

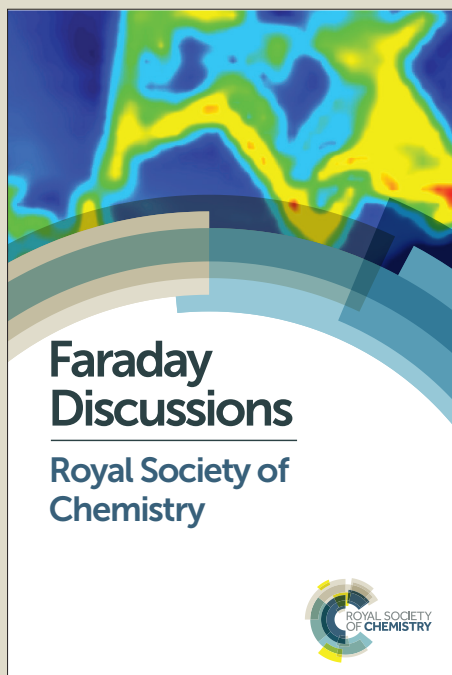
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Proceedings of the Royal Society of Chemistry

ARTICLE

Towards witnessing quantum effects in complex molecules

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Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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Whether many-body objects like organic molecules can exhibit full quantum behaviour, including entanglement, is an open fundamental question. We present a generic theoretical protocol for entangling two organic molecules, such as dibenzoterrylene in anthracene. The availability of organic dye molecules with two-level energy structures characterised by sharp and intense emission lines are characteristics that position them favourably as candidates for quantum information processing technologies involving single-photons. Quantum entanglement can in principle be generated between several organic molecules by carefully interfering their photoluminescence spectra. Major milestones have been achieved in the last 10 years showcasing entanglement in diverse systems including ions, cold atoms, superconductors, photons, quantum dots and NV-centres in diamond, but not yet in molecules.

1 Introduction

Quantum mechanics has only one mystery, and all of it is contained in the double-slit experiment, said Richard Feynman¹. The image of a single particle going through two slits simultaneously and interfering with itself jars with our perception of reality, yet countless experiments have shown the effect to be as real as anything our eyes see.

Although interference has long been known classically, it is also a key signature of quantum phenomena, because it requires the quantum phase of superposed states to stay in step over the timescale of the experiment. In quantum mechanics, we are of course, talking about interference at the level of a single particle like a photon or an atom, or even a molecule undergoing a double-slit diffraction. Two closely related quantum phenomena are superposition and entanglement. The paradigm bench-top

demonstration of quantum superposition is again the diffraction of photons or electrons that pass one-at-a-time through a double-slit and gradually build-up interference fringes. The superposition here refers to the spatial superposition of different paths that the system can take when going through the slits to reach a particular spot at the detection screen.

One of the questions this throws up is the relationship between the notions of superposition and entanglement. To be able to talk about entanglement we need first to be able to identify two subsystems. In that experiment we can think of the paths that the electron takes as interfering, resulting from the superposition of the two paths. This can also be viewed as entanglement in the picture where the paths are seen as the entangled sub-systems (this is also known as mode-entangled). In this picture, a path containing zero electrons is still counted as a state, $|0\rangle$, and the path with 1 electron is counted as state $|1\rangle$. Hence the entangled state arises where the electron is present equally in both paths is $|01\rangle + |10\rangle$. But

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this is not sufficient for entanglement. We also need to be able to measure two different complementary properties of each subsystem. In this case, this implies not only being able to measure the presence or absence of the electron in each of the paths, but also being able to measure in the complementary basis containing superpositions of zero and one electrons. This in itself is the main challenge. Looking ahead, it would be fascinating to conduct experiments that study and compare the fundamental relationship between spatial and temporal coherence, superposition, entanglement, and non-locality².

Whether complex organic objects can maintain full quantum behaviour, including entanglement, is an open fundamental question. Until recently, the detection and characterisation of quantum mechanical effects has been confined to the scale of simple objects like atoms or particles (mostly on over microscopic distances). That was before a series of experiments³ in the last few years showed that quantum effects could also be observed in relatively large objects, such as proteins⁴.

The strongest manifestation of quantum coherence is usually considered to be quantum entanglement. There is a particularly strong interest in entanglement within many-body physical systems, rather than at the level of single-atoms or particles. This shift, from the small to the large, is remarkable considering that in less than one hundred years, we have gone from disbelieving entanglement, or “spooky action at a distance” as Einstein poked fun at it, to regarding it as being ubiquitous in the macroscopic world^{5,6,7}. The overarching question, then, is in which kind of molecular structures are we most likely to find quantum coherence, and which can show interference and entanglement? And how will we

know it when we see it? In other words, what are the practical ways in which we can witness entanglement? Here we suggest one.

2 Methods

2.1 Witnessing quantum properties

Quantum coherence, discord, and entanglement are quantum effects with an increasing degree of complexity. Quantum coherence, technically defined as the existence of off-diagonal elements in some pre-assigned measurement basis, is necessary in order to have entanglement.

Quantifying first-order derivatives of free energy (such as magnetization) as well as second and higher order quantities⁸ (such as magnetic susceptibility and heat capacity) allow bounds to be obtained for different quantum and classically correlated states. The general logic is that we use correlation functions of the type

$$\langle \sigma_1 \otimes \sigma_2 \rangle$$

whose averages are sensitive to the nature of correlations and return different values depending on whether the state is fully separable (i.e. without any quantum entanglement)

$$\rho = \sum_i p_i \rho_1^i \otimes \rho_2^i$$

or if it contains quantum correlations. Note that the above state, which is considered a general disentangled states, can still contain quantum coherence within each subsystem 1 and 2. If none of the subsystems have any coherence (as defined with respect to their particular basis) then the state is merely classically correlated.

After this very brief tour of quantum entanglement we will look at one possible protocol with single

organic molecules (used as qubits) to explore the kind of quantum effects that can be generated and observed.

2.2 Entangling molecules

Researchers still argue about whether quantum physics fully applies to more complex systems and where the classical-to-quantum transition occurs. Entangling two organic molecules would offer a direct proof of (non-trivial) quantumness⁶.

An added motivation for testing the ability of single molecules to maintain entanglement comes from quantum information technologies, such as cluster state quantum computation⁹ and quantum key distribution, where entanglement can be used to establish a communication channel.

Many of these technologies encode information into single-photons and rely on traditional solid-state photon sources. Often, these have limitations in terms of reproducibility, photon-emission efficiency, indistinguishability, and high cost. All these reasons make it urgent to fully assess the technological potential, such as in entanglement of readily-available single organic molecules.

Fig.1 illustrates a generic protocol for entangling two molecules, where they are projected into the state $|01\rangle + |10\rangle$ (designating entanglement between the internal energy levels of the two molecules) by impinging a single-photon on a beam-splitter such that it coherently interacts with both molecules.

The scheme uses path degrees of freedom (or modes) to construct a two-particle measurement where certain measurement outcomes reveal information about the combined state, but not about the individual particles.

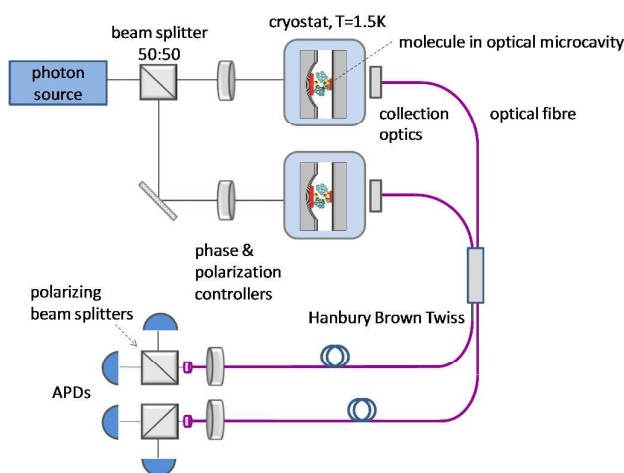


Figure 1: generic scheme¹⁰ for entangling two molecules via interaction with single-photons. Entanglement has been realised with various systems, including large objects¹¹, but not with organic molecules.

The experiment must be constructed in such a way that no decoherence or information loss occurs that could provide information on the state of the individual molecules. The photons emitted from the two physical qubits must also be *indistinguishable*.

The ability to control emission into optical cavity modes is highly desirable as it offers a means of achieving indistinguishability without the application of molecular control fields (e.g. electric fields, strain)¹².

The aim of this experiment is primarily to demonstrate that entanglement between complex molecules separate by macroscopic distances (meters) is indeed possible.

The protocol comprises three steps:

The first entails generating a mode-entangled state $|01\rangle + |10\rangle$ consisting of a single-photon and a vacuum state by impinging a single-photon on a 50-50 beam splitter¹³.

The second step requires the coupling of the optical mode of the microcavity to the mode-entangled state, or driving field. Treating the optical cavity as an imperfect mirror, we can model the interaction between its optical mode and the field using beam-splitter formalism where we trace over the cavity mode and the external field together, resulting in the cavity field¹⁴

$$\hat{\rho}_c = \text{Tr}_f[\hat{B}(\theta)\hat{\rho}_f|0\rangle_c\langle 0|\hat{B}^\dagger(\theta)|]$$

where f is the field mode injected into the cavity, \hat{B} is the beam splitter operator and θ is a control parameter of the mirror, i.e. transmissivity.

The protocol is completed by a third step whereby the cavity field and molecule are coupled. The rate of coupling is given by the Jaynes-Cummings model¹⁵ where only linear interaction coupling is considered. This is given by the Hamiltonian

$$\hat{H} = \hbar\delta\frac{\hat{\sigma}_z}{2} + \frac{\hbar\Omega}{2}(\hat{a}\hat{\sigma}_+ + \hat{a}^\dagger\hat{\sigma}_-)$$

where δ is the detuning frequency between the driving field and the two-level molecule, \hat{a} and \hat{a}^\dagger are the cavity field mode ladder operators, and $\hat{\sigma}_\pm$ are the spin raising and lowering operators.

Confirmation of entanglement is possible by measuring the fluorescence fields from the two cavities. Absence of coincidence counts in the two arms of the detection apparatus after the decay of the excited state following a characteristic lifetime (approximately 8ns in the case of DBT in anthracene) finally confirms entanglement between two molecules.

2.3 Single-molecule spectroscopy

How does this translate into the laboratory? Coupling single photons to a molecular transition is hard and places experimental constraints¹⁶ on

the photon energy and polarisation, environmental noise and the brightness of the output signal. However, there is cause for optimism thanks to the development of novel tuneable Fabry–Pérot micro-cavities¹⁷ (Fig.2 below) into which single molecules can be embedded, promising to make the task of interrogating single molecules with single-photons easier by increasing the interaction strength and light-collection efficiency.

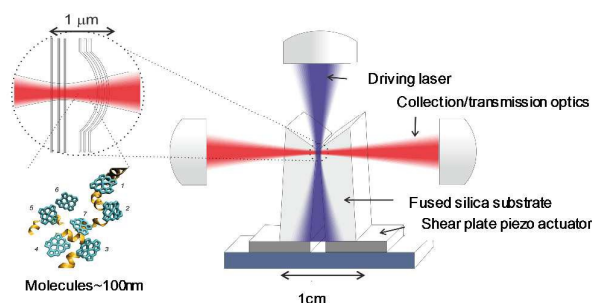


Figure 2: Schematic of our half-symmetric optical micro-cavity assembly allowing laser excitation of single molecules either through a mirror into a cavity mode or in the transverse direction. A blow-up of the semi-convex geometry of the cavity is shown (top right). The optical mode is fully tuneable in-situ with respect to its wavelength and position, as shown in experiments designed by J.M. Smith and R.A. Taylor¹⁷. The cavities have femto-litre mode volumes and offer high-finesse, quality factors around $>10^4$, and coupling efficiencies into detectors $\sim 30\%$ ¹⁸.

3 Discussion

Erwin Schrödinger founded quantum mechanics believing that in practise we could never achieve a sufficient degree of experimental precision that would let us experiment on single molecules¹⁹. It is normal that experiments can only test some aspects of theoretical predictions, while others remain beyond technical reach, for a while. The

development and startling success of single-molecule spectroscopy^{20,21,22,23} in the last 20 years (recognised in last year's Nobel Prize for chemistry) today enables us to select the fluorescence of individual molecules from ensembles, realizing experiments that Schrödinger once thought unlikely.

Single-molecule spectroscopy offers unprecedented access to information on properties masked by the averaging of ensemble populations, and today is the cutting-edge in the study of structure, chemical kinetics, and tracking in-vivo biological processes in single cells²⁴. A series of landmark experiment^{25,26} in the last few years demonstrated that single organic molecules compare favourably to quantum dots and nanocrystals as emitters of indistinguishable single-photons. Beside this immediate technological benefit, organic molecules also represent one of the frontiers in the study of complex quantum states, and so are ideally married to theoretical objectives in realising entanglement in many-body systems such as two (and possible more) molecules. '

A typical example of an organic molecule that acts as a highly efficient single-photon emitter is dibenzoterrylene (DBT). Our preliminary spectroscopic characterisation of DBT in anthracene crystal is shown Fig.3. Optical transitions in most organic dye molecules, including DBT_{AC}, reduces to an effective two-level systems with a dark triplet state with negligible intersystem crossing yield ($< 10^{-7}$). At cryogenic temperatures, the spectral properties of DBT_{AC} in bulk exhibit a bimodal distribution of inhomogenously broadened spectral peaks centred on 785nm and 794nm, corresponding to the two lattice insertion/substitution sites of DBT in anthracene.

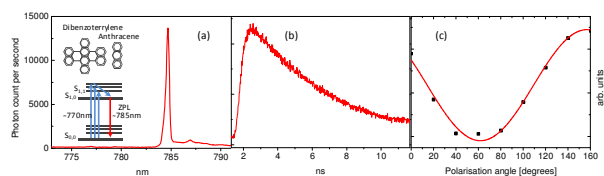


Figure 3: (a) bright and sharp photoluminescent peak from organic molecules (dibenzoterrylene - DBT) in an anthracene crystal at 4K, and (b) its corresponding time-resolved PL trace with characteristic exciton decay lifetime of 5ns. The molecule is a highly promising source of single IR photons relevant for telecommunications. (c) Polarisation control of photon emission from dibenzoterrylene. Inset in (a) shows the structure of DBT and anthracene comprising benzene rings in 2D corrugated sheets. Samples²⁶ of DBT were kindly provided by Prof. M. Orrit and his group at Leiden University, Holland.

The narrow linewidth of the Zero Phonon Line (ZPL) in single DBT molecules (20-40 MHz)²⁶ and fixed polarisation makes them highly attractive as sources of indistinguishable photons. Below $T \sim 2K$, phonon modes are suppressed and transitions can be excited resonantly or quasi-resonantly by pumping either the purely electronic state $S_{1,0}$, or the $S_{1,1}$ and higher-order vibrational states. These are non-radiative short-lived states (5-10 picoseconds) that relax into the $S_{1,0}$ level before decaying fluorescently to $S_{0,0}$. This produces an intense and narrow ZPL with wavelength $\sim 785nm$ or $\sim 794nm$ and a bright source of photons, which makes DBT a near-ideal test-system for experiments on entanglement.

4 Conclusions

There are two motivations driving the search for entanglement. The first is fundamental. We would like to know if complex organic objects can support entanglement and, if so, under what conditions. Conventional wisdom would have it

that a system consisting of a large number of subsystems (say 10^{24} , bathing in a hot environment) ought to behave fully classically. Large and hot bodies should not, then, be entangled. Yet mounting experimental evidence suggests otherwise. Studying entanglement in "messy" systems such as organic molecules (even in relatively small ones consisting of tens of atoms) is a step towards probing the quantum-to-classical transition, should any such thing exist at all. The implication is that life itself may rely on non-trivial quantum effects to survive.

The second motivation is technological since entangled molecules could act as efficient encoders of quantum bits, crucial for future applications in quantum information processing. If the power of entanglement is to benefit future quantum computers, we need to be able to handle larger and larger entangled systems²⁷ in terms of complexity as well as the number of quantum bits.

While atoms, superconductors, quantum dots and nano-diamonds have all been shown to exhibit entanglement, a similar milestone remains to be achieved for single organic molecules. The protocol for entangling two molecules presented here, if realised, would showcase the ability of many-body organic systems to compete with their solid state counterparts as viable candidates for applications in quantum information processing.

Acknowledgements

The authors thank Professor Michel Orrit and his group at Leiden University for kindly providing samples of dibenzoterrylene and for helpful discussions. Financial support from the Oxford Martin Programme on Bio-Inspired Quantum Technologies, the Singapore Ministry of Education and National Research Foundation is gratefully acknowledged. V.V. is

Fellow of Wolfson College, Oxford, and T.F. is James Martin Fellow of the Oxford Martin School.

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