**Rama Dhali**

Relation on the activity as Assegnista di Ricerca 15th February 2019 – 15th February 2022

* **Research activity:**

Thermally activated delayed fluorescence (TADF) is a rare phenomenon occurring in systems where a triplet state sits very close in energy to the lowest excited singlet. Once the triplet state is populated, either upon intersystem crossing (ISC) following photoexcitation or upon injection of charges in a device, it may transfer its population to the nearby singlet state via a reverse ISC (RISC), provided that the energy gap between singlet-triplet is very low ($ΔE\_{ST}\~k\_{B}T$). The TADF requirement of singlet and triplet states lying close in energy is easily met in dyes with low-energy charge transfer (CT) states, provided the conjugation between the electron-donor (D) and electron acceptor (A) is weak. Dyes with the D and A units arranged almost orthogonally were immediately recognized as target systems. However, strictly orthogonal (non-conjugated) systems also have vanishingly small spin–orbit coupling between relevant states, hindering RISC, as well as negligible transition dipole moments from the excited singlet to the ground state, strongly suppressing emission intensity. An enormous effort towards the design of novel and more efficient TADF dyes includes multipolar dyes, where several D and A groups are linked together in different geometries, macromolecular and dendritic systems. Conformational flexibility, modulating the D–A conjugation, and hence affecting both the singlet–triplet energy gap and spin–orbit coupling is crucial to get efficient TADF. To make the picture even more intricate, the matrix properties, including dielectric properties, mobility, viscosity etc., may affect in different ways states with different nature, with dramatic effects on the relative energies of excited states. In my research over the last three years in the University of Parma (Guide: Prof. Anna Painelli), we are trying to get a clear picture of TADF process and different affecting parameter from extensive experimental and theoretical studies. Here I shortly summarize main results.

>> Choosing the DFT functional:

Density functional theory (DFT) and time-dependent density functional (TD-DFT) are the most widely used methods to study ground and excited states of medium to large molecular systems. Our TADF dyes have charge-transfer as well local-excited states. The most delicate issue is the choice of the functional to treat all the states properly. Recent studies propose the use of range-separated exchange functionals to solve the problem for CT states by obtaining the optimal mixing of short- and long-range exchange component, for each molecule of interest. We have tried to address this problem and discussed our findings in these following publications.

*Rama Dhali, D.K. Andrea Phan Huu, Francesco Bertocchi, Cristina Sissa, Francesca Terenziani and Anna Painelli “Understanding TADF: a joint experimental and theoretical study of DMAC-TRZ”, Phys. Chem. Chem. Phys., 2021,23, 378-387*

*Rama Dhali, D.K. Andrea Phan Huu, Francesca Terenziani, Cristina Sissa and Anna Painelli “Thermally activated delayed fluorescence: a critical assessment of environmental effects on the singlet-triplet energy gap”, J. Chem. Phys. 154, 134112 (2021)*

>> Environmental effects on excited states:

The dielectric properties of local environment largely affect the relative energies of CT and LE states and therefore alter the properties and behaviour of TADF dyes. Continuum solvation models are largely exploited to address the issue. However there are different implementations of continuum models leading to wildly different results. We traced the origin of this behavior to a fundamental problem of continuum model implementations in dealing with fast solvation, i.e. the solvation component associated with the electronic degrees of freedom of the solvent and usually described in continuum models in terms of the solvent refractive index. Relevant results and discussion are published in these articles.

*D. K. Andrea Phan Huu, Rama Dhali, Carlotta Pieroni, Francesco Di Maiolo, Cristina Sissa, Francesca Terenziani, and Anna Painelli “Antiadiabatic View of Fast Environmental Effects on Optical Spectra”, Phys. Rev. Lett. 124, 107401*

*Rama Dhali, D.K. Andrea Phan Huu, Francesca Terenziani, Cristina Sissa and Anna Painelli “Thermally activated delayed fluorescence: a critical assessment of environmental effects on the singlet-triplet energy gap”, J. Chem. Phys. 154, 134112 (2021)*

>> Understanding DMACTRZ: A joint experimental and theoretical study:

Now we know the right functional and right approach to treat the solvation effects for TADF dyes. As discussed before, the efficiency of TADF emitters is affected by several factors – (a) nature of excited states, (b) spin-orbit coupling, (c) conformational degree of freedom, (d) environmental effects, etc. Towards this ambitious aim, we did an extensive spectroscopic study of a typical TADF dye (DMAC-TRZ) in liquid and glassy solvents. TD-DFT results for the same molecule in gas-phase and under an applied electric field are exploited to build a reliable model for the dye, rigorously validated against experiment. The model, accounting for charge transfer and local singlet and triplet states, spin–orbit coupling, conformational and vibrational degrees of freedom, sets the basis for a sound understanding of the photophysics of TADF dyes in different environments. The charge-transfer nature of the fluorescent state and of the almost degenerate phosphorescent state is unambiguously demonstrated. The concurrent role played by conformational degrees of freedom and the matrix polarizability in governing TADF is also addressed. A full discussion and relevant results are available publicly available in the following article.

*Rama Dhali, D.K. Andrea Phan Huu, Francesco Bertocchi, Cristina Sissa, Francesca Terenziani and Anna Painelli “Understanding TADF: a joint experimental and theoretical study of DMAC-TRZ”, Phys. Chem. Chem. Phys., 2021,23, 378-387*

*D. K. Andrea Phan Huu, Sangeeth Saseendran, Rama Dhali, Larissa Gomes Franca, Kleitos Stavrou, Andrew Monkman, and Anna Painelli “Thermally Activated Delayed Fluorescence: Polarity, Rigidity, and Disorder in Condensed Phases”, J. Am. Chem. Soc., 2022, 144, 15211–15222*

>> Large dihedral angle relaxation of DMAC-py-TRZ:

In this work, we present the novel emitter DMAC-py-TRZ, which comes from a modification of the previously known, and discussed above, emitter DMAC-TRZ. The interest in this material was sparked by the unusual crystal structure that was found. Instead of presenting the usual ~90° dihedral angle, the x-ray showed a very small twist of 19.73° and a v-shaped bent molecule. The interesting molecular geometry led us to carry out an in-depth computational study of the dihedral angle relaxation and excited-state properties, together with a complete optoelectronic and photophysical characterization. This is carried out with a close collaboration with Prof Eli Zysman-Colman, University of St Andrews, Scotland. A manuscript is under preparation for this work.

Currently, we are also trying to extend our understanding towards quadrupolar and octupolar dyes.

* **Teaching activity: list student you have followed in tirocinio or thesis work (if any)**

Co-supervisor: Francesco Azzolin, Master thesis in Industrial Chemistry.

*Molecules for TADF: a joint theoretical and experimental study of DMAC-pyTRZ*

* **International Secondments:**

1. **Device Simulation in Setfos**

Date: January – March 2021 (3 months)

Host: Fluxim, Switzerland (Online mode)

2. **Computational and spectroscopic analysis on TADF dyes**

Date: October – December 2021 (2 months)

Host: Prof Eli Zysman-Colman, University of St. Andrews, Scotland

* **Publications during PhD: (including in preparation)**

1. D. K. Andrea Phan Huu, Rama Dhali, Carlotta Pieroni, Francesco Di Maiolo, Cristina Sissa, Francesca Terenziani, and Anna Painelli “Antiadiabatic View of Fast Environmental Effects on Optical Spectra”, Phys. Rev. Lett. 124, 107401

2. Rama Dhali, D.K. Andrea Phan Huu, Francesco Bertocchi, Cristina Sissa, Francesca Terenziani and Anna Painelli “Understanding TADF: a joint experimental and theoretical study of DMAC-TRZ”, Phys. Chem. Chem. Phys., 2021,23, 378-387

3. Rama Dhali, D.K. Andrea Phan Huu, Francesca Terenziani, Cristina Sissa and Anna Painelli “Thermally activated delayed fluorescence: a critical assessment of environmental effects on the singlet-triplet energy gap”, J. Chem. Phys. 154, 134112 (2021)

4. Ettore Crovini, Rama Dhali, Dianming Sun, Tomas Matulaitis, Timothy Cromberfield, David B. Cordes, Alexandra M. Z. Slawin, Cristina Sissa, Francesco Azzolin, Francesco Di Maiolo, Anna Painelli and Eli Zysman-Colman, “Understanding Large Dihedral Angle Relaxation of DMAC-py-TRZ : A joint Experimental and Computational Study of TADF Dye”, Under Preparation

5. D. K. Andrea Phan Huu, Sangeeth Saseendran, Rama Dhali, Larissa Gomes Franca, Kleitos Stavrou, Andrew Monkman, and Anna Painelli “Thermally Activated Delayed Fluorescence: Polarity, Rigidity, and Disorder in Condensed Phases”, J. Am. Chem. Soc., 144, 15211–15222 (2022)

* **Participation to schools**

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|  | Date |
| TADF Spring school, Garda:Materials design, Photophysics part 1, Modeling | 26-29 March 2019 |
| TADF School, Frankfurt:personal career development plan | 28-30 October 2019 |
| Introduction to molecular dynamicscourse by Dr. Luca Grisanti, 10 hours | 12-19 December 2019 |
| Organic optoelectronicsCourse by Prof. F. Cacialli, 48 hours | Second semester 2019 |
| Computational School on Electronic Excitations in Novel Materials Using the Yambo CodeOrganizer: ICTP, Trieste | 27-31 January 2020 |
| TADF school, VilniusDevice design and optimization, self-organization and time management | 11-13 February 2020 |
| Virtual Winter School on Computational Chemistry | 17-20 February 2020 |
| TADF schoolPaper Writing Workshop |  9 October 2020 |
| Virtual Winter School on Computational Chemistry | 15-18 February 2021 |
| TADF School, Palma:Grant Writing Workshop; Communication Skills I, Work life balance, Poster Presentation, Outreach Training, Training on device design & optimization, Career Perspectives, Outreach programme |  4-8 October 2021 |
| TADF School, Zell am See:Communication Skills II, Outreach programme | 21-25 February 2022 |
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* **Participation to conferences**
1. **CpiC virtual symposium**

Date: 18-20 January 2021

*Poster: Understanding TADF: a joint experimental and theoretical study of DMAC-TRZ*

1. **Non-equilibrium dynamical solvent effects on excited states: From spectroscopy to photoreactivity (online)**

Date: 14 – 17 June 2021

*Talk: Understanding large dihedral angle relaxation of DMAC-py-TRZ: a joint experimental and computational study of thermally-activated delayed fluorescence dye*

1. Quantum Dynamics and Spectroscopy of Functional Molecular Materials and Biological Photosystems (online)

Date:3-7 May 2021

1. **Light-matter Interactions from scratch: Theory and Experiments at the Border with Biology; (online)**

Date: 22 - 25 Nov 2021

*Talk: Understanding large dihedral angle relaxation of DMAC-py-TRZ: a joint experimental and computational study of thermally-activated delayed fluorescence dye*

1. **International Conference on the Science and Technology of Synthetic Metals (ICSM)**

Date: 17 – 22 July 2022 (Glasgow)

*Talk: Understanding large dihedral angle relaxation of DMAC-py-TRZ: a joint experimental and computational study of thermally-activated delayed fluorescence dye*

*Talk: Understanding TADF: a joint experimental and theoretical study of* ***DMAC-TRZ***

1. The 6th International TADF Workshop (online); Date: 9-10 December 2021
2. The 5th International TADF Workshop (online); Date: 7-8 December 2020
3. TADFlife Spring School, Garda; Date: 25 -29 March 2019
4. TADFlife Network Meeting, Frankfurt; Date: 28-30 October 2019
5. TADFlife Network Meeting, Vilnius; Date: 10-13 February 2020
6. TADFlife Network Meeting (Online); Date: 8-9 October 2020
7. TADFlife Network Meeting (Online); Date: 8-11 February 2021
8. TADFlife Network Meeting (Online); Date: 29th June – 1st July 2021
9. TADFlife Network Meeting, Palma; Date: 4 - 8 October 2021
10. TADFlife Network Meeting, Zell am See; Date: 21 – 25 February 2022