

**Plasmonic surface enhancement of dual fluorescence and
phosphorescence emission from organic semiconductors: effect of
exchange gap and spin-orbit coupling**

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Supporting Information

Sample Preparation

1. Silver nanoparticle film

Silver nanoparticle films were prepared by Tollens silver mirror reaction, as described in Ref. 1. For a reaction time of 45-150 sec, the morphology of the silver films was rough. When restricted to these reaction times, the resultant silver film exhibited similar degree of rate enhancement.

2. Organic fluorophore film

The compounds were co-dissolved with polystyrene (Aldrich, average M. W. 82000) in toluene. The concentration of polystyrene in toluene was kept at 10 g/L. The films were coated on quartz and Tollens substrates (16×8 mm²) using the following spin-coating parameters: volume of solution = 30 μL, speed = 2 krpm and time = 60 s. In the finally dried organic film, the compounds are homogenously dispersed at ~1% wt. ratio in polystyrene.

Fluorescence and Phosphorescence Lifetime

Time-resolved fluorescence measurements were performed using a Hamamatsu streak camera system with up to ~4 ps time resolution. Samples were excited using a 140 fs, 80 MHz repetition rate, frequency doubled Ti:Sapphire laser. During measurements, the samples were placed in dynamic vacuum of ~10⁻⁶ mbar.

Phosphorescence lifetimes were recorded in a cold-finger closed-cycle helium cryostat using a pulsed solid-state laser at 355 nm and an Andor intensified gated CCD camera with a time resolution of ~1 ns.

Absorbance Spectra

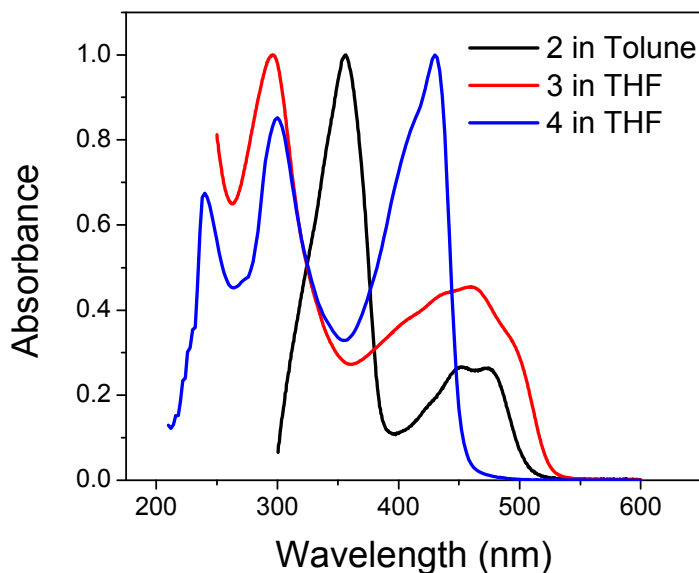


Fig. 1. Solution phase uv-vis absorption spectra of compounds 2, 3 and 4 at room temperature

Singlet-Triplet Energy Difference

The singlet and triplet energy levels are split by the exchange gap. For rigid-rod conjugated polymers, the exchange gap was known to be universally 0.7 ± 0.1 eV.² However, we recently showed that by careful chemical design it is possible to achieve different extents of delocalization of the singlet and triplet excited states, thereby achieving wide tunability in their energy difference.³ Compounds 3 and 4 are such copolymers where the exchange gap could be tuned to much lower values (0.017 and 0.4 eV, respectively). It is, of course, conceivable that triplet emission actually occurs from a higher lying (hot) triplet state and that Kasha's law is violated in the triplet manifold. At present, we do not have a way of proving this. As commented on in Ref. 2, we did not observe any long-lived triplet features at lower energy, but, of course, lower-energy triplet transitions may be dark.

References

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3. D. Chaudhuri, H. Wettach, K. J. vanSchooten, S. Liu, E. Sigmund, S. Höger and J. M. Lupton, *Angew. Chem. Int. Ed.*, 2010, **49**, 7714.