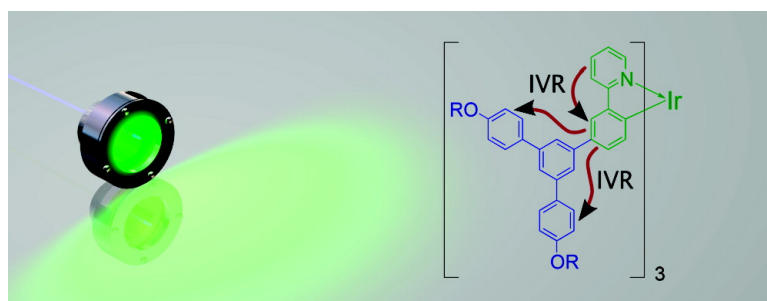Communication

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Iridium Metal Complexes as an Unambiguous Probe of Intramolecular Vibrational Redistribution

Gordon J. Hedley,[†] Arvydas Ruseckas,[†] Zehua Liu,[‡] Shih-Chun Lo,[§] Paul L. Burn,[§] and
Ifor D. W. Samuel*,[†]

*Organic Semiconductor Centre, SUPA, School of Physics and Astronomy, University of St Andrews, North Haugh,
St Andrews, Fife, KY16 9SS, United Kingdom, Department of Chemistry, University of Oxford, Chemistry Research
Laboratory, Mansfield Road, Oxford, OX1 3TA, United Kingdom, and Centre for Organic Photonics and
Electronics, School of Molecular and Microbial Sciences, University of Queensland, Chemistry Building,
Queensland 4072, Australia*

Received May 15, 2008; E-mail: idws@st-andrews.ac.uk

Intramolecular vibrational redistribution (IVR) determines energy flow between vibrational modes within a molecule and is important in isomerization reactions, including the primary steps in vision,[1] the formation and breaking of chemical bonds,[2] and charge transfer reactions.[3] As a predominantly ultrafast process, observation and understanding of IVR has presented substantial difficulties, requiring both complex experimental setups and subtle analysis of data for systems in the ground or excited state. In this paper we utilize the specific luminescence properties of phosphorescent transition metal complexes associated with mixing of the singlet and triplet states to monitor IVR and cooling in a straightforward manner. In these compounds IVR manifests itself as a photoluminescence (PL) decay, thus enabling unambiguous observation of the process. In contrast, IVR studies on fluorescent materials rely on spectral shifts which can be affected by solvation. We show that addition of dendrons to the phosphorescent core opens up new channels for the dissipation of vibrational energy, enabling ultrafast luminescence experiments on these materials to be utilized as a method for unequivocally investigating IVR.

IVR has traditionally been studied in the time domain, principally in the gas phase, using a number of techniques, including time-resolved fluorescence,[4] pump–probe spectroscopy,[5] time-resolved stimulated emission pumping,[6–8] and Raman spectroscopy.[9,10] Femtosecond PL studies have utilized the dynamical shift of the PL spectrum,[11] as well as directly detected luminescence,[12] to monitor IVR. In the condensed phase, spectral dynamics are affected by solvation or matrix reorganization and hence can make IVR difficult to separate out, particularly in large molecules because of broad spectral features. Comprehensive reviews of IVR present some historical background and outline the current work in this large field.[13–17]

Dendrimers have been pursued[18,19] as an attractive method for attaining the most efficient solution-processable phosphorescent materials for organic light emitting diodes (OLEDs). Here we have used two $Ir(ppy)_3$ cored dendrimers, G1M and G1P (structures shown in the inset to Figure 1), to monitor vibrational energy flow. The dendrimers were synthesized following reported methods.[20] Solutions were prepared in toluene and tetrahydrofuran with concentrations in the range 1–10 mg/ml. No differences in the ultrafast dynamics were observed for the different solvent concentrations, with femtosecond dynamics being identical across this range. Absorption and PL spectra for $Ir(ppy)_3$ and the two dendrimers are shown in Figure 1; the 10 nm redshift in G1P is

† University of St Andrews.
‡ University of Oxford.
§ University of Queensland.
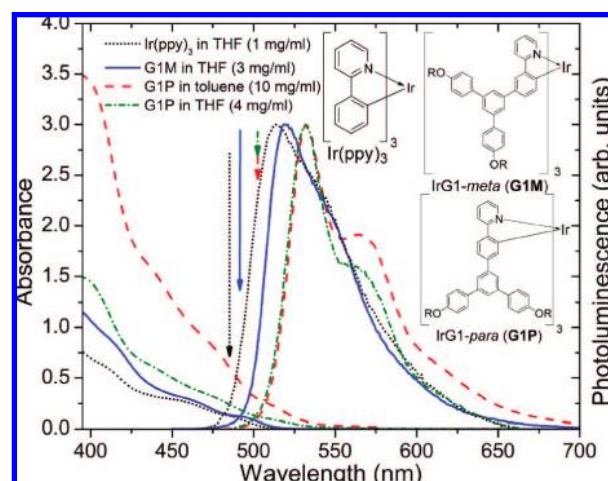
Figure 1. Steady state absorption and photoluminescence spectra (λ_{ex} = 400 nm) of the three compounds under investigation. The chemical structures are shown inset, where OR represents 2-ethylhexyloxy groups. Arrows indicate detection wavelengths at 140 meV above the steady state PL peak for PL kinetics shown in Figure 2.

due to the extension of electron delocalization between the ligand and the first phenyl of the dendron.[21] All ultrafast PL dynamics were recorded using excitation of 400 nm and luminescence upconversion in a BBO crystal.[22] We note that such measurements are demanding for phosphorescent materials because of their low radiative rates.

Energy dissipation by IVR and cooling manifest themselves as ultrafast luminescence decays due to the decrease in the admixture of singlet character of the emitting triplet state. At the peak of the PL and on its red side, the ultrafast dynamics in the dendrimers are similar to $Ir(ppy)_3$,[22] with a partial decay of the PL observed with time constants of 230 fs and 3 ps. As detection moves to shorter wavelengths the decay becomes faster; at 140 meV above the PL peak the recorded dynamics for the dendrimers and the $Ir(ppy)_3$ core are as shown in Figure 2. Biexponential decays using time constants of 150 fs and 3 ps can be fitted to the data, with the amplitude of the femtosecond component higher in the dendrimers. On the basis of previous work[22] we attribute the 150 fs time constant to IVR and the 3 ps component to cooling by energy transfer to the solvent. The different behavior at higher energy confirms that IVR is occurring. Observing luminescence dynamics at even larger values of excess energy in the dendrimers showed a 70 fs decay at 310 meV above the PL peak. Unfortunately this could not be compared with $Ir(ppy)_3$ due to the strong Raman signals from the
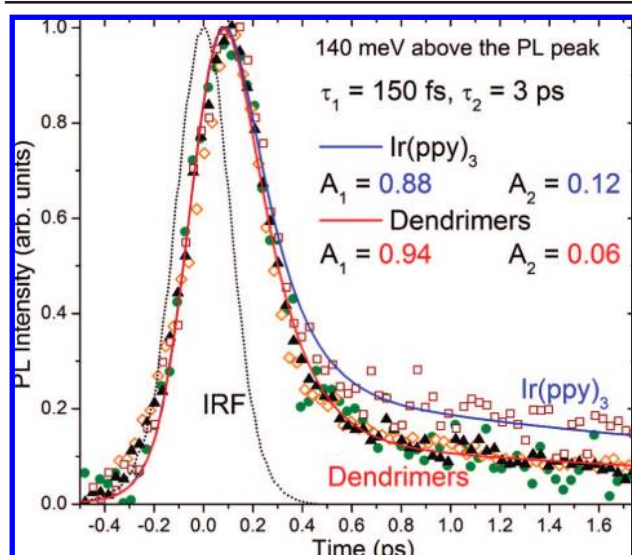
Figure 2. Luminescence dynamics recorded for Ir(ppy)$_3$ (open squares), G1M (closed triangles), G1P in toluene (closed circles), and G1P in THF (open diamonds) at the specific energy of 140 meV above the PL peak. Solid lines indicate biexponential fits with 150 fs and 3 ps time constants, in which the dendrimers have more of the femtosecond component. The dotted line indicates the instrument response function (260 fs, fwhm).

solvent, which in turn is due to the poor solubility of this material compared with the dendrimers.

Both dendrimers show an identical increase in the amount of the decay component associated with IVR at 140 meV of excess energy (Figure 2). No significant change in the rate of IVR is observed at this energy with the addition of the dendrons. This can be explained by the fact that the energy of the stretch of a single C−C bond, which links the biphenyl units of the dendron to the phenylpyridine ligand of the core, is ∼170 meV, which is larger than the vibrational excess energy of 140 meV. Thus only around one-quarter of the dendrimers will have the C−C bond thermally activated and thus would have a faster rate of IVR. Since this occurs on a very short time scale (<150 fs), it is difficult to discriminate any faster decay rate component for the quarter that are activated, however this appears as an increase in the amount of the femtosecond component. More of the excess energy is able to dissipate via IVR when the dendrons are present, with vibrational energy transferring from the core out onto the dendrons, which act as heat sinks for the excess energy. It is important to note that the difference observed is reproducible and has been monitored in several freshly prepared solutions of both dendrimers. As well, the identical nature of the decay of G1M and G1P at the value of 140 meV of excess vibrational energy, despite the 10 nm shift between the actual detection energies, is a clear sign that the dendrons are playing a role in the increasing amount of IVR that takes place. Other processes such as solvation can be ruled out, as studies in toluene and THF, two solvents with differing polarities, both give identical decays at all wavelengths measured.

Looking at the IVR dissipation time constants in the compounds under study can allow a wider picture of the dissipation rate dependence on vibrational energy to be generated. By monitoring the luminescence decays at different values of excess energy above the lowest excited ^{3}MLCT state (representing the PL peak wavelength) the rate dependence can be observed. The results for the dendrimers are shown in Figure 3. An increasing decay rate is found at increasing values of excess energy and can be explained
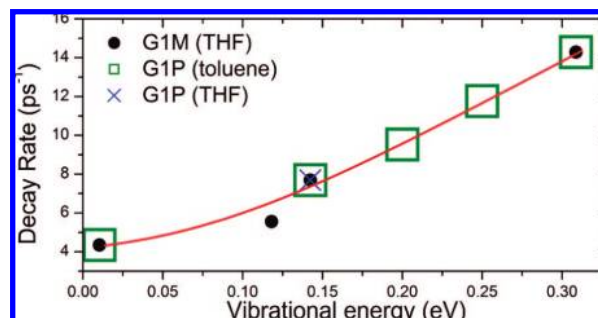
Figure 3. PL decay rate as a function of the energy interval between the detected PL and the steady state PL peak. The red line is a guide for the eye. Higher vibrational energies dissipate faster, consistent with a larger density of vibrational states.

by a growth in the vibrational density of states available for energy dissipation and vibrational coupling at higher energies.[15] This dependence, for values of excess energy of 0.1−0.3 eV, has an approximate gradient of 43 ps^{-1} eV^{-1}.

To summarize, we have used the photophysical properties of iridium cored phosphorescent dendrimers and the parent complex to monitor the flow of vibrational energy inside the molecules on the femtosecond time scale. Using luminescence spectroscopy has allowed us to directly measure IVR, enabling a straightforward unambiguous assignment of the processes involved; contrasting with other methods of measuring IVR. It was found that the addition of dendrons to the Ir(ppy)$_3$ core increases the amount of excess energy that can dissipate by IVR, the extra heat capacity of the dendrons enabling more dissipation. The technique used enables the study of IVR as a function of the excess vibrational energy.

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