

PL, magneto-PL and PLE of the trimetallic nitride template fullerene $\text{Er}_3\text{N}@C_{80}$

Mark A. G. Jones^{*,1}, John J. L. Morton¹, Robert A. Taylor², Arzhang Ardavan², and G. Andrew D. Briggs¹

¹ QPIRC, Department of Materials, University of Oxford, Parks Road, Oxford, OX1 3PH, UK

² Clarendon Laboratory, Department of Physics, University of Oxford, Parks Road, Oxford, OX1 3PU, UK

Received 20 April 2006, revised 15 May 2006, accept 1 August 2006

Published online 19 September 2006

PACS 75.25.+z, 78.30.Na, 78.66.Tr

$\text{Er}_3\text{N}@C_{80}$ exhibits sharp optical emission lines in the near-infrared attributed to fluorescence from the Er^{3+} ion. Here we demonstrate that high magnetic fields cause this spectrum to split, corresponding to transitions from the lowest field-split Kramers doublet of the $^4I_{13/2}$ manifold to the four lowest field-split levels of the $^4I_{15/2}$ manifold. The internal structure of these fullerenes can be spatially aligned with a preferred orientation under high magnetic field; the effect of alignment is to reduce the broadening associated with the isotropic spatial averaging characteristic of powder or frozen-solution spectra. Using a tunable 1.5 μm laser, we directly observe non-cage-mediated optical interactions with the Er^{3+} ion. This spectroscopic method provides the opportunity to map the energy level structure of the incarcerated ion and to coherently control its quantum state. These qualities suggest that rare-earth endohedral fullerenes have characteristics that could be employed as a readout pathway for fullerene-based quantum information processing.

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1 Introduction

Proposals for quantum information processing (QIP) [1–3] employ the spin state of an ‘endohedral’ species trapped inside a fullerene cage [4] to encode quantum information. Despite recent progress [5] in developing this architecture, readout from such a qubit has only been demonstrated within the ensemble paradigm, as single-spin detection is technically challenging. Optical techniques have been successfully used to read out a single spin-qubit in a diamond N–V defect [6, 7]. To apply this method to readout in fullerene systems requires qubits that respond to both optical and magnetic manipulation [3].

Rare-earth endohedral fullerenes have been extensively studied with a variety of techniques; in particular electron paramagnetic resonance (EPR) has been widely employed in metallofullerene characterisation [8]. Optical techniques are less used due to the opacity of the fullerene cage at infrared and shorter wavelengths [9]. Crystal-field effects have been observed using these techniques and these act as a diagnostic on the local ionic environment [10]. Charge transfer from the incarcerated ion to the fullerene cage modifies the cage electronic structure and can permit optical interaction with the ions. Several of the erbium fullerenes have 1.5 μm luminescent emission [11–13], while EPR has been observed in others [14, 15]. This provokes speculation as to the possibility for using this class of species as a method of introducing optical control and measurement techniques into the field of fullerene-based QIP.

* Corresponding author: e-mail: mark.jones@materials.ox.ac.uk, Phone: +44 1865 273719, Fax: +44 1865 273730

This work examines $\text{Er}_3\text{N}@C_{80}$, a *trimetallic nitride template* (TNT) fullerene [16]. The structural and chemical properties of this class of materials are well characterised [17–19], indicating a structure whereby the TNT group is planar and aligned with one cage threefold axis [20].

Photoluminescence has already been demonstrated in this system at 77 K and 1.6 K [13]. Under illumination of a frozen solution of $\text{Er}_3\text{N}@C_{80}$ above the cage bandgap, photoluminescence is observed. At liquid helium temperatures, the near-infrared emission consists of eight lines between 1510 nm and 1610 nm.

This luminescence is interpreted as emission from the Er^{3+} ion, resulting from transitions from the $^4I_{13/2}$ manifold to the $^4I_{15/2}$ manifold (Fig. 2). For a free ion, this transition is observed at 1543 nm, but the electrostatic crystal field of the neighbouring ions and cage lifts the m_j degeneracies and Stark-splits these levels into a maximum of 7 and 8 sublevels respectively. The low-temperature luminescence is interpreted as emission from the lowest level of the $^4I_{13/2}$ manifold to all levels of the $^4I_{15/2}$ manifold. Emission is not observed from other levels due to the dominance of cage-mediated nonradiative processes.

2 Magneto-photoluminescence

The Er^{3+} ion is a Kramers ion [21], with residual magnetic degeneracy in the Stark-split crystal field levels. In principle, it is possible to lift this degeneracy and isolate transitions between different spin states.

To observe the magnetic field response, a sample of the material, purified by high pressure liquid chromatography (HPLC), was dissolved in carbon disulphide (CS_2) to form a saturated solution and was placed in a delrin cuvette inside the variable-temperature insert of a 21 T superconducting magnet. 532 nm excitation was applied via a fiber bundle inserted into the sample solution, and observed luminescence was collected via separate fibers in the same bundle. Detection was achieved by dispersing the collected luminescence via a grating monochromator coupled to a germanium detector. The sensitivity of the detection was enhanced by chopping the laser light and using lock-in amplification to generate the recorded signal.

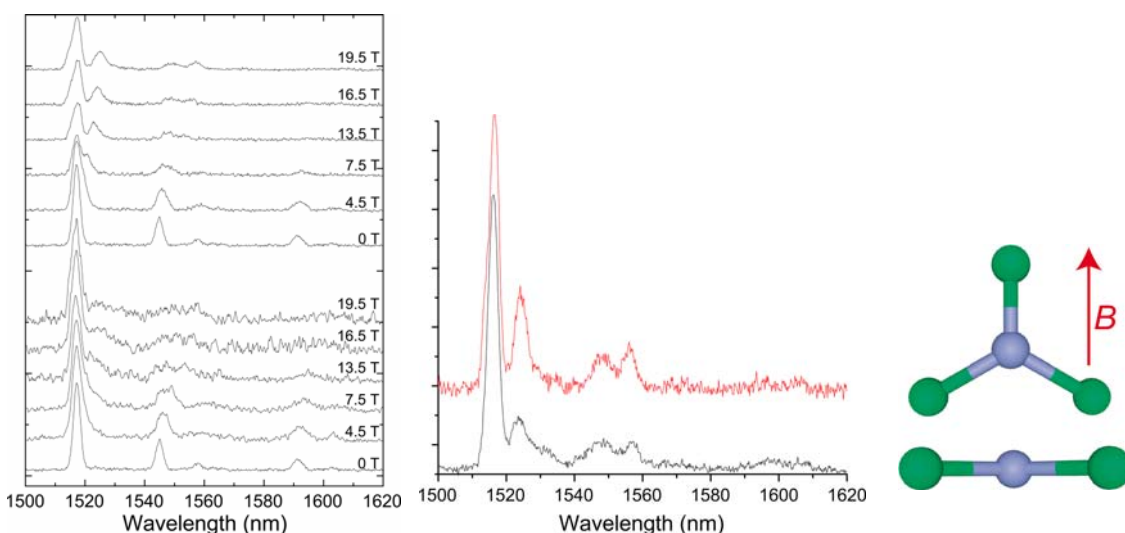


Fig. 1 (online colour at: www.pss-b.com) Left: 1.55 μm photoluminescence observed from $\text{Er}_3\text{N}@C_{80}$ in frozen solution in CS_2 at 4.2 K at a range of magnetic fields from 0 T to 19.5 T. Upper sequence is field-cooled, lower sequence is without field cooling. Centre: Normalised comparison of the spectrum obtained at 19.5 T after the sample was cooled under field (upper) and the spectrum after the sample was cooled without field (lower). Right: Cartoon showing two possible orientations of the Er_3N group with respect to applied magnetic field (B).

The sample was cooled to 4.2 K and then the magnetic field was applied. As the field was increased from zero, a Zeeman-like splitting of the observed spectrum, linear with field, became evident, with the principal peak exhibiting a splitting in transition energy of $1.8 \text{ cm}^{-1}/\text{T}$, as shown in Fig. 1.

The sample was warmed to 181 K (above the solvent melting point) and allowed to melt. The sample was then re-cooled to 4.2 K with the 19.5 T field applied. Observation of the photoluminescence revealed a change in the observed spectrum, with the peaks becoming more well-defined and redistributing intensity between the field-split components (Fig. 1).

Locally, the symmetry of the electrostatic crystal field of the Er^{3+} ion is approximately C_{2v} (Fig. 1). This defines a set of axes. The splitting of the energy levels in field depends on the direction of this field with respect to these axes, equivalent to an anisotropic g -factor in electron paramagnetic resonance. Before field-cooling, the spectrum is an isotropic average of all possible orientations of the field with respect to the local axis of the erbium. Since the degree of splitting depends on the orientation of the cage, some configurations will have a lower ground-state energy than others, and the population of these orientations will be enhanced under field. Freezing the solvent preserves this orientation imbalance, and leads to a modified and sharpened field-split spectrum. However, as there are three erbium ions in a each molecule, fixed in a planar triangular configuration, the lowest energy orientation for one ion may not be the lowest for the others, and this leads to imperfect alignment and a less well defined effect. This alignment is expected to be more visible in heterogenous TNT species, such as $\text{ErSc}_2\text{N}@C_{80}$, as these contain only one magnetically-active ion per molecule, reducing orientational competition between the ions.

3 Direct excitation

Rather than exciting incoherently via the cage [13], direct excitation of the ionic levels is also possible [22]. If the the excitation wavelength is not too strongly absorbed by the cage, the ion can be excited directly and luminescence will be stimulated without involving the cage as an intermediate pathway. This technique is useful in two ways. Firstly, by tuning the laser across the upper manifold, the absorptive transitions may be mapped. Secondly, by direct interaction with the ion, its quantum states can be manipulated in a controlled manner. This has utility in fullerene qubit manipulation or in fullerene quantum optics.

A sample of the purified material was dissolved in CS_2 to form a saturated solution and was placed in a sealed quartz tube suspended in a continuous flow exchange gas cryostat arranged for fluorescence. The sample was frozen and cooled to 5 K. Excitation was performed with a continuously tunable $1.5 \mu\text{m}$ diode laser. The luminescence, collected perpendicular to the incident beam, was postfiltered with a double subtractive single dispersive monochromator to exclude laser scatter. Detection was performed

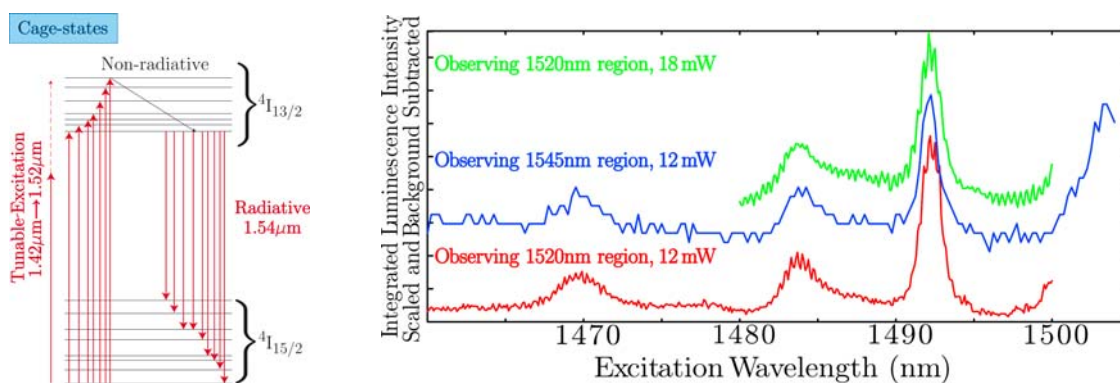


Fig. 2 (online colour at: www.pss-b.com) Left: Level scheme for direct excitation of the $\text{Er}^{3+} \ ^4I_{13/2}(1) \rightarrow \ ^4I_{15/2}(1 \dots 8)$ transitions. Right: Integrated luminescence intensity as function of excitation wavelength. Traces corresponding to different powers and observation regions have been offset for legibility.

with a 1024-pixel InGaAs array detector. The intensities of each of the two strongest emissive transitions were monitored as a function of excitation wavelength.

Figure 2 shows the integrated area of different emission peaks as a function of excitation wavelength. Background subtraction was used to remove the effect of remaining stray light. The peaks correspond to Er³⁺ ⁴I_{15/2}(1) → ⁴I_{13/2}(1 . . . 7) transitions. Observing different emission peaks confirms that the ion is being directly excited, and eliminates the possibility of exciting a different emission process. As the transitions are being probed with a laser of sub-MHz width, the linewidths observed are not instrument-limited. The sharpness and moderate splitting of the upper manifold transitions reinforces the picture of a substantially ionic character.

4 Summary

Er₃N@C₈₀ is a magneto-optically active endohedral fullerene; such a species has great potential for endohedral fullerene-based QIP. We have demonstrated that magnetically-split luminescent transitions of the ion are accessible experimentally, and that direct optical excitation of the ion is possible at these wavelengths. Encoding quantum information in, for example, the ground state Kramers doublet, and using direct non-cage-mediated optical interaction with the incarcerated ion, it may be possible to manipulate and measure the qubit optically. This technique may also be extended to any metallofullerene with ionic states that are accessible via cage transparency. The ability to align the magnetic axis of anisotropic endohedral fullerenes has been demonstrated which has applications in the creation of useful fullerene qubit arrays. The techniques described in this work are directly applicable to the range of existing rare-earth-doped fullerenes with suitable cage transparency. Furthermore, they are applicable to other endohedral fullerenes that have been chemically modified to vary the cage bandgap. Application of these techniques may identify suitable candidates for the optical readout of quantum information from a fullerene-based quantum computer.

Acknowledgement This research is part of the QIP IRC www.qipirc.org (GR/S82176/01). The work also forms part of the DARPA Slow Light programme through support from Hewlett-Packard Co. (contract FA9550-05-C-0017). GADB thanks EPSRC for a Professorial Research Fellowship (GR/S15808/01). AA is supported by the Royal Society. MAGJ is supported by an EPSRC DTA Scholarship. JJLM is supported by St. John's College, Oxford. Fullerene samples were obtained from Luna Nanomaterials Inc. The authors acknowledge R. Nicholas and L. Li. for use of and assistance with the Clarendon 21 T magnet, and I. Walmsley, M. Reid, K. Porfyrikis, R. Davies and R. Beausoleil for valuable discussions.

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