

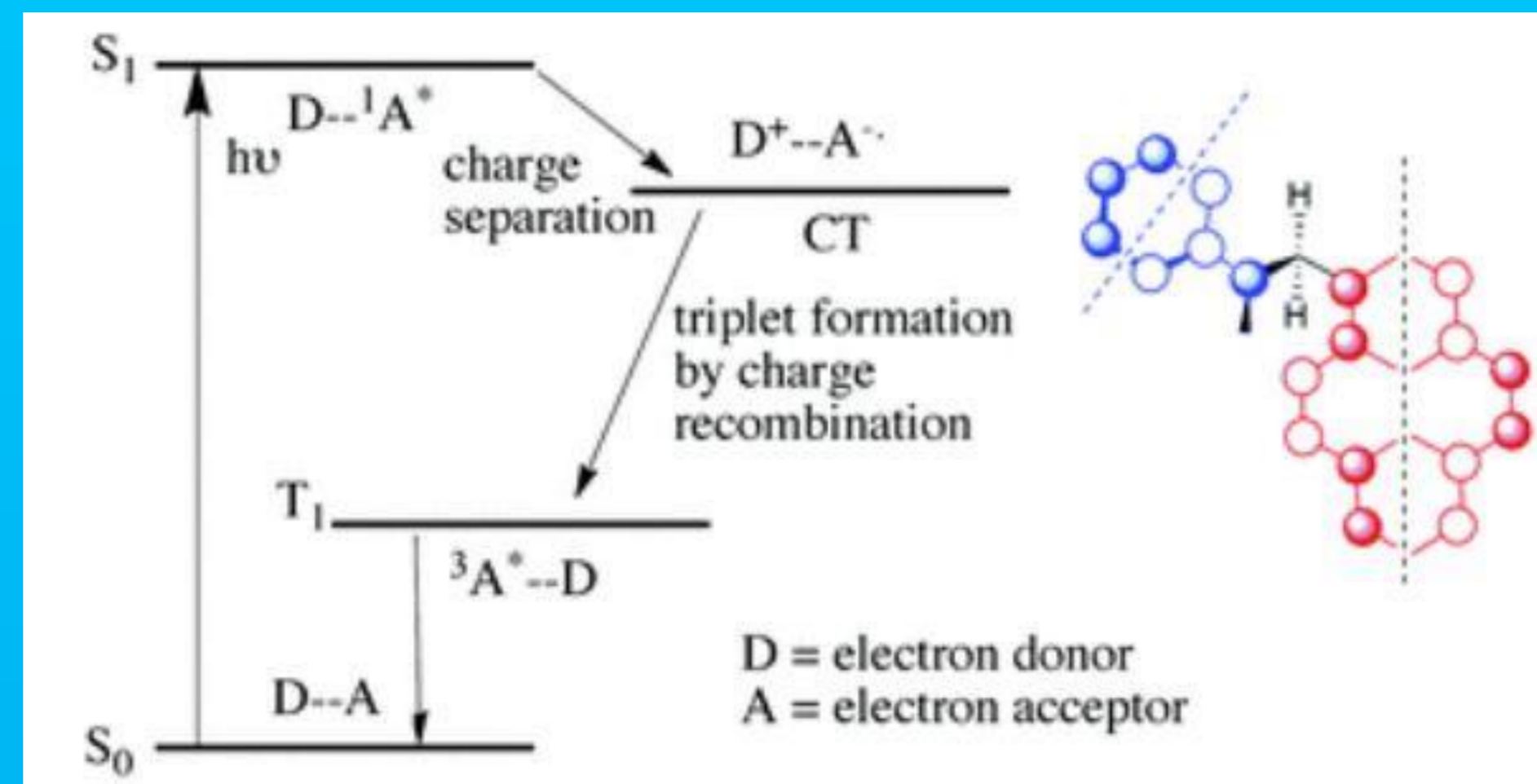
Dáire Gibbons,<sup>a,b</sup> Nicolas Villandier,<sup>b</sup> Stéphanie Leroy-Lhez<sup>b</sup> and René M. Williams<sup>a</sup>

<sup>a</sup>Molecular Photonics Group, Van 't Hoff Institute for Molecular Sciences (HIMS), University of Amsterdam, 1090 GD Amsterdam, The Netherlands  
<sup>b</sup>Laboratoire PEIRENE - EA 7500, Faculté des Sciences et Techniques, Université de Limoges, 123 avenue Albert THOMAS, 87060 Limoges, France

D. J. Gibbons *et al.*, *Photochem. Photobiol. Sci.*, 2020, 19, 136–158. DOI: 10.1039/C9PP00399A.

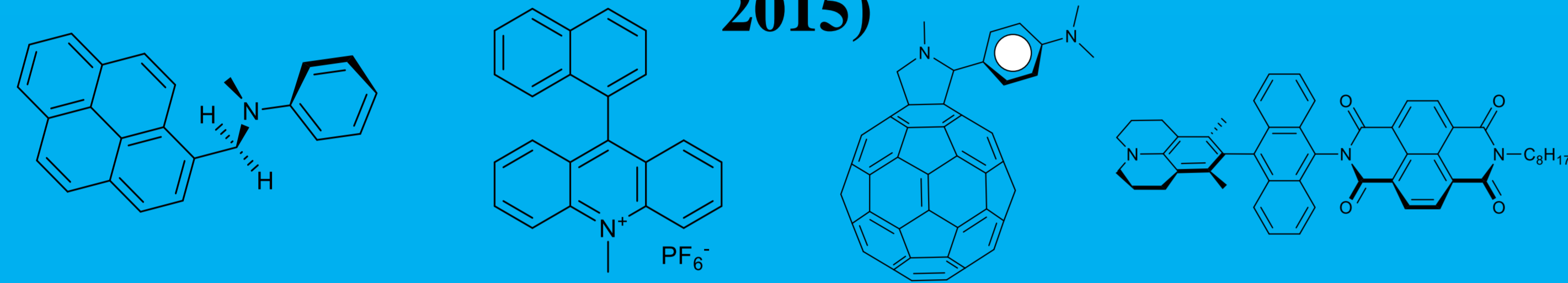
## 1. Introduction

- Triplet excited states are very important and have been used in photo-initiators for photo-polymerization,<sup>1</sup> photodynamic (anti-cancer) therapy (PDT)<sup>2</sup> and photodynamic antimicrobial chemotherapy (PACT).<sup>3</sup>
- Common method involves the use of the **heavy atom effect (HAE)**.<sup>4</sup> The common drawback of HAE is its cost (for example Pd or Pt) and toxicity, etc.
- Herein,<sup>4</sup> we present an innovative triplet forming mechanism: Triplet formation by charge recombination (TCR).
- Attaching an **electron donor** to an **electron acceptor**, molecules can be converted into systems with high triplet yields that undergo the triplet formation by charge recombination mechanism.



**Figure 1:** Simplified Jablonski diagram of donor-acceptor dyad (D-A) showing pathway to the triplet via charge recombination.<sup>4</sup>

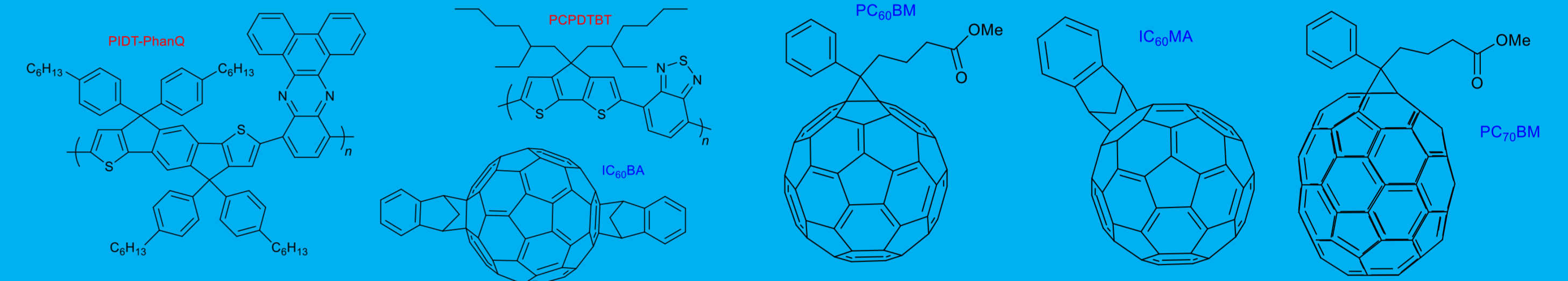
## 2. Fast molecular electron donor - acceptor systems (pre-2015)



**Figure 2:** Aromatic structures that exhibit TCR.<sup>5–8</sup>

Orientation of the  $\pi$ -systems of the donor-acceptor is a key factor in TCR (Fig. 2).

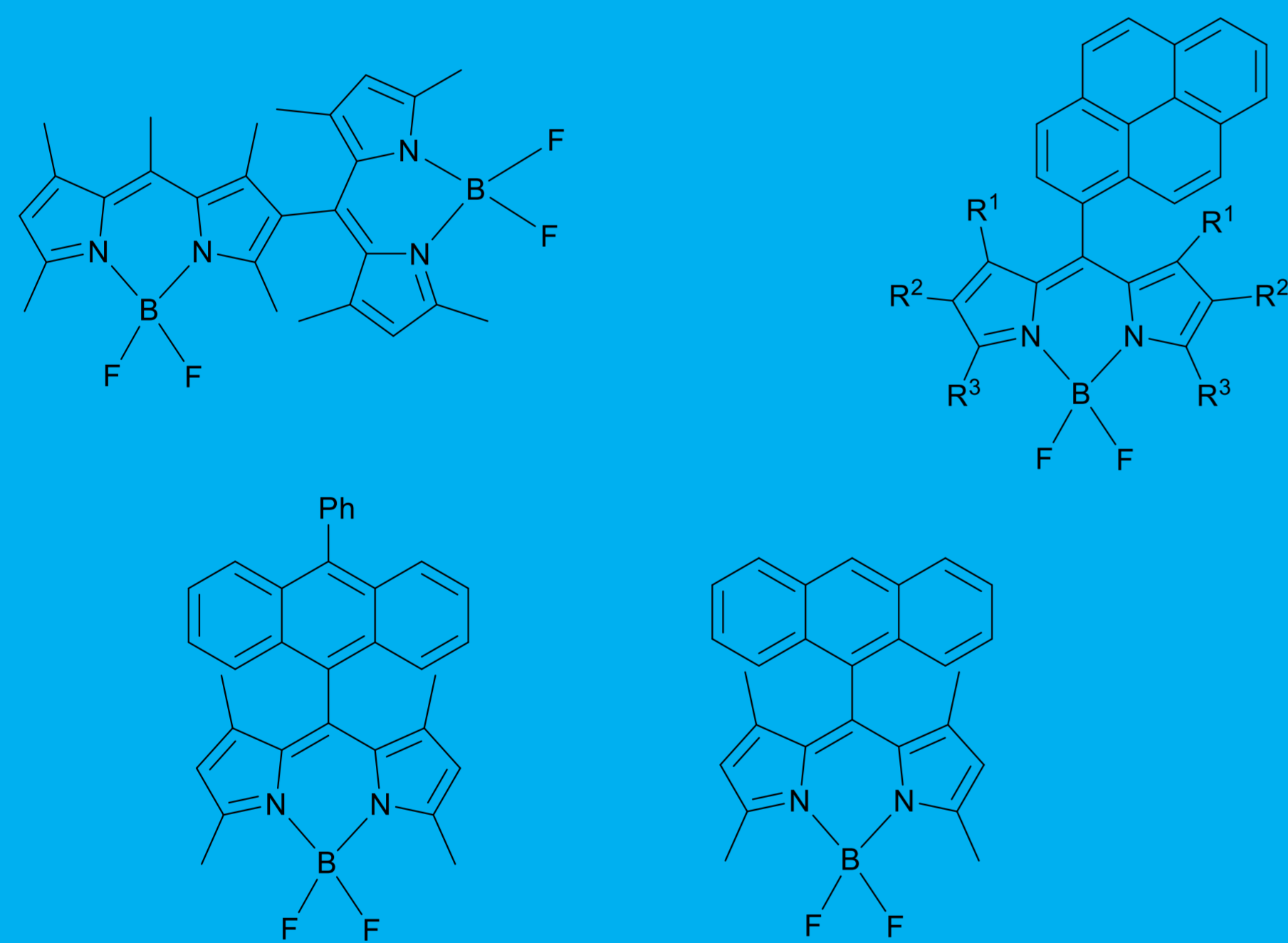
## 4. Polymer–fullerene blends



**Figure 5:** Chemical structures of fullerene based thin film blends that undergo TCR.<sup>14</sup>

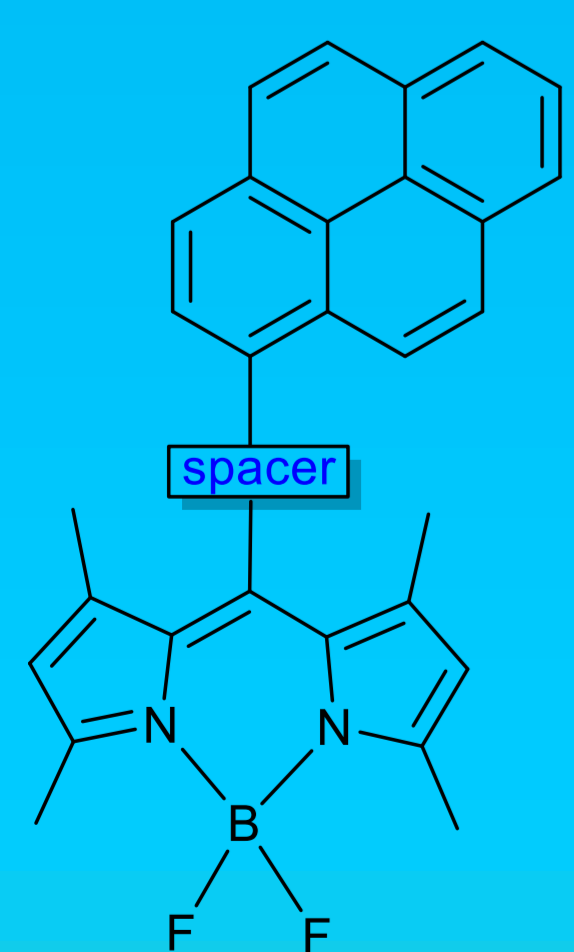
- TCR occurs in fullerene-polymer based thin-film blends (Fig. 5).<sup>14</sup>

## 3. BODIPY-based systems – Heavy atom-free Photosensitizer



**Figure 3:** (Top left): BODIPY dimer; (Top right): BODIPY-pyrene dyads and (Bottom): BODIPY-anthracene dyads.<sup>9–13</sup>

- BODIPY dyads exhibit orthogonality (Fig. 3).
- Orthogonality & manipulation of solvent polarity enhances SOCT-ISC.<sup>9–11</sup>

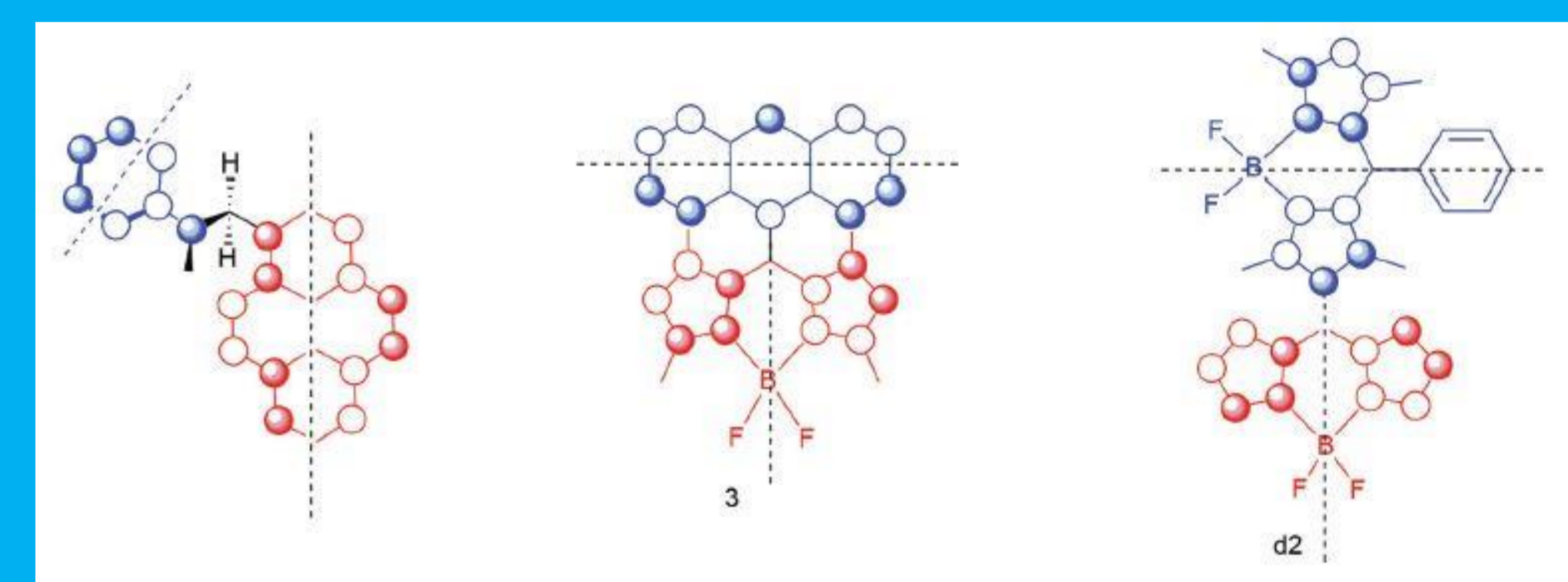


- Water-soluble BADs show efficacy against breast cancer cells via PDT<sup>12</sup>
- Structural and media polarity determine dominant photophysical pathway.<sup>13</sup>

**Figure 4:** BODIPY-pyrene dyad exhibiting reduced TCR due to spacer between subunits.<sup>13</sup>

## 5. TCR mechanistic aspects

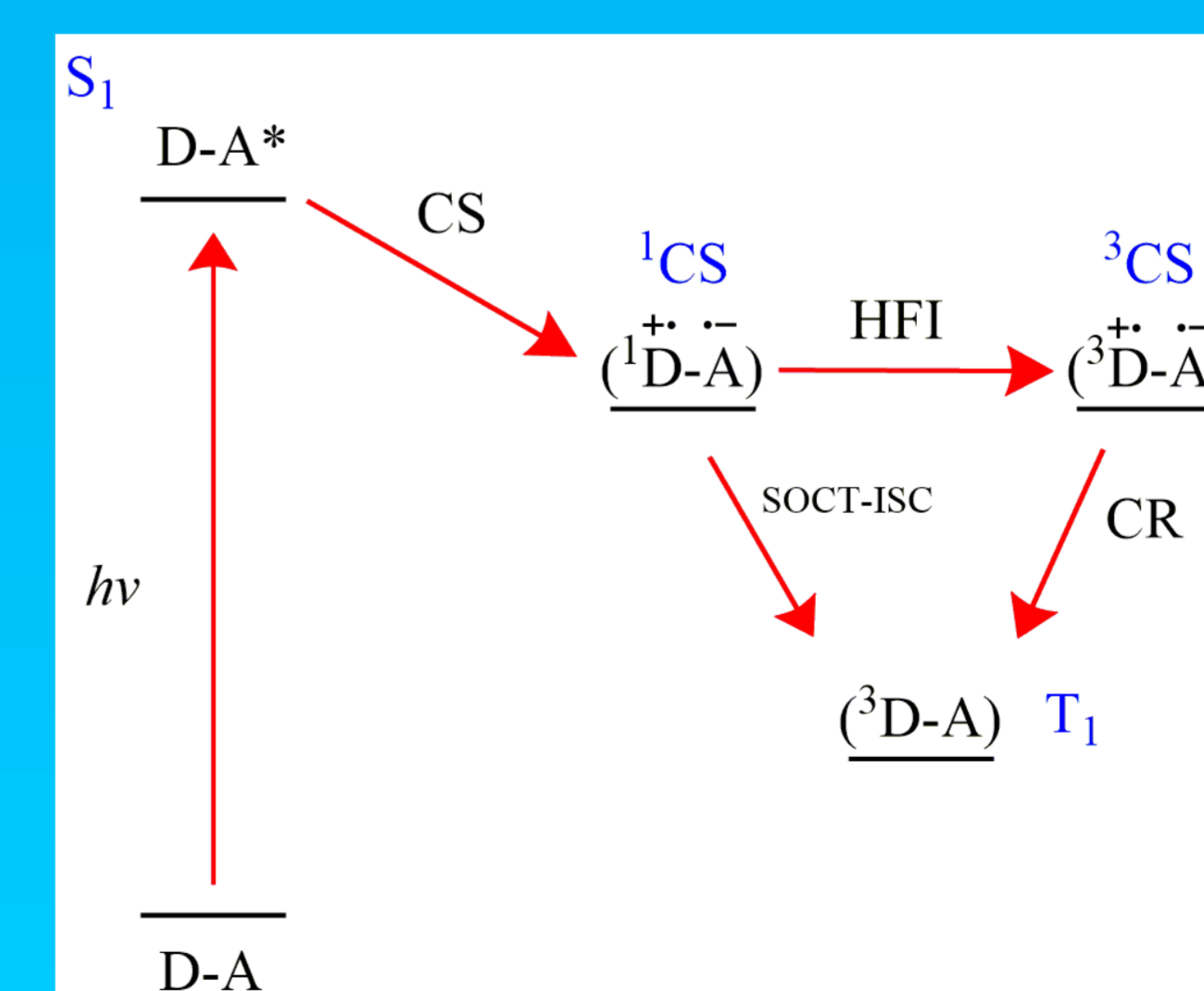
### HFI vs SOCT-ISC



**Figure 6:** Orthogonality of nodal planes is an important feature SOCT-ISC that leads to TCR.<sup>4</sup>

## 6. Conclusions

- Long-lived CS state (~10 ns) undergoes HFI to form a <sup>3</sup>CT state
- Short-lived CS state (~40 ps) undergoes SOCT-ISC to form triplet if:
  - **Short distance** between donor and acceptor
  - **Double orthogonality**



**Figure 8:** Jablonski diagram of donor-acceptor dyad (D-A) showing pathway to the triplet via charge recombination. In this triplet state, singlet oxygen can be produced.<sup>4</sup>

## 7. Outlook

- Exploration of many other aromatic/fluorophore dyads to determine whether TCR occurs
- Guidelines for structural design of TCR

### Acknowledgements:

This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement n°764837.