Exciton and Spin Chemistry of Luminescent Trityl Radicals

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The spin of ground and excited levels in molecular materials dictates the exciton mechanisms for any photonic, optoelectronic and quantum technology applications. Recent interest in organic radicals containing unpaired electrons has emerged from the design of new materials that undergo efficient light absorption and emission from transitions between doublet spin ($S = 1/2$) ground and excited levels. I will present our work on trityl radicals as the functional emitters in light-emitting devices, in which we explore designs that couple their optical, spin and magnetic properties in molecular excitons that could enable future technology platforms.

Optically Functional Material Design based on the Weak Exchange Interaction in Multi-radical Systems

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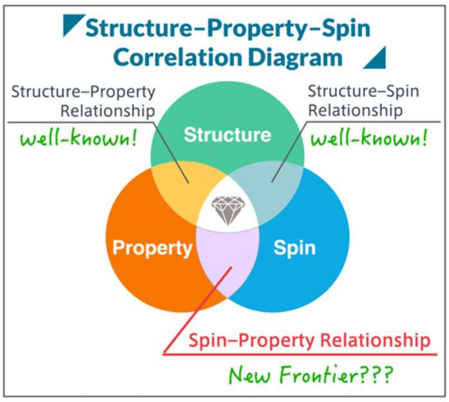
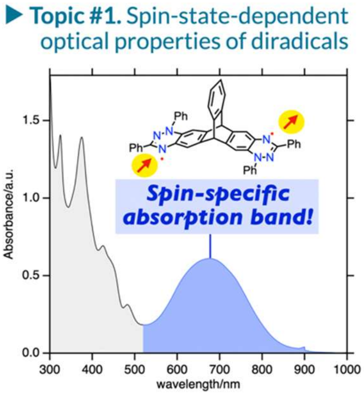
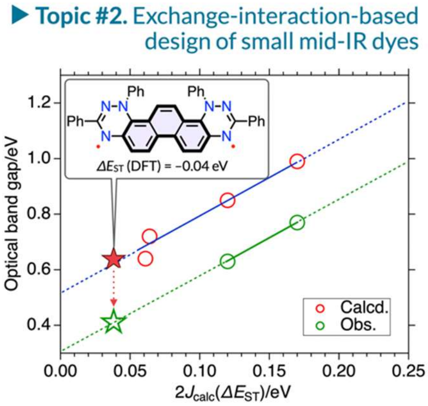
The properties of discrete molecular systems are determined by their structure, charge, and spin state. Therefore, it is important to comprehensively design the three factors (structure, charge, and spin) for novel functional materials. The spin-property relationship is less explored, while structure-property and structure-spin relationships have been extensively studied. From such a perspective, we have investigated the spin-state-dependent properties of molecules and the exchange-interaction-driven molecular design approach for functional materials. In this presentation, two of our recent research topics will be reported in addition to the latest results.







The first topic is the spin-state-dependent optical properties of organic multi-radical systems.[1,2] Organic diradicals generally exhibit a small energy gap between their spin-states, which leads to a population of excited spin-states even at room temperature. However, it has been considered that such an interaction as weak as the thermal energy does not make a significant difference in the photophysical properties of the different spin states. We found di- and tri-radical systems with weak through-space spin-spin interactions exhibiting absorption spectra strongly dependent on their spin states. The spin-dependent absorption feature allowed spin-selective photoexcitation, revealing spin-dependent excited-state dynamics.

The second topic is exchange-interaction-based molecular design for exceptionally small optical band gaps.[3,4] Near- to mid-IR responsive chromophores, characterized by their ability to produce exciton across the electronic transition to the vibrational energy region, hold significant potential for various applications. We experimentally established a linear correlation between the exchange interaction of diradicals and the optical band gap of their 1e-oxidized radical cation state. By taking advantage of the relationship, we designed a chromophore with only 590 Da, showing a mid-IR electronic transition reaching 2000 cm^{-1} (5000 nm).

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New Developments Towards Highly Luminescent Diradicals

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Quantum sensing enables the detection of magnetic and electric fields with extraordinary sensitivity, surpassing classical sensors in precision and resolution. A key breakthrough in this field has been the use of nitrogen-vacancy (NV) color centers in diamond, which combine spin readout with optical detection. However, great challenges remain in their scalability, spatial control, and fabrication complexity of color centers in diamond preventing their widefield application.

As a promising alternative, we explore the potential of molecular color centers – specifically, organic diradicals – as scalable, tunable, and chemically well-defined spin-active systems.

In this talk, I will introduce a new class of fluorescent diradicals derived from tris(trichlorophenyl)methyl (TTM) radicals, bridged via indolocarbazoles. These molecules exhibit near-pure diradical character ($y_0 \approx 1$) and an exceptionally high photoluminescence quantum yield of up to 18%, representing a significant advancement over previously reported luminescent diradicals. Unlike traditional Kekulé or Schlenk-Brauns type diradicals, our symmetric donor-bridged diradicals show unique charge-transfer features in the excited state, tunable through molecular design.

I will discuss the relationship between donor–radical orientation, excited-state properties, and spin–spin coupling, as well as implications for quantum sensing. Our findings demonstrate that organic diradicals can achieve the long-sought combination of spin multiplicity, photostability, and strong emission, offering a chemically versatile platform for single-molecule quantum technologies.

Relation between Electron-Electron Repulsion and Emission Spectrum

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The wavelengths of photon emission generally become red-shifted with extended conjugation for a molecule. However, carbazole-dendronized tris(2,4,6-trichlorophenyl)methyl (TTM) radicals exhibit a blue shift of the fluorescence spectrum when increasing the generation number of dendrons [1]. Carbazole oligomer substituted TTM radicals also show similar behaviors, although the degree of blue-shift is weakened compared to the dendron-substituted ones [2]. These unusual observations cannot be explained by the one-electron picture, i.e., the HOMO-LUMO gap.

In this study, to clarify the relation between the emission wavelength and the Coulomb repulsion, we constructed a Hubbard model represented by the electron configurations consisting of the fragment orbitals for the dendron/oligomer and TTM radicals [1,2]. Then, we showed that the emission wavelength is blue-shifted when the Coulomb interaction of the dendron fragment orbital decreases while that of the TTM fragment orbital remains constant. This model, applicable to a general donor-acceptor charge-transfer (CT) system, provides a design principle for spectral blue shift with the extended conjugation.

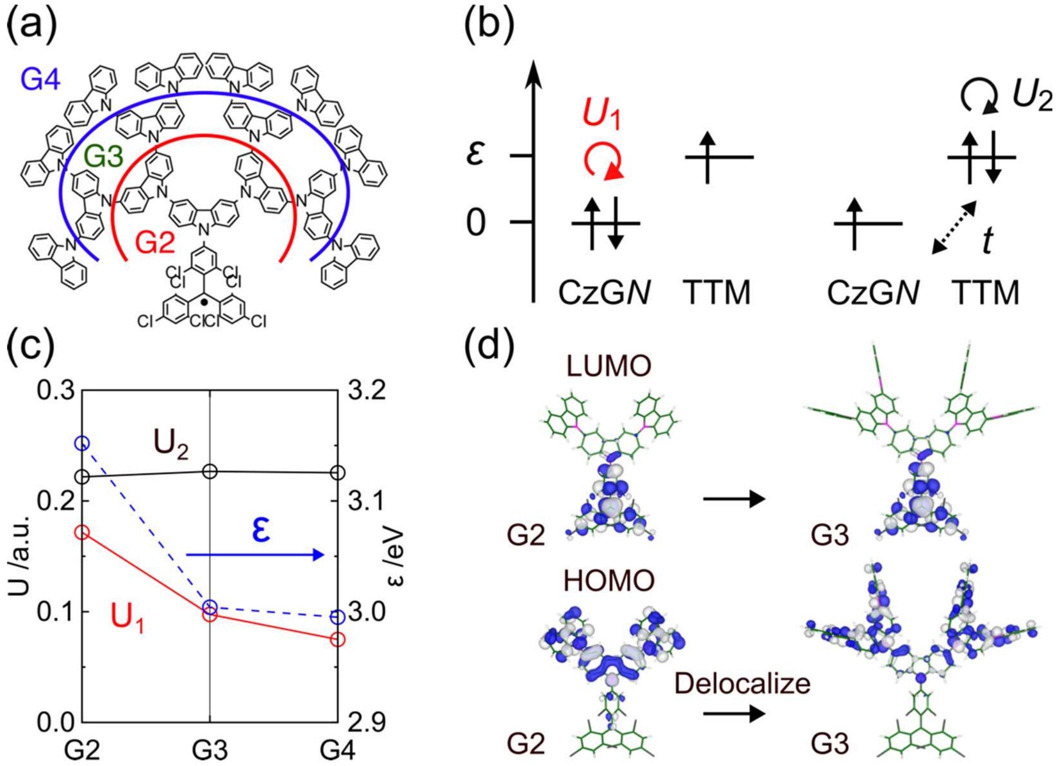

Fig. 1 (a) Structure of carbazole-dendronized TTM radicals. (b) Hubbard model. (c) Hubbard parameters. (d) Frontier orbitals.

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Quantification of Cellular Functions using Quantum Sensors

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Recent advancements in nanoscale quantum sensors—capable of optical detection under ambient conditions—are driving major progress in quantum technologies for biochemical detection in biological systems. Notably, enzyme-linked immunosorbent assays (ELISA) enhanced by quantum techniques have achieved detection limits as low as 82×10^{-21} M in a biotin-avidin model system. In parallel, quantum-based intracellular measurements of biochemical parameters such as temperature and radicals are expanding the frontiers of quantum life science. The core advantage of quantum measurement in these contexts lies in its high-precision quantification capabilities, exemplified by temperature detection with sub-0.1 °C accuracy and nanoscale nuclear magnetic resonance (NMR) measurements with spatial resolution below 1 nm [1,2,3].

In this presentation, I will introduce two emerging approaches for quantifying cellular functions: (1) nanoscale two-dimensional quantum imaging for analyzing radical generation on cell membranes, and (2) Molecular Quantum Nanosensors (MQNs). By embedding molecular qubits within host materials, MQNs provide enhanced spectral uniformity and improved sensitivity—surpassing that of nanodiamond-based quantum sensors. Utilizing biocompatible MQNs, we demonstrate organelle-specific intracellular quantum thermometry, enabling the detection of heat shock responses within the nucleus of cancer cells. Our results reveal a temperature response that spatially correlates with DNA concentration, underscoring the practical utility of MQNs for monitoring cellular activity with molecularly enhanced precision at subcellular resolution [4].

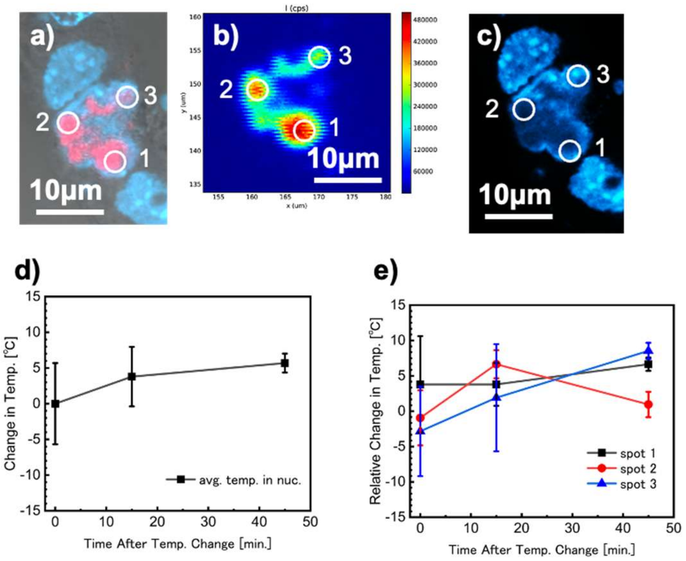

Figure 1. a), b) Measurement of MQNs inside nucleus. c) DNA concentration measured within nucleus. d) Average temperature change inside nucleus of cancer cells. e) Change of temperature at spot1,2 and 3 inside nucleus of cancer cells.

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Persistent trityl radicals for molecular (opto)electronic applications

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Perchlorotriphenyl methyl (PTM) radical is a persistent organic free radical with a multifunctional character, displaying paramagnetic, redox, fluorescent and chiral activity. [1,2] Towards applications, PTM radicals have been grafted on different surfaces, including silicon, gold, ITO and HOPG, via alkene, thiol, silane and diazonium groups, respectively. [3,4] This presentation will provide an overview of the different strategies used to immobilize PTM radicals on surface and how these approaches have opened new avenues for diverse (opto)electronic applications. On the one hand, we have demonstrated that PTM radicals bearing terminal alkynes exhibit extraordinarily long coherence times,[5] a crucial feature for quantum technologies. However, long coherence times alone are not sufficient and integrating molecular qubits into functional electronic devices architectures remains a major challenge. In this context, the functionalization of Au via terminal alkyne emerges as a particularly very promising approach. On the other hand, a significant part of the presentation will focus on the modification of single-walled carbon nanotubes (SWCNTs) via diazonium chemistry, being this, the first example of SWCNTs covalently modified with PTM radicals. It is well known that diazonium salts react with SWCNTs generating luminescent sp^3 defects (also called quantum defects or organic color centers). [6] In our study, the performed photoluminescence (PL) studies reveal that the presence of the radical leads to partial quenching of the sp^3 defects PL. The mechanism to explain this phenomenon is a combination of a photoinduced electron transfer process and population transfer to triplet states enabled by radical-enhanced intersystem crossing. [7] To gain deeper insight into this mechanism, these materials are currently being investigated by Optically Detected Magnetic Resonance (ODMR) which is a technique that combines the spin-sensitive magnetic resonance technique with optical spectroscopy to very sensitively detect triplet excitons in SWCNTs. The results using this technique will be also discussed.

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Spin communication in TTM-based triplet–radical dyads

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Photogenerated organic triplet–doublet systems hold great promise for a range of technological applications in the emerging field of molecular spintronics, including quantum sensing and optoelectronic devices.[1] Typically, they consist of an organic chromophore covalently attached to a stable radical. Upon photoexcitation, the chromophore triplet state is rapidly generated by a process referred to as radical-enhanced intersystem crossing. If the exchange coupling between the chromophore triplet state and the radical spin centres is strong, compared to other electronic or magnetic interactions active in the system, quartet states may be formed by spin mixing.[2-4]

In particular if an optical read-out of the spin state can be achieved,[5] these spin-optical interfaces may be regarded as molecular analogues to the frequently used NV^- color centers in diamond. Compared to solid-state defect centers, molecular spin qubit systems have the advantage that they may be scalable by formation of well-defined multi-qubit arrays and their optical and spin properties may be adapted to specific needs by rational synthetic design.

Here, we present our recent results on a series of chromophore–radical dyads based on the luminescent radical tris(trichlorophenyl)methyl (TTM). Combining insights from transient UV-vis and EPR spectroscopy, we illustrate the influence of the chromophore energetics on the quartet state formation yields and spin-optical properties.

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Luminescent radical materials and devices

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Due to the single unpair electron in mono-radical materials, the spin configurations of their excited states and ground state are both doublets. So, the emission process is spin-allowed. We exploited a luminescent radical, TTM-1Cz, as the emitter to fabricate the first OLED with doublet emission.[1] The problem caused by the spin-forbidden transition of triplet exciton in traditional fluorescent OLEDs is circumvented. After continually optimizing materials and device, a D-A type luminescent radical emitter, TTM-3NCz, was used as the emitter of an OLED with a maximum external quantum efficiency of 27 %, and the first-excited state is thought to be a charge-transfer doublet state.[2] Through exploiting a TADF host, the energy transfer from singlet and triplet excitons to doublet excitons was confirmed and the efficiency roll-off was improved,[3] and a maximum EQE of 9.6 % of an near infrared OLED with 800 nm EL emission was achieved.[4]

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Substituent Effects in Luminescent Organic Radicals and Diradicaloids

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Luminescence of stable organic radicals has gained substantial recent attention for both its practical applications, e.g. in organic light-emitting diodes evading the non-emissive triplets as well as fundamental interest in the photophysical phenomena it involves, including the violation of Aufbau principle and the formation of exotic quartet states.

This presentation will summarize the recent work at McGill exploring the luminescent properties of trityl radicals and related Thiele's diradicaloids, in solution and solid state.[1-3] The focus will be on understanding the effects of very simple structural modifications, and the role of substituents defining the chemical and photo-stability, energy levels and the excited states dynamics of such materials will be discussed.

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Spin-correlated luminescence from assembled molecular spins

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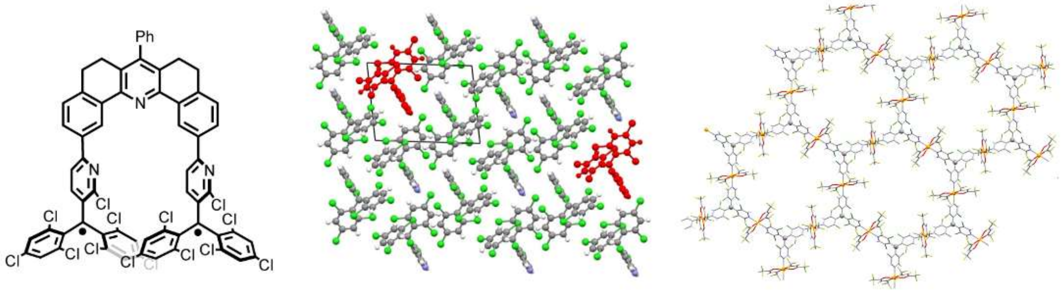
Radicals can exhibit photofunctions unique to their open-shell electronic states, such as efficient electroluminescence, spin-allowed doublet-singlet and doublet-triplet energy transfer, and the absence of heavy atom effect [1]. These characteristics distinguish radicals from conventional closed-shell molecules, making them a new class of molecular emitters [2-7].

We have shown that spin-correlated photofunctions emerge when radicals are assembled to interact with each other. PyBTM, a luminescent stable radical molecule, doped into host molecular crystals displayed radical-pair and excimer-like emission bands in the emission spectrum upon photoexcitation, and the intensity ratio of these two bands changed drastically by applying a magnetic field of up to 18 T at 4.2 K [2,3]. This is the first demonstration of magnetoluminescence in radicals. Magnetoluminescence was also observed in radical-based coordination polymers [4]. Diradical molecules, dispersed and isolated in PMMA matrices, demonstrated magnetoluminescence as a single molecular property [5,6]. Elucidating the mechanisms underlying these magnetoluminescence characteristics revealed that the spin degree of freedom in the ground state of assembled radicals plays a key role in realizing spin-correlated photofunctions.



Diradicals

Radical-doped molecular crystals

Radical-based coordination polymers

Fig. 1. Radical-assembled molecular systems demonstrating magnetoluminescence.

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