Comprehension of how molecular entities behave in their normal operating environment is indispensable information required in many areas of science, including biology, chemistry and medicine. Probing a species and gaining insightful information can be a major challenge, however, particularly in what sometimes can be difficult surroundings. Many of the developed molecular probes rely on the emission of visible light (fluorescence or phosphorescence) as a non-intrusive signalling method. An important advantage of emission spectroscopy relates to the realisation that detection can be carried out by either steady-state or time-resolved modes. A major problem associated with luminescent chemical sensors concerns resolving the ‘real’ signal from background fluorescence and/or scatter. Time-gated techniques have alleviated, at least to some extent, the problem but necessitate the use of stable molecules that emit strongly on relatively slow time scales (i.e., milliseconds). Luminescent lanthanide complexes have been identified as the most promising candidates for such sensors, essentially because they possess inherently long lifetimes and emission profiles that occur in the visible to near-infrared spectral region. However, since molar absorption coefficients associated with lanthanide f-f transitions are weak, sensitization from aromatic moieties attached to the complexes is needed.

In an attempt to improve existing sensor technology based on fluorescent molecules, we have turned our attention to the use of delayed fluorescence (DF). A versatile way to generate DF is via intramolecular triplet-triplet annihilation (TTA). The process of TTA forms a ground-state molecule and a molecule promoted to the first-excited singlet state (Fig. 1). The key feature of TTA is that the fluorescence lifetime matches that of the excited triplet state. Instead of the normal fluorescence lifetime of a few nanoseconds, DF can survive for some tens of microseconds.

We have synthesised and characterised by $^1$H NMR spectroscopy and more importantly mass spectrometry, a series of molecular dyads comprising two pyrene units separated by a spacer (Fig. 1). The carefully positioned bulky groups attached to the pyrene groups hinder to different extents their possible closest approach. Delayed fluorescence is observed for the molecular dyads and represents a potential new way forward in imaging technology.

Reference

Fig. 1. An example of a di-pyrene dyad that displays DF by the mechanism shown.