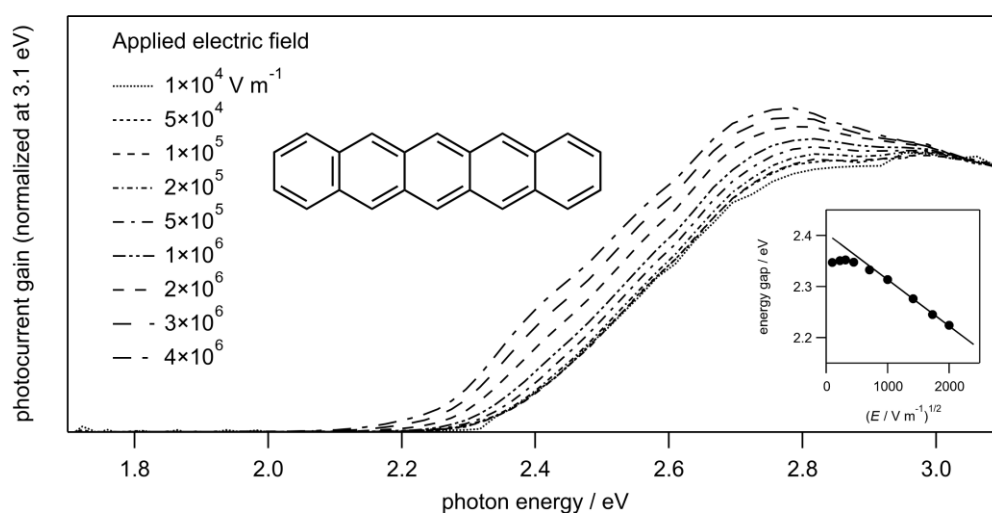


## Electric field induced shifts of the intrinsic charge separation energies in pentacene thin films.

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Crystalline pentacene has two remarkable optical features that affect charge generation processes. First, singlet fission – the spontaneous decay of a singlet exciton into two triplet states – is unusually efficient<sup>1</sup>, and, second, the first singlet transition is strongly coupled to nearby charge transfer (CT) states, leading to a high degree of mixing<sup>2</sup>. The two phenomena are in fact closely related<sup>3</sup> and in combination facilitates intrinsic charge generation in the bulk. Provided the purity of material is kept sufficiently high, CT transitions make up the principle peaks in the photocurrent action spectra of pentacene thin films<sup>4</sup>.



**Fig. 1.** Photocurrent yield spectra of 10 nm pentacene thin film as a function of applied field. *Inset:* The corresponding change in the energy gap with field strength.

In the present work, we examine how the manifold of CT transitions responds to changes in the local electric field. At high applied voltages, we find the relative efficiency of charge pair separation originating from the low energy CT states is enhanced, and that the transport energy decreases following the Poole-Frenkel effect.

<sup>1</sup> M.B. Smith and J. Michl, *Chem. Rev.* **110**, 6891 (2010).

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<sup>4</sup> R. Murdey and N. Sato, in *Adv. Org. Cryst. Chem.* (Springer Japan, Tokyo, 2015), pp. 627–652.