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The influence of changing from fluorenone to fluorenyl-malonitrile on the excited state dynamic of tetraphenylbenzene-fluorene based donor-acceptor systems

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Abstract

Understanding the photophysical properties of a donor-acceptor system, and how it is linked to and controlled by structural modification is key to the systematic design of new materials to fulfil a particular role. In this study two series of tetraphenylbenzene-fluorene based donor-acceptor systems are compared. Between the series the fluorene unit is changed from fluorenone to fluorenyl-malonitrile. The series with the fluorenone acceptor (series 1) was found to show high environment sensitivity and green emission (530 nm). By adding the more electron withdrawing malonitrile the electronic absorbance and emission was red shifted, with the absorbance moving from the UV region to blue region and emission shifting to 650 nm. However, the near complete quenching of the emission was also observed.

The combination of transient absorbance and emission spectroscopy, resonance Raman spectroscopy, time resolved IR and computational modelling was used to build up a detailed understanding of what was occurring. Overall it was found in the first series the excited state and emissive properties were dominated by fluorenone-like behaviour, with minimal influence from the tetraphenylbenzene unit. In the second series it was found that quenching of the emission could be linked to rotation in the excited state opening up new, non-radiative, decay pathways.

Fig. 1: Key processes giving rise to the variation in emissive properties on going from fluorenone to fluorenyl-malonitrile.

Keywords: transient absorbance, transient emission, DFT, Raman spectroscopy, resonance Raman spectroscopy, time resolved IR