## **Electronic Supplementary Information**

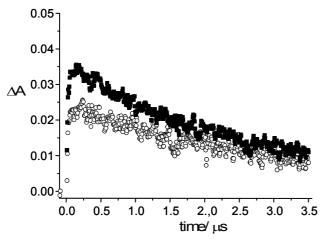
## Triplet exciplexes as energy transfer photosensitisers

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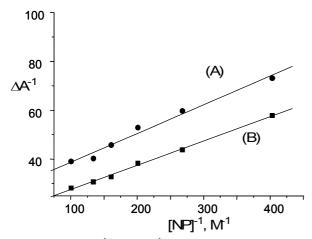
- **ESI 2:** Transient kinetic traces observed at 430 nm after laser flash photolysis (355 nm) of a deareated solution of (S,S)-1 containing (S)-5 and (R)-5 in acetronitrile. Plot of  $\Delta A^{-1}$  vs. [NP]<sup>-1</sup> for deareated acetonitrile solutions of (S,S)-1 (0.7 mM) containing increasing amounts of (S)-5 (A) and (A)-5 (A).
- **ESI 3:** Transient kinetic traces observed at 430 nm after laser flash photolysis (355 nm) of a deareated solution of (S,S)-1 containing (S)-6 and (R)-6 in acetronitrile. Plot of  $\Delta A^{-1}$  vs. [NP]<sup>-1</sup> for deareated acetonitrile solutions of (S,S)-1 (0.7 mM) containing increasing amounts of (S)-6 (A) and (A)-6 (A).
- **ESI 4:** Plot of  $\Delta A^{-1}$  vs. [NP]<sup>-1</sup> for deareated acetonitrile solutions of (R,S)-2 (0.7 mM) containing increasing amounts of (S)-5 (A) and (R)-5 (B).
- **ESI 5:** Transient kinetic traces observed at 430 nm after laser flash photolysis (355 nm) of a deareated solution of (R,S)-2 containing (S)-6 and (R)-6 in acetronitrile. Plot of  $\Delta A^{-1}$  vs.  $[NP]^{-1}$  for deareated acetonitrile solutions of (R,S)-2 (0.7 mM) containing increasing amounts of (S)-6 (A) and (R)-6 (B).
- **ESI 6:** Transient kinetic traces observed at 430 nm after laser flash photolysis (355 nm) of a deareated solution of (S)-3 containing (S)-5 and (R)-5 in acetronitrile. Plot of  $\Delta A^{-1}$  vs. [NP]<sup>-1</sup> for deareated acetonitrile solutions of (S)-3 (1.1 mM) containing increasing amounts of (S)-5 (A) and (R)-5 (B).
- **ESI 7:** Transient kinetic traces observed at 430 nm after laser flash photolysis (355 nm) of a deareated solution of (S)-3 containing (S)-6 and (R)-6 in acetronitrile. Plot of  $\Delta A^{-1}$  vs. [NP]<sup>-1</sup> for deareated acetonitrile solutions of (S)-3 (1.1 mM) containing increasing amounts of (S)-6 (A) and (R)-6 (B).
- **ESI 8:** Transient kinetic traces observed at 430 nm after laser flash photolysis (355 nm) of a deareated solution of (S)-4 containing (S)-5 and (R)-5 in acetronitrile. Plot of  $\Delta A^{-1}$  vs. [NP]<sup>-1</sup> for deareated acetonitrile solutions of (S)-4 (1.1 mM) containing increasing amounts of (S)-5 (A) and (R)-5 (B).
- **ESI 9:** Transient kinetic traces observed at 430 nm after laser flash photolysis (355 nm) of a deareated solution of (S)-4 containing (S)-6 and (R)-6 in acetronitrile. Plot of  $\Delta A^{-1}$  vs. [NP]<sup>-1</sup> for deareated acetonitrile solutions of (S)-4 (1.1 mM) containing increasing amounts of (S)-6 (A) and (R)-6 (B).
- ESI 10: (U)B3LYP/6-31G\*-optimised geometry of an intramolecular <sup>3</sup>(BT-InH)\* exciplex

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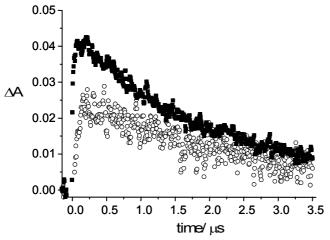
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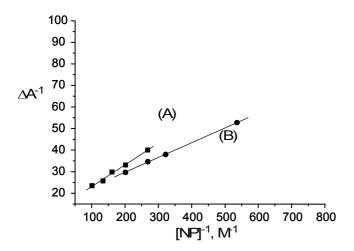
**Fig. 4** Transient kinetic traces observed at 430 nm after the laser Flash photolysis (355 nm) of a deareated solution of (S,S)-1 (0.7 mM) containing 9.9 mM of (R)-5 ( $\blacksquare$ ) and (S)-5 ( $\bigcirc$ ) in acetonitrile.



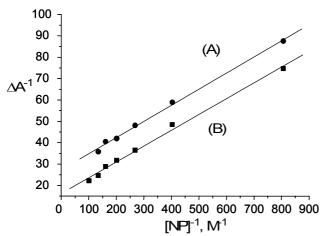
**Fig. 5** Plot of  $\Delta A^{-1}$  vs. [NP]<sup>-1</sup> for deareated acetonitrile solutions of **(S,S)-1** (0.7 mM) containing increasing amounts of **(S)-5** (A) and **(R)-5** (B).



**Fig. 6** Transient kinetic traces observed at 430 nm after the laser Flash photolysis (355 nm) of a deareated solution of **(S,S)-1** (0.7 mM) containing 9.9 mM of **(R)-6** ( $\blacksquare$ ) and **(S)-6** ( $\bigcirc$ ) in acetonitrile.



**Fig. 7** Plot of  $\Delta A^{-1}$  vs. [NP]<sup>-1</sup> for deareated acetonitrile solutions of **(S)-1** (0.7 mM) containing increasing amounts of **(S)-6** (A) and **(R)-6** (B).



**Fig. 8** Plot of  $\Delta A^{-1}$  vs. [NP]<sup>-1</sup> for deareated acetonitrile solutions of (*R*,*S*)-2 (0.7 mM) containing increasing amounts of (*S*)-5 (A) and (*R*)-5 (B).

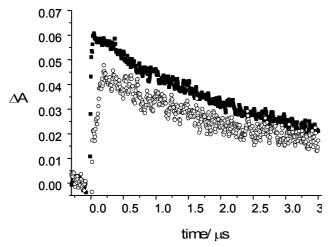
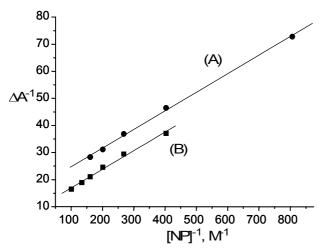
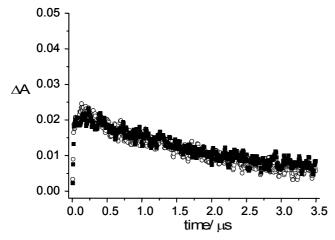


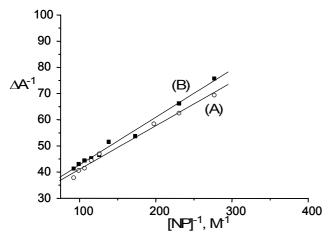
Fig. 9 Transient kinetic traces observed at 430 nm after the laser flash photolysis (355 nm) of a deareated solution of (R,S)-2 (0.7 mM) containing 9.9 mM of (R)-6 ( $\blacksquare$ ) and (S)-6 ( $\bigcirc$ ) in acetonitrile.



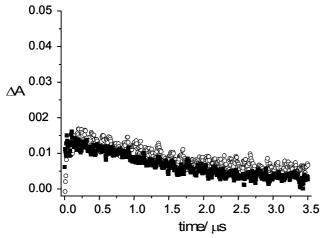
**Fig. 10** Plot of  $\Delta A^{-1}$  vs. [NP]<sup>-1</sup> for deareated acetonitrile solutions of **(R,S)-2** (0.7 mM) containing increasing amounts of **(S)-6** (A) and **(R)-6** (B).



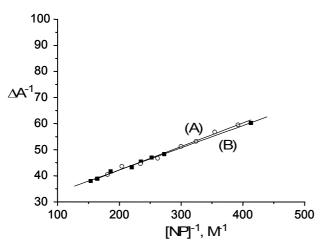
**Fig. 11** Transient kinetic traces observed at 430 nm after the laser Flash photolysis (355 nm) of a deareated solution of **(S)-3** (1.1 mM) containing 9.9 mM of **(R)-5** ( $\blacksquare$ ) and **(S)-5** ( $\bigcirc$ ) in acetonitrile.



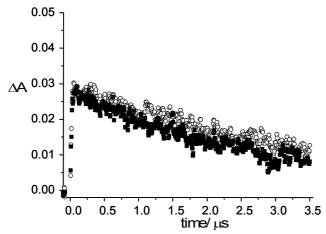
**Fig. 12** Plot of  $\Delta A^{-1}$  vs. [NP]<sup>-1</sup> for deareated acetonitrile solutions of **(S)-3** (1.1 mM) containing increasing amounts of **(S)-5** (A) and **(R)-5** (B).



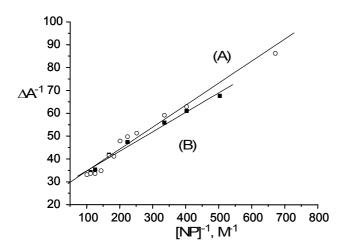
**Fig. 13** Transient kinetic traces observed at 430 nm after the laser flash photolysis (355 nm) of a deareated solution of **(S)-3** (1.1 mM) containing 9.9 mM of **(R)-6** (■) and **(S)-6** (○) in acetonitrile.



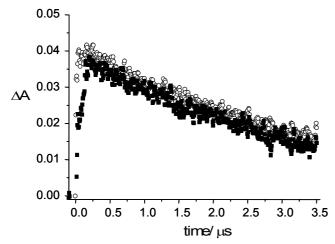
**Fig. 14** Plot of  $\Delta A^{-1}$  vs. [NP]<sup>-1</sup> for deareated acetonitrile solutions of **(S)-3** (1.1 mM) containing increasing amounts of **(S)-6** (A) and **(R)-6** (B).



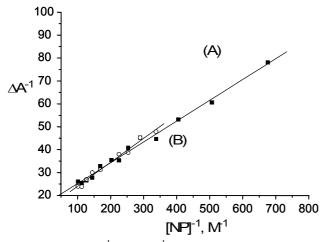
**Fig. 15** Transient kinetic traces observed at 430 nm after the laser flash photolysis (355 nm) of a deareated solution of **(S)-4** (1.1 mM) containing 9.9 mM of **(R)-5** ( $\blacksquare$ ) and **(S)-5** ( $\bigcirc$ ) in acetonitrile.



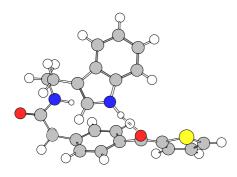
**Fig. 16** Plot of  $\Delta A^{-1}$  vs. [NP]<sup>-1</sup> for deareated acetonitrile solutions of **(S)-4** (1.1 mM) containing increasing amounts of **(S)-5** (A) and **(R)-5** (B).



**Fig. 17** Transient kinetic traces observed at 430 nm after the laser flash photolysis (355 nm) of a deareated solution of **(S)-4** (1.1 mM) containing 9.9 mM of **(R)-6** ( $\blacksquare$ ) and **(S)-6** ( $\bigcirc$ ) in acetonitrile.



**Fig. 18** Plot of  $\Delta A^{-1}$  vs. [NP]<sup>-1</sup> for deareated acetonitrile solutions of **(S)-4** (1.1 mM) containing increasing amounts of **(S)-6** (A) and **(R)-6** (B).



**Fig. 19** (U)B3LYP/6-31G\*-optimised geometry of an intramolecular <sup>3</sup>(BT-InH)\* exciplex.