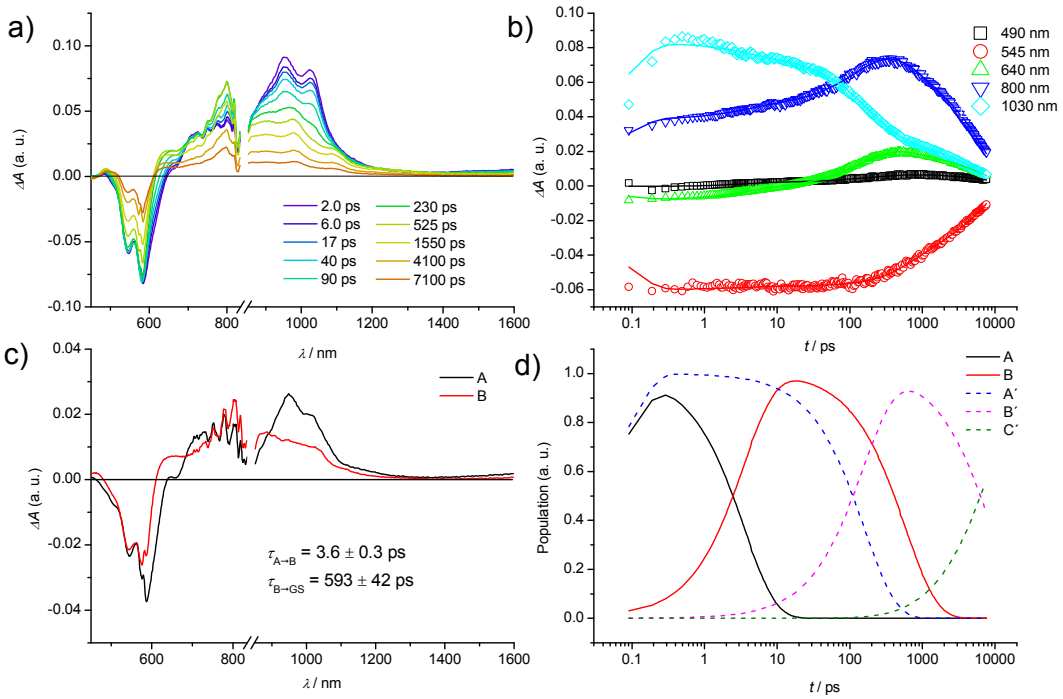

Fig. S7 a) Femtosecond transient absorption of the pyrene@ **Cy-PBI** complex in dichloromethane showing excited state dynamics after photoexcitation; b) plots of selected kinetic traces superimposed with matching curves at different wavelength; c) species-associated spectra plots; d) kinetic model plots (λ_{ex} = 580 nm, 1.0 μJ/pulse, 298 K). A: singlet excited state S_1; B: charge transfer state CT; A´, B´ and C´ correspond to the free **Cy-PBI** and are not shown in c) for clarity reasons.

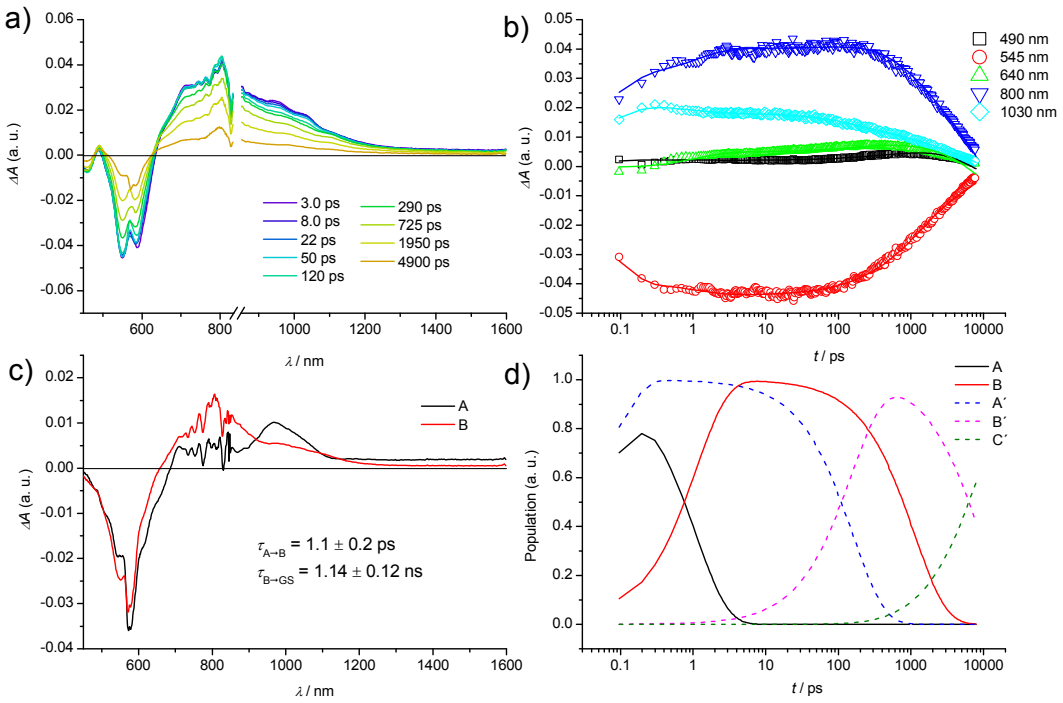

Fig. S8 a) Femtosecond transient absorption of the anthracene@**Cy-PBI** complex in dichloromethane showing excited state dynamics after photoexcitation; b) plots of selected kinetic traces superimposed with matching curves at different wavelength; c) species-associated spectra plots; d) kinetic model plots (λ_{ex} = 580 nm, 1.0 μJ/pulse, 298 K). A: singlet excited state S_1; B: charge transfer state CT; A´, B´ and C´ correspond to the free **Cy-PBI** and are not shown in c) for clarity reasons.

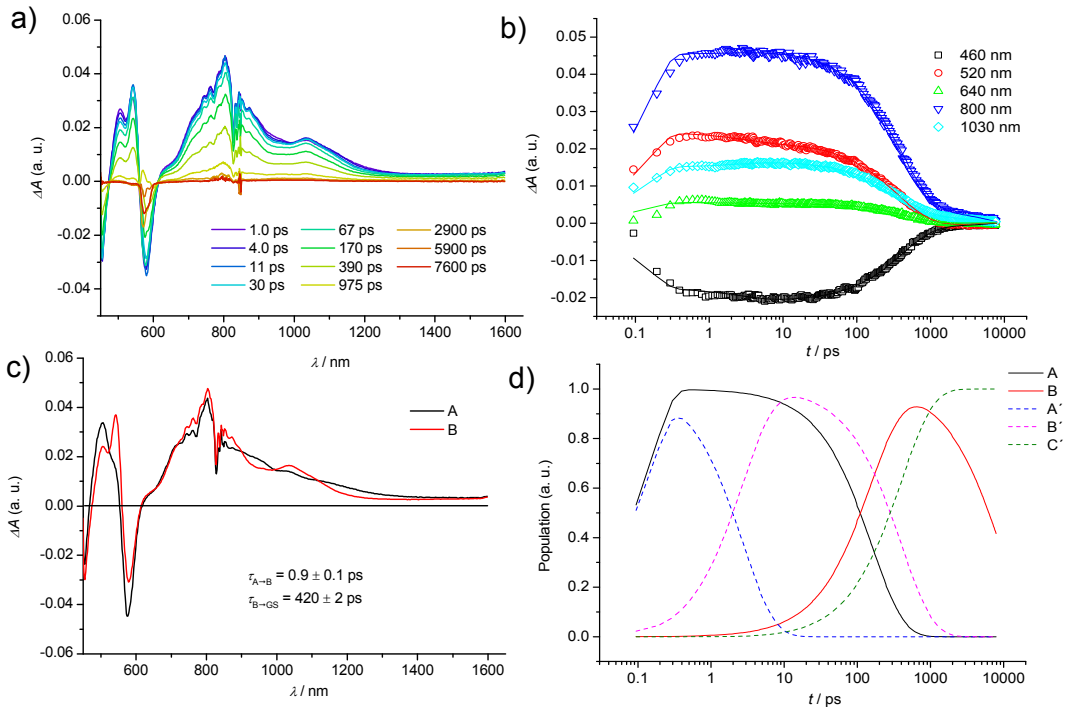

Fig. S9 a) Femtosecond transient absorption of the perylene**@Cy-PBI** complex in dichloromethane showing excited state dynamics after photoexcitation; b) plots of selected kinetic traces superimposed with matching curves at different wavelength; c) species-associated spectra plots; d) kinetic model plots (λ_{ex} = 580 nm, 1.0 μJ/pulse, 298 K). A: singlet excited state S_1; B: charge transfer state CT; A´, B´ and C´ correspond to the free **Cy-PBI** and are not shown in c) for clarity reasons.