



Light-matter Interactions from scratch: Theory and Experiments at the Border with Biology | (SMR 3637)

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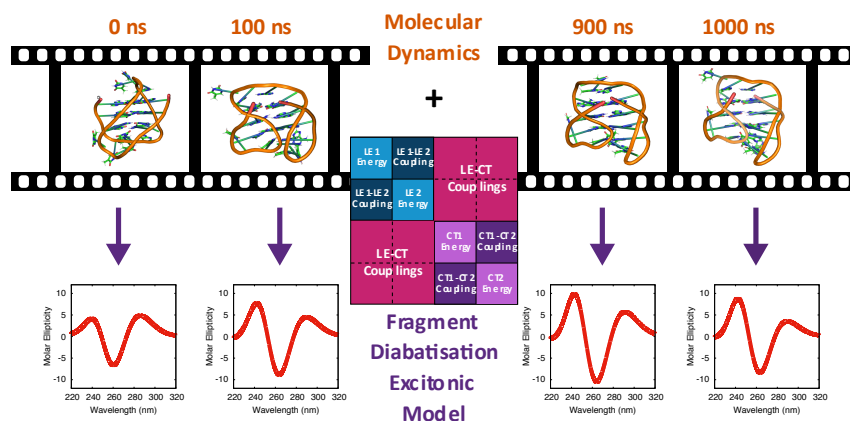
Electronic Dichroism Spectra of Guanine Quadruplexes by integrating Excitonic calculations and MD Simulations

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Excitonic Hamiltonians are widely employed cost-effective tools to model photoactivated processes in multichromophoric arrays. We have developed a Fragment Diabatization based Excitonic (FrDEx) model, a general and flexible approach, which incorporates charge transfer states [1]. Using FrDEx we have computed the electronic circular dichroism (ECD) and absorption spectra of two guanine-rich DNA sequences arranged in Quadruple helices (guanine quadruplex, GQs), i.e. a fragment of the human telomeric sequence (Tel21, antiparallel), and (TGGGGT)₄ (TG4T, parallel). The FrDEx spectra are in are fully consistent with the experimental ones and in good agreement with that provided by the quantum-mechanical method used for the parametrization of FrDEx model. When applied to different structures generated by molecular-dynamics simulations on Tel21, we found that ECD spectrum is moderately sensitive to the conformation adopted by the bases of the loops and more significantly to the thermal fluctuations of the guanine tetrads. In particular, we show how changes in the overlap of the tetrads modulate the intensity of the ECD signal. We illustrate how this correlates with changes in the character of the excitonic states at the bottom of the La and Lb local excitation bands, with larger involvement of local excitation and charge transfer states of bases that are more closely stacked.



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Extremely fast triplet formation by charge recombination in a Nile Red/Fullerene flexible dyad

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A donor/acceptor dyad in which Nile Red (donor) and fullerene (acceptor) are anchored through flexible spacers to a calix[4]arene scaffold was synthesized and spectroscopically characterized [1]. After selective photoexcitation of Nile Red, the almost quantitative formation of a triplet state localized on the fullerene moiety was observed on a fast timescale ($\sim 10^{-10}$ s⁻¹) in solvents of different polarity. The mechanism of this process was investigated combining sub-picosecond transient absorption spectroscopy and spectroelectrochemical measurements. Results suggest the formation of a short-lived charge-separated state followed by fast charge recombination yielding a triplet state localized on the fullerene moiety. The fast and efficient formation of the fullerene triplet after photoexcitation in the visible range suggests interesting applications of this system, among which singlet oxygen production in photodynamic therapy.

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Assessing the Contribution of Lysine to the UV-visible Spectra of Charged Amino Acid Rich Proteins by Acetylation

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Recent studies have revealed that monomeric proteins rich in charged amino acids exhibit charge transfer transitions which form a broad UV-visible absorption band spanning 200-800 nm [1]. The new band termed as Protein Charge Transfer Spectra (ProCharTS) opens up a new label free window to probe proteins and their interactions. However systemic studies on the contributions of specific charged amino acid species to the spectra are required in order to develop ProCharTS as a potent biophysical probe. Here we examine the possibility of using acetylation of Lys amino groups to assess their contributions to the ProCharTS profile of charged amino acid rich proteins. We present the UV-visible absorption of monomeric Human Serum Albumin (HSA) and acid extracted Histone proteins from human cells whose sequence is rich (> 30%) in both positively and negatively charged amino acids including Lys, Arg, Glu, and Asp. These proteins are found to show a prominent ProCharTS profile exhibiting a distinctive tail which extends up to 800 nm. Titration of HSA with acetic anhydride (chemical acetylation) and treatment of human U2OS cells in culture with Sodium Butyrate (inhibition of HDAC mediated enzymatic deacetylation) are shown to perturb the ProCharTS profile of these proteins. HSA purity was ascertained by HPLC and SDS-PAGE, while its acetylation was confirmed by mass spectrometry and its effects on HSA structure ascertained using CD spectroscopy. The purity of the acid-extracted Histones from human cells were checked using SDS-PAGE with the aim of obtaining ProCharTS of the acetylated and modified histones. The ProCharTS on individual recombinant histones and their complexes will be studied after cloning, expressing and purifying these core histones. We present computational studies based on molecular dynamics simulations and electronic structure calculations to understand the impact of Lys acetylation on the ProCharTS profiles of HSA and Histones. Our studies indicate that the modulation of the ProCharTS profile by selective acetylation of Lys in a diverse pool of positively and negatively charged amino acids is sensitive to the salt-bridge forming propensities for these amino acids.

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Addressing the Frenkel and charge transfer character of exciton states with a dimer-based model Hamiltonian: application to large aggregates of Perylene Diimide

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The interchromophoric arrangements influence the intermolecular interactions inside an aggregate, which in turn, determine the unique optical properties, photo-induced processes and new functionalities of the aggregate. To mention just one example, the aggregate induced emission (AIE) [1], which consists in stronger fluorescence at aggregate level and finds applications in fluorescence detection of biomolecules and biomolecular processes. Generally, when talking about the excited states in aggregates, we always refer to exciton states. The nature of exciton states can generally be classified as Frenkel (FE)-dominated, charge-transfer (CT)-dominated or mixed CT/FE. The CT character has a crucial role in the photo-induced processes of an aggregate. [2–7] It is therefore fundamental to assess the CT/FE contributions to exciton states. Generally, from a quantum-chemical (QC) calculation, exciton states are expressed in terms of delocalized excitations (DEs). In order to extract the CT/FE character, we present a diabaticization procedure with diabatic states chosen to coincide with local excitations within a restricted orbital space. On the other hand, a QC calculation will soon become unfeasible when considering very large aggregates. In this regard, we propose a model Hamiltonian (mH) approach built on the basis of QC calculations carried out only on dimers composing the aggregate [8]. Perylene Diimide (PDI) is chosen as a model system. Excitation energy profiles and CT/FE character modulations as a function of the interchromophore rearrangement are studied for aggregates of PDI up to tetramer. The dimer-based approach closely reproduces the results of full-aggregate calculations and the results demonstrate how the CT/FE interactions modulate the interchange of the H-/J- type aggregate for small longitudinal shifts of the chromophores.

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Testing micelles stability exploiting RET: an important warning

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Micelles are extensively exploited in biomedical applications as nanocarriers for different applications, including drug-delivery, bioimaging, etc [1]. The colloidal stability of nanocarriers is a crucial parameter, and resonance energy transfer (RET) phenomenon can be exploited to evaluate the stability of the nanocarrier [2]. In fact, a RET signal is detected only when the energy donor and the energy acceptor are close, i.e. when the nanocarrier is intact and both dyes are loaded on the same nanoparticle. Upon disaggregation of the nanocarrier, the dyes are expected to move far apart, and RET signal drastically decreases. In this work [3], a comprehensive spectroscopic characterization of two indocarbocyanines, DiI (1,1'-dioctadecyl-3,3,3',3'-tetramethyl- indocarbocyanine perchlorate) and DiD (1,1'-dioctadecyl-3,3,3',3'- tetramethylindodicarbocyanine perchlorate), in water suspensions in the presence of CTAB surfactant both above and below the critical micellar concentration is presented. DiI and DiD are compatible dyes for RET, since absorption of DiD (the energy acceptor) overlaps emission of DiI (the energy donor). RET is observed in micelles loaded with both dyes: the large local concentration of dyes allows to observe RET, even if the total dye concentration is low. Interestingly, the efficiency of RET is significantly increased when diluting the sample below the critical micellar concentration. This counterintuitive observation is rationalized in terms of the very large affinity between the dyes and CTAB, that favors the dynamical formation of molecular clusters, different from micelles, containing both cyanines. This work raises an important warning for the studies that rely on the observation of RET to investigate the stability of nanoparticles decorated with two (or more) dyes.

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Interferometric Broadband Optical Activity Spectroscopy with Fourier Transform Balanced Detection

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Optical activity spectroscopy such as circular dichroism (CD) and optical rotatory dispersion (ORD) is frequently employed to investigate (bio)-molecular structures and chiroptical responses of materials. However, standard CD and ORD measurements techniques rely on a scanning narrowband approach which limits their further development and wider utilization towards advanced applications.

The development of broadband chiroptical spectroscopy is challenging,[1-3] as chiral signals are 3–5 orders of magnitude smaller than achiral signals. Moreover, wavelength-dependent polarization sensitivity of optical components introduces significant polarization artifacts in the measurements, often masking the chiral signal.

We present a novel configuration for high-sensitivity and rapid measurement of broadband CD and ORD spectra spanning the visible and near-infrared.[4] The setup utilizes a linearly polarized light that creates an orthogonally polarized weak chiral free-induction-decay field, along with a phase-locked achiral transmitted signal which serves as the local oscillator for heterodyne amplification. By scanning the delay between the two fields with a birefringent common-path interferometer and recording their interferogram with a balanced detector, broadband CD and ORD spectra are retrieved simultaneously with a Fourier transform. Using a thermal light source, we achieve state-of-the-art sensitivity for CD and ORD across a broad wavelength range with a measurement time of just a few seconds. The setup allows high-sensitivity measurement of glucose concentration and real-time monitoring of fast asymmetric chemical reactions.

The interferometric approach demonstrated here, with its sensitivity to the electric field shifts, has a great potential for time-resolved optical activity measurements of stereochemical and structural changes. The setup accepts ultrashort laser pulses and will allow high-speed modulation of the pump beam, thus paving the way for high-sensitivity measurements of femtosecond chiral dynamics, which remains a holy grail in the field of ultrafast spectroscopy.

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Mechanical deformation of red blood cells assisted by optical tweezers: a comparison between healthy and diabetic individuals.

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In this work we present a systematic study of mechanical deformation on red blood cells using a home made optical tweezers system operating at 1064 nm. Stretching of the erythrocytes is performed at several laser powers. Eight clinically diagnosed diabetics and eight healthy individuals donated blood samples. The blood cells were subject to nine different laser powers, then information of the diameter change of the cell, compared with its original diameter is produced, in total 2786 individual cells were used in the results presented here. After statistical analysis and using a linear regression model we can affirm that this type of experiment can differentiate between healthy or diabetic individuals with a around 80% of confidence for the cases when “high laser intensities” are used, although there are many parameters susceptible to be optimized and hence evaluate with better confidence the damage in the red blood cell membrane of diabetic individuals.

Revealing the excited state dynamics of 1,4-Dicyanodibenzodioxin derivatives.**Vikas Kumar Jha¹, Subhadeep Banerjee², E Siva Subramaniam Iyer¹**¹*School of Chemical and Materials Sciences, Indian Institute of Technology Goa, Farmagudi, Ponda, Goa, India 403401*²*Department of Chemistry, BITS-Pilani K.K. Birla Goa, India- 403726*
Email: essiyer@iitgoa.ac.in**Abstract**

1,4-Dicyanodibenzodioxin derivatives (X-DCDBDO) are a fancy and bright candidate for labelling and visualizing photophysical, photochemical and photobiological processes [1,2, 3]. Previous studies of these molecules facilitate us with different biological activities of these molecules. Previous studies show in vitro cytotoxicity against glial C6 and HeLa tumor cell lines [1]. In conjugation, these molecules contain electron-withdrawing and electron-donating groups and behave as donor-acceptor systems exhibiting intramolecular charge transfer. In this work, we have systematically studied the excited state processes and the dynamics of derivatives of 1,4-Dicyanodibenzodioxin (X-DCDBDO). The molecules have been selected in such a way that they have different donor-acceptor moiety and the environment. Femtosecond transient absorption was performed to study the charge transfer processes. The samples were analyzed in two different solvent systems with different polarities and characters. Steady-state spectra are evidence of the minute effect of polarity of the solvent systems. The transient absorption spectra were recorded to understand the dynamics. UV Visible pulses pumped the prepared liquid samples, whereas UV and Visible white light generated on CaF₂ and sapphire crystals, respectively, were used as probe light. Before performing Time-resolved measurement, steady-state absorption and emission spectra were recorded. The OD of all the samples was maintained between 0.3 to 0.4 in a 2 mm cuvette. Molecules containing electron-withdrawing group in the vicinity of the dicyano group shows a larger stokes shift of about 90 nm. In comparison, molecules containing electron-donating groups in the vicinity of the dicyano group show a smaller stokes shift of about 60 nm and change upon substituting different groups on the donor side. The addition of an electron-withdrawing group at the donor side stabilizes the excited state in the absence of an electron releasing group at the acceptor end. In our primary inferences, the rate of charge transfer process follows the trend X-DCDBDO-NHR < X-DCDBDO-F at the acceptor end upon taking the same donor. In Fluoro substituted acceptor end, the rate of formation of charge-transfer states follows the trend Br > H > CN > NO₂ on the donor side, while in the case of NHR substituted acceptor end, the rate of formation of charge-transfer states follows the trend CN > H > Br > NO₂. The fastest charge transfer process is happening in DCDBDO-F derivatives in THF.

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Cell-Permeable Fluorescent Chemical Sensors for Imaging Phosphoinositides

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Phosphoinositides, a class of essential signaling anionic phospholipids, mediate key cellular processes like membrane trafficking, ion-channel regulation, and signal transduction.¹ Dynamic changes in localization and concentration of phosphoinositides on the membrane act as initiating flags for cell-signaling events. Hence, the ability to follow phosphoinositide dynamics in live cells can provide mechanistic insights into fundamental cellular processes. Detecting phosphoinositide distribution changes can also guide therapeutic interventions for diseases like cancer, type-2-diabetes, and bipolar disorder which are linked to impaired metabolism of these lipids.¹ Since, phosphoinositides are mostly present in the inner leaflet of the plasma membrane and intracellular organelle-membranes at low concentrations, a major challenge is to develop selective, sensitive, and cell-permeable sensors. Additionally, tracking phosphoinositide dynamics demands a reversible sensing strategy. Optical imaging can afford the requisite spatiotemporal resolution to image phosphoinositide dynamics. We have devised a peptide-based reversible fluorescent sensing strategy for tracking phosphoinositides and have applied the strategy in a proof-of-concept study to detect phosphatidylinositol-(4,5)-bisphosphate (PI(4,5)P2).² Our sensing strategy is modular and appropriate selection of phosphoinositide binding scaffolds can potentially lead to sensors for the entire phosphoinositide family. We have performed molecular dynamics simulations on phosphoinositide binding peptides in the presence of phosphoinositide containing lipid bilayers to guide our sensor design. As a result, we have successfully developed two orthogonally emitting sensors with high selectivity toward PI(4,5)P2 and phosphatidylinositol-(3,4,5)-trisphosphate (PI(3,4,5)P3), respectively. Both sensors have been tested for in vitro selectivity against other biologically relevant phospholipids and are cell-permeable. Current studies are focused on tracking phosphoinositide dynamics in live cells using our novel sensors. The comparative levels and distributions of these two phosphoinositides are important determinants in the regulation of cell proliferation and migration. Our ultimate aim is the simultaneous imaging of PI(4,5)P2 and PI(3,4,5)P3 to obtain molecular insights into these crucial cellular processes under physiological and pathophysiological conditions. I will present details of our phosphoinositide sensing strategy, sensor design, and live cell imaging studies with our novel sensors.

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Raman spectroscopy technique as an effective tool to monitor dilution effects on ionic liquids

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Ionic liquids (ILs) properties are very flexible as a function of addition of water or other solvents. This property makes them interesting candidates as solvation media to assess the stability and structural changes of dissolved biomolecules. Yet, the molecular structure of the mixtures itself needs to be understood. In this work four imidazolium-based ionic liquids (1-methylimidazolium Cl, 1-methylimidazolium tfo, 1-methylimidazolium NO₃, 1-methylimidazolium HSO₄) have been studied by Raman spectroscopy using two excitation wavelengths, one in the UV range (266 nm) and the other in NIR range (785 nm). Most of the imidazolium cation bands show intensity enhancement at UV excitation as a result of the phenomenon of pre-resonance. Specific spectral differences among the different samples were identified, at high and moderate IL concentrations, attributed to changes on cation-anion interactions. In a highly diluted samples (water ratio > 90%) all samples tend to have more similar spectra, suggesting analogous hydration features of the cation in these conditions. The results from the present Raman investigation contribute to a more comprehensive view of the water-mediated interactions in IL/water mixtures. This could facilitate the design of effective stabilizing ILs for their exploitation in the fields of biomedicine and life science.

Distance-dependent Through-Space Intervalence Charge Transfer in Thiazolothiazole-based Metal-Organic Frameworks

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Metal-Organic Frameworks (MOFs) are crystalline organic-inorganic hybrid materials comprised of the metal centers and organic linkers, well-known for their high surface area, well-defined pore, tunable structures.¹ MOFs are not generally electrically conductive. Electrically conductivity in MOFs can be achieved using redox-active metal nodes or organic linkers, stable radical-based ligands.² In fact, MOFs are a unique platform to investigate the charge transfer mechanism where the metal ions or organic linkers are well organized in a highly crystalline rigid system. Charge transfer can be achieved by either the through-space or through-bond approach.³ The through-bond mixed-valance charge transfer has been well explored whereas, through-space inter-valency in MOF is elusive.⁴ We have synthesized a new Co(II) based metal-organic framework using redox-active organic linker, N,N'-di(4-pyridyl)thiazolo-[5,4-d]thiazole. The framework exhibits through-space intervalence charge transfer (IVCT) arising from cofacially arranged N,N'-di(4-pyridyl)thiazolo-[5,4-d]thiazole linkers. The IVCT has been elucidated computationally using time-dependent density functional theory (TD-DFT) methods. Moreover, we have compared the extent of IVCT with a similar reported framework structure.⁵ The computational study also exploits the distance-dependent through-space intervalence charge transfer (IVCT) in both systems. Here, I present experimental observation and comparative study of through-space intervalence charge transfer (IVCT) using redox-active organic linkers in two metal-organic frameworks and their computational supports. This interrogation of the charge transfer mechanism and electrical conductivity in MOF provides a better understanding of conducting materials.

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TADF in polar matrices: understanding environmental effects

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Materials capable of thermally-activated delayed fluorescence (TADF) find potential applications in many research fields, such as organic light-emitting devices, catalysis, fluorescence imaging and biosensing.[1, 2, 3]

Donor-acceptor (DA) dyes with poorly conjugating bridges were immediately recognized as promising systems, due to the small energy gap between the lowest energy singlet and triplet states. However, TADF efficiency depends on several interrelated factors, including the nature of the excited states and the conformational flexibility of the molecule. Moreover, the photo-physical behaviour of TADF emitters is deeply affected by the surrounding environment.

Recently, an essential state model (ESM) was proposed for a typical TADF dye, 9,9-dimethyl-9,10-dihydroacridin-4,6-triphenyl-1,3,5-triazine (DMAC-TRZ).[4] The ESM includes four diabatic electronic states, an effective molecular vibration and an effective torsional mode. The ESM is parametrized on density functional theory calculations and validated against optical spectra in solution.

In this work, the same ESM is exploited to address environmental effects on TADF dynamics. Following recently proposed strategies to account for the dielectric properties of the medium[5] we propose an original approach to inter-system crossing (ISC) and reverse inter-system crossing (RISC) rates fully accounting for non-adiabatic vibrational and conformational modes. ISC and RISC rates are largely suppressed when going from gas phase to a polarizable matrix. Inhomogeneous broadening phenomena rationalize the anomalous behaviour of time-resolved spectra of DMAC-TRZ in polar matrices.[6]

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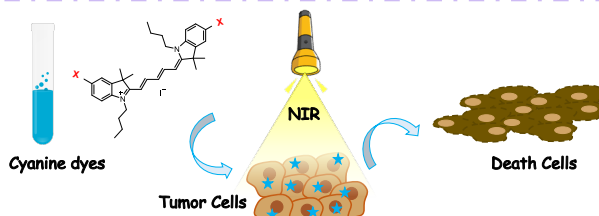
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AIM

INTRODUCTION

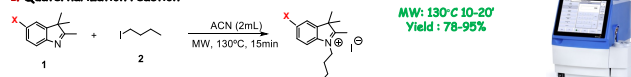
The effectiveness of photodynamic therapy (PDT) has been proved to be closely related to the intrinsic features of the photosensitizer (PS). Over the recent years, several efforts have been devoted to the discovery of novel and more efficient near-infrared (NIR) photosensitizers showing higher efficacy and lower side effects, compared to the currently commercially available (*i.e.* porphyrins - Photofrin®, chlorins, derivatives of chlorins - Foscan®, bacteriochlorins, and phthalocyanines). Among different NIR organic dyes, polymethine dyes (PMDs) are the most retaining attentions for wide application in various fields of science and technology. In particular, cyanines can be considered as innovative photosensitizers (PS) due to the easy and low-cost synthesis along with remarkable absorption property in the far-red NIR region, perfectly matching the biological tissues' transparency window (600-900 nm) [1, 2]. The advantage of cyanines over other classes of PSs relies in the possibility of easily tuning their structure to get the proper photophysical and photochemical properties for the desired applications [3]. Even though the clinical application of Cyanines as PSs for PDT is limited compared to other classes of PSs such as phthalocyanines and most first-generation PS, porphyrins and their derivatives, they could be considered more promising PSs, thanks to their broad absorption spectral range with high extinction coefficients, high fluorescence quantum yield (QY), photostability, relatively high selectivity to tumor cells, low dark toxicity and side effects [3].

The present contribution deals with the design, synthesis and characterization of a new series of CY polymethine dyes to be used as innovative PSs for PDT, based on indolenine ring and with different substitution groups, with the aim to highlight a structure-activity relationship.

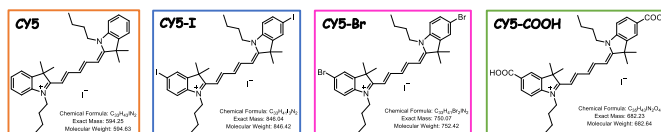
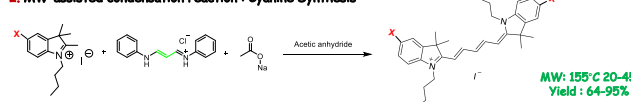


SYNTHESIS AND CHARACTERIZATION OF CYANINES

1. Quaternization reaction



2. MW-assisted condensation reaction: Cyanine Synthesis



METHODS

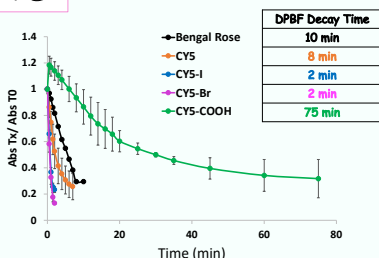
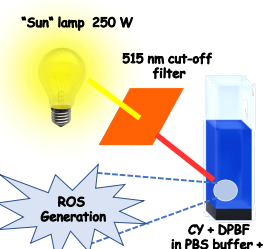
IN VITRO PDT TESTS

The photodynamic activity of cyanines was evaluated in terms of cell viability (MCF-7 cell line) before and after 15 min of irradiation, by using a compact LED array-based illumination system produced by Cicci Research s.r.l.

RED-LED array (light source with excitation wavelength: 640 nm, and voltage: 15 volt) composed of 96 LEDs in a 12 × 8 arrangement.

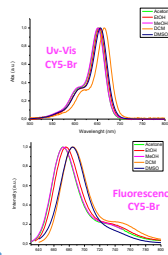
MTS assay was performed 24h after irradiation in order to evaluate cell viability.

RESULTS



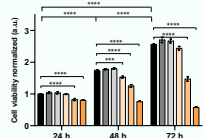
All CYs possess ROS generation ability, excepted for CY5-COOH, which need long time to promote the decay of DPBF

PHOTOCHEMICAL PROPERTIES EVALUATED BY UV-VIS AND FLUORESCENCE

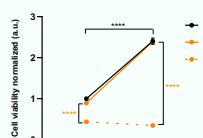


	QY in DMSO	ϵ (M ⁻¹ cm ⁻¹) in DMSO	Abs _{max} (DMSO)	Fuo intensity _{max} (DMSO)	Stokes shift (nm)
CY5	0.59±0.01	1.52 × 10 ⁵	652	670	20
CY5-I	0.65±0.01	2.00 × 10 ⁵	662	691	29
CY5-Br	0.58±0.02	2.65 × 10 ⁵	657	684	27
CY5-COOH	0.51±0.01	2.19 × 10 ⁵	661	682	21

In order to correlate ROS production and PDT activity, cytotoxicity and PDT tests were performed on CY5, CY5-Br and CY5-I



All cyanines resulted Biocompatible up to 200 nM



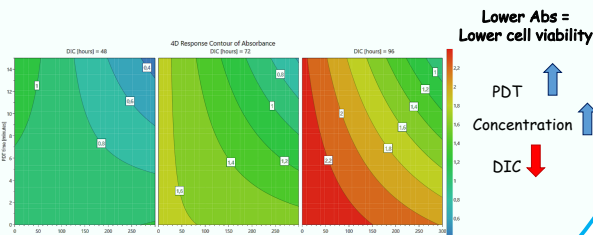
All cyanines showed cytotoxicity after irradiation

CONCLUSIONS

- ✓ We have reported the synthesis of new symmetrical pentamethine cyanine dyes varying the substituent group.
- ✓ The absorption maxima around 650-660 nm are not affected by the different substituent on the indolenine ring.
- ✓ The heavy atom effect leads to a more rapid ROS generation but the resulting effect on the PD activity is similar.
- ✓ All resulted biocompatible and showed an interesting *in vitro* PD activity, at very low concentration (200 nM).

Design of Experiment (DoE)

- To perform a multivariate statistical analysis
- To maximize the information content, precision and accuracy in the results
- To keep the number of experiments low.



$$Abs = 1.35 - 0.21 PDT - 0.31 Conc + 0.52 DIC - 0.25 PDT \cdot Conc - 0.11 PDT \cdot DIC - 0.14 Conc \cdot DIC$$

ACKNOWLEDGEMENTS

The authors acknowledge the financial support from the University of Torino (Ricerca Locale ex-60%, Bando 2020) and from the Fondazione Cassa di Risparmio (CRT) of Torino, Italy.

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Monitoring Protein Unfolding and DNA Binding using Protein Charge Transfer Spectra

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CT (Charge Transfer) transitions involving Lys/Glu sidechain charged groups and peptide backbone accounted for the novel absorbance in the Near UV-Visible region (250–800 nm) observed in protein α_3C (devoid of aromatic amino acids)¹. In a subsequent computational study, CT spectra was elucidated for other charged amino acids (including Arg, His, Asp and the phosphorylated forms of Serine, Threonine and Tyrosine) using TDDFT calculations². Weak luminescence from charged monomeric proteins characterized by significant overlap between excitation/emission spectra, large Stokes shifts and multiexponential intensity decays were additionally reported³. In the present investigation, ProCharTS was used to study protein unfolding and DNA-Protein binding.

α_3C , α_3W and Human Serum Albumin (HSA) are alpha-helical proteins with multiple charged atoms in close proximity. Upon chemical denaturation by guanidine.HCl (GdnCl), a prompt decrease in α_3C ProCharTS absorption was observed even at 1M GdnCl concentration which decreased further to a baseline value beyond 3M denaturant concentration. The decrease in ProCharTS was attributed to a substantial loss of charged amino acid contacts upon protein unfolding. Interestingly, the α_3C ProCharTS at 5M GdnCl was slightly higher, hinting towards residual structure. Upon unfolding by GdnCl, HSA absorbance reduces in the 325–800 nm region and there is a shift in Trp emission maximum from 329 to 348 nm. The loss in helicity in CD spectrum and redshift in Trp emission maximum (for mutant α_3W and HSA) correlated with decrease in the ProCharTS absorbance and luminescence. Thus ProCharTS can serve as a novel LABEL-FREE spectroscopic tool to monitor protein unfolding.

Efficient DNA condensation by PRM (salmon protamine) is a crucial step in sperm maturation which is monitored *in-vitro* by conventional techniques like EMSA. TDDFT calculations predict significant CT absorbance in the near UV region for Arg-rich protein PRM. PRM absorbs moderately in the 250–350 nm region inspite of complete absence of aromatic amino acids. Upon binding of PRM to calf-thymus genomic-DNA and subsequent condensation, ProCharTS in the soluble fraction of PRM decreased by ~50 % between 250–320 nm. Electrophoretic mobility shift of calf-thymus DNA in the presence of PRM confirmed PRM-DNA binding. The decrease in PRM ProCharTS was used to quantify its DNA binding ability in a LABEL-FREE manner.

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Multidimensional Electronic Spectroscopy with Combined Spectral, Temporal, and Spatial Resolutions

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Two-dimensional electronic spectroscopy (2DES) is a state-of-the-art spectroscopic tool which provides contour map snapshots of ultrafast quantum dynamics with high temporal and spectral resolution. However, all conventional 2DES approaches rely on non-collinear or partially-collinear geometry. This allows for directional filtering of 2DES signal field, at the cost of poor or no spatial resolution. For instance, in the conventional BoxCARS geometry, signal detection relies on creating a phase and amplitude grating in the sample and because of this, spatial resolution can not be better than $10^4 \mu\text{m}^2$ [6]. Due to lack of spatial resolution and sensitivity limitations, several open questions remain. For instance, it is known that the initial steps of photosynthetic energy transfer may involve quantum superpositions between mixed vibrational-electronic states. But because such wavepackets decay rapidly due to ensemble averaging[1] of the 2DES signal[2], their functional relevance is uncertain. Similarly, in the context of photovoltaic thin films morphological averaging leads to uncertainty about mechanistic details of the correlations between morphology and device photocurrent [3].

We present a home-built spatially-resolved fluorescence detected 2DES (SF-2DES) spectrometer which address the issues on limited sensitivity and spatial resolution in conventional 2DES. Our SF-2DES setup is based on a visible white-light continuum with spectral bandwidth capable of sub-10 fs temporal resolution, along with sub-micron spatial resolution made possible by combining the setup with a reflective microscope objective. We follow the all-collinear acousto-optic phase-modulation (AOPM) approach[4] to separate the fluorescence-detected 2DES signal using phase-sensitive lock-in detection. This represents the first implementation of SF-2DES based on a *visible* white-light continuum where broadband visible wavelengths present specific set of challenges[6] not present in near-IR[7] or non-white-light based approaches[6].

We further demonstrate the enhanced detection sensitivity of fluorescence-detection over heterodyne-detection employed in conventional 2DES. Preliminary 2DES spectra are obtained with high signal-to-noise ratio at optical densities as low as ~ 0.02 , which is more than 10x lower than what is possible with conventional 2DES. This represents the first such report of enhanced sensitivity of fluorescence detection at such ODs. Future applications of our spectrometer include spatially-resolved measurements of sub-100 fs exciton dissociation[5] in organic thin films, and measurements of exciton interactions in photosynthetic proteins.

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Emergence of Aggregation Induced Emission (AIE), Room Temperature Phosphorescence (RTP) and Multi-Stimuli Response from a Single Organic Luminogen by Directed Structural Modification.

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Metal free organic luminogens are often conventional fluorophores with fast deactivation of the excited state in nano second time scale. A large S1-T1 energy gap as well as a very weak spin-orbit coupling often limits their application to be used as a potential phosphorescent emitter; however, a smart designing and choosing an appropriate pair of donor and acceptor can effectively solve this problem. Herein, naphthalene monoimide and phthalimide based donor-acceptor luminogens have been designed and synthesized. All the designed luminogens are able to exhibit room temperature phosphorescent behavior in ambient condition due to presence of a very small ΔE_{ST} value. Moreover, introduction of cyano-ethylene moiety in between donor and acceptor moiety can increase its lifetime further due to enhanced non-covalent interactions in crystalline state.

Metastable Chiral Azobenzenes Stabilized in a Double Racemate

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The self-assembly of chiral organic chromophores is gaining huge significance due to the abundance of supramolecular chirality found in natural systems. We report an interdigitated molecular assembly involving axially chiral octabrominated perylene diimide (OBPDI) which transfers chiral information to achiral aromatic moieties.¹ The crystalline two-component assemblies of OBPDI and electron-rich aromatic units were facilitated through π -hole $\cdots\pi$ donor–acceptor interactions,² and the charge-transfer characteristics in the ground and excited states of the OBPDI cocrystals were established through spectroscopic and theoretical techniques.³ The OBPDI cocrystals entail a remarkable homochiral segregation of P and M enantiomers of both molecular entities in the same crystal system, leading to twisted double-racemic arrangements. Synergistically engendered cavities with the stored chiral information of the twisted OBPDI stabilize higher-energy P/M enantiomers of trans-azobenzene through non-covalent interactions.

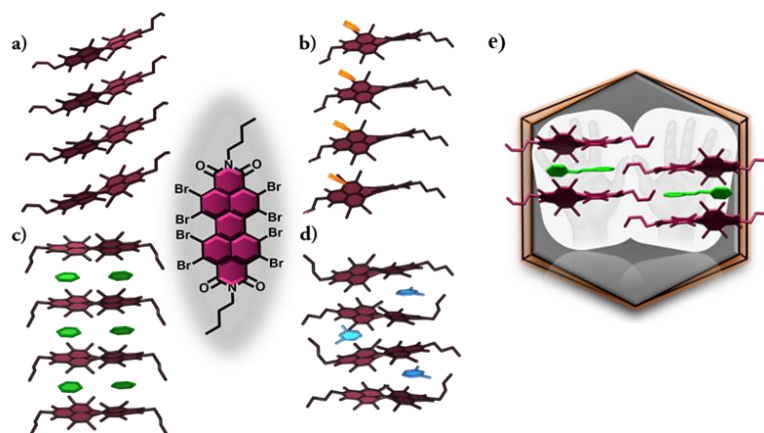


Figure 1: Crystal packing of OBPDI in a) DCM-hexane, b) THF, c) benzene, toluene, o-xylene and d) m-xylene, p-xylene, mesitylene (representation of only one enantiomer is given for clarity in a-d); e) Double racemic cocrystal generated by induction of twist from OBPDI host to achiral azobenzene guest through noncovalent interactions.

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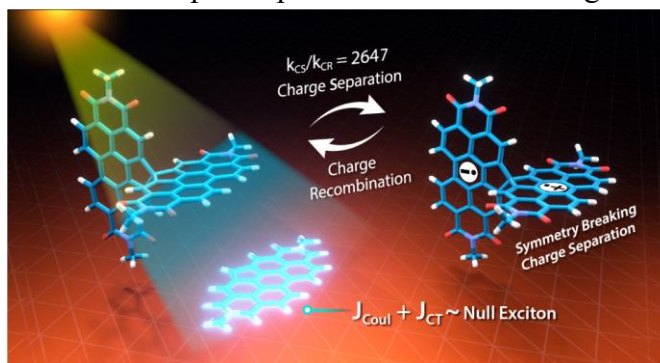
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Null Exciton-Coupled Chromophoric Dimer Exhibits Symmetry-Breaking Charge Separation

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A comprehensive understanding of the structure-property relationships in multichromophoric architectures has pushed the limits for developing robust photosynthetic mimics and molecular photovoltaics [1,2]. The elusive phenomenon of null exciton splitting has gathered immense attention in recent years owing to the occurrence in unique chromophoric architectures and consequent emergent properties [3-5]. Herein, we integrated two fundamental concepts, null exciton splitting and symmetry-breaking charge separation, as an innovative strategy to generate an efficient long-lived charge-separated state. Spiro-conjugated perylene diimide dimer (Sp-PDI₂) in Greek cross (+)-arrangement exhibits negligible excitonic coupling as evidenced from spectroscopic methods. Theoretically calculated Coulombic and charge transfer coupling validated the minimal excitonic interaction among the orthogonally arranged Sp-PDI₂. The rotational angle-dependent Coulombic and charge transfer coupling calculations provided significant values for lower rotational angles manifesting impeccable evidence for the ability of Greek cross-architecture in lowering excitonic coupling. The Sp-PDI₂ exhibits a remarkably selective hole transfer phenomenon which aids in the ultrafast SB-CS. As predicted by Marcus theory of electron transfer, the rate of charge recombination shows an inverted dependence on the driving force upon changing the solvent polarity. Ultrafast charge separation and decelerated charge recombination render unequivocal evidence for the prolonged SB-CS state ($k_{CS}/k_{CR}=2,647$ in ACN) in the null exciton coupled Sp-PDI₂ is the most long-lived charge-separated state obtained so far among the multichromophoric PDI derivatives. The study providing explicit correlation of the relative orientation of chromophoric system and its frontier molecular orbital interaction in dictating complex excited-state dynamics offers potential design principles for the design of advanced molecular photovoltaics and hence has implications in both fundamental and applied research.



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Carbon dots used as responsive drug nanocarriers to deliver Squaraines: an *in vitro* evaluation of their Photodynamic activity

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Over the recent years, extensive efforts have been devoted to the development of near-infrared (NIR) dyes for biological applications, especially for photodynamic therapy (PDT). Polymethine dyes can be considered as innovative photosensitizers (PS) due to the easy and low-cost synthesis along with remarkable absorption property in the far-red NIR region, perfectly matching the biological tissues' transparency window (600-900 nm). In particular, NIR polymethine cyanines (CY) and squaraines (SQ) are well suited for this purpose and have been extensively studied for these applications, thanks to their high molar absorption coefficients, remarkable brightness, fluorescence and photostability, especially in organic media [1]. Despite their excellent photochemical properties, their chemical instability and self-aggregation when in contact with biological media still limit their effective clinical application. To overcome these drawbacks, the development of a nanocarrier in which the dye is incorporated into biocompatible nanoparticles could be considered a promising approach to prevent the formation of dye aggregates and thus increase its solubility in aqueous environment. Carbon nanodots (C-dots) are a new class of carbon-based nanomaterials with exclusive features, such as unique optical properties, aqueous solubility, excellent biocompatibility and low toxicity. For these reasons, they have been studied and applied in a wide range of biomedical fields, including drug delivery [2].

The present contribution deals with the preparation of C-dots complexes with a SQ dye active in *in vitro* PDT, to promote its use in physiological conditions. Preliminary results showed that C-dots-dye complex exhibit good optical properties, good biocompatibility and *in vitro* photodynamic activity.

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Studying the effect of internal electric and magnetic field on electric current on a periodic of poly(dA)-poly(dT) DNA structure.

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Abstract. *Peierls phase factor* is used in studying the internal magnetic field effect on electric current on a periodic structure, the poly(dA)-poly(dT) DNA molecule structure. In the tight-binding Hamiltonian model, the electric field-dependent electron hopping amplitudes are employed for investigating the effect of the internal electric field built up along the structure. The electric current at a certain voltage is calculated using the Landauer-Buttiker formalism from the electron transmission probability, which is obtained using Green's function technique. It is observed that the electric current oscillates with the internal magnetic field.

Triplet Excitonic States Character Description in Perylenebismide Dimers

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Perylene-3,4:9,10-bis(dicarboximide) (PDI) and its derivatives are well known visible organic chromophores with excellent optoelectronic properties for energy and charge transport [1]. Moreover, their molecular rigidity results in robust thermal and photochemical stabilities, and strong absorption capabilities of visible and near-infrared (NIR) light. Photophysical properties of PDI aggregates are of special interest as light-harvesting materials in organic photovoltaics [2].

While low-lying singlet excitations of PDI have been largely investigated, much less is known about the triplet state. Despite that the triplet manifold is not initially accessible through photoexcitation, recent studies have identified spin triplets as the final photoproduct states upon exciton decay processes in PDI covalent dimers [3] and in the crystal[4].

Recently a simple diabaticization procedure within a restricted orbital space has been used to analyse the Frenkel Exciton (FE) and Charge Transfer (CT) character of singlet adiabatic states of PDI aggregates[5]. By contrast, few investigations have been reported for the analysis of triplet states[6]. In the present work we aim to analyse the lowest excited triplet states of molecular dimers of PDI.

To that end, we have computed the vertical adiabatic triplet excited states by means of the time-dependent (TDDFT) version of the Density Functional Theory (DFT) for a number of molecular configurations along the intermolecular longitudinal translation coordinate. We have then applied the simple diabatic approach of [5] to analyze the character (CT/FE) of the triplet states and the interplay of inter-molecular interactions determining the adiabatic energy profiles of the lowest triplet exciton states.

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