**Supporting Information:** Singular Temperatures Connected to Charge
Transport Mechanism Transitions in Perylene Bisimides from Steady-State
Photocurrent Measurements

José A. Quintana, <sup>a</sup> José M. Villalvilla, <sup>b</sup> Alejandro de la Peña, <sup>c</sup> José L. Segura, <sup>c</sup> and María A. Díaz-García<sup>\*, b</sup>

<sup>a</sup> Departamento de Óptica, Instituto Universitario de Materiales de Alicante y Unidad Asociada UA-CSIC, Universidad de Alicante, 03080 Alicante, Spain.

<sup>b</sup> Departamento de Física Aplicada, Instituto Universitario de Materiales de Alicante y Unidad Asociada UA-CSIC, Universidad de Alicante, 03080 Alicante, Spain.

<sup>c</sup> Departamento de Química Orgánica, Facultad de Química, Universidad Complutense de Madrid, 28040 Madrid, Spain.

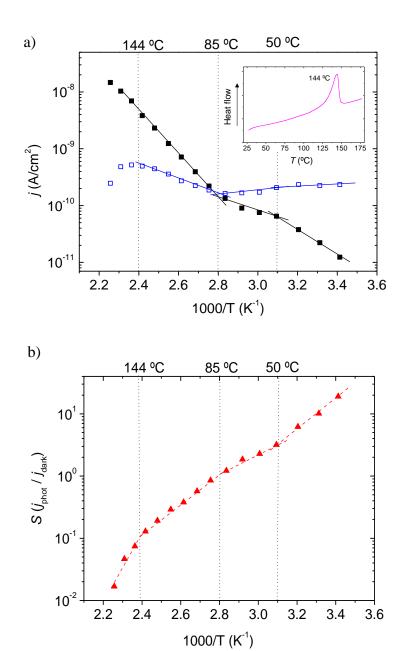
Data for N,N'-Bis(1-hexylheptyl)-perylene-3,4:9,10-bis-(dicarboximide) (PBI-C6)

## 1. Molecular Structure

$$C_6H_{13}$$
 $C_6H_{13}$ 
 $C_6H_{13}$ 
 $C_6H_{13}$ 

Figure S1

## 2. Photocurrent Dependence on Temperature



**Figure S2.**- Arrhenius plots of (a) dark current,  $j_{dark}$  (black full squares) and photocurrent  $j_{phot}$  (blue empty squares) and (b) photosensitivity  $S = j_{phot} / j_{dark}$  at an electric field of 0.4 V/ $\mu$ m, and a light intensity of 10 mW/cm<sup>2</sup> at 633 nm for PBI-C6. Inset in a) shows DSC taken from Ref. 9.

BPI-C6 shows activation energy transition temperatures at 50 and 85 °C (Fig. S2a), at which no structural or phase changes occur (the material is crystalline in the whole temperature range explored). But these transitions are observed in the dark current, in contrast to PBI-W+CL, in which the transition temperatures were observed in the photocurrent, but not in the dark current. The alterations in the dark current observed in PBI-C6 remind the temperature dependence of the conductivity of a typical doped (extrinsic) semiconductor with an exhaustion range of 35 °C. In the presence of light, the photocurrent is weakly dependent on temperature, so the current behavior seems to be determined by dark current and indeed the transition temperatures observed in the photocurrent occur at the same temperatures as for the dark current. Further studies should be done to confirm that the origin of the transition temperature at 85 °C, at which  $S \sim 1$ , is the same than that of PBI-W+CL. At temperatures higher than 85 °C, the photocurrent is lower than the dark current, indicating that the photogenerated carrier concentration is smaller than that of the thermal carriers. A decrease in the photocurrent, after reaching the isotropic phase at 145 °C, is also observed. With regards to S (Fig. S2b), even though the transition temperatures can be distinguished by slope changes (at 50, 85 and 145 °C), the response is dominated by the dark current, and a decrease is observed in the whole range of temperatures.