

# Ultrafast Optical Control of Charge Dynamics in Organic and Hybrid Electronic Nanodevices

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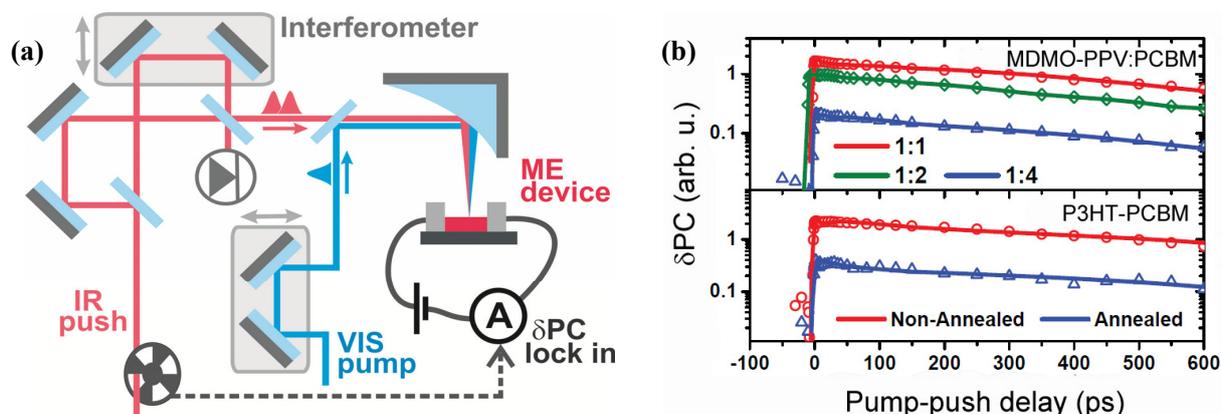
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**Abstract:** Using ultrafast visible/IR pulse-sequence spectroscopy combined with electric current detection, we engage vibronic and charge-delocalization phenomena to control the performance of optoelectronic devices based on organic semiconductors, colloidal quantum dots and conductive oxides.

**OCIS codes:** (320.7130) Ultrafast processes in condensed matter, semiconductors; (300.6340) Spectroscopy, infrared

Molecular electronics is a growing field with an ultimate goal of using organic and biological macromolecular systems such as conjugated polymers, molecular crystals, photochromic proteins or organic/inorganic hybrids in the development of nano-scale electrical circuits. Within the last decade it became clear that charge (de)localization, energetic disorder and vibronic coupling effects can be important roles for the conductivity of molecular-based materials. Until now, most efforts to control and use these effects have been confined to synthetic and material-processing approaches, aiming to develop materials of better quality by mostly trial-and-error exhaustive search.

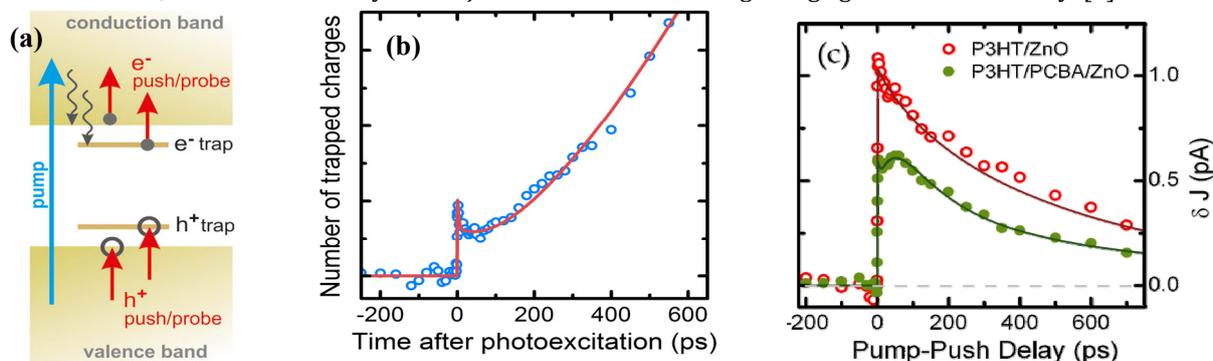
In this work, we report a pioneering attempt to engage the charge-localization and vibronic-coupling effects optically, using ultrafast IR excitation of the vibrational or/and sub-gap electronic transitions. For this we combine ultrafast spectroscopy, photocurrent detection,[1] and ultrafast IR interferometry [2] providing the spectral resolution for selective vibrational excitation. We show that optical manipulation of vibrational and electronic states of the molecule gives control over charge separation and transport dynamics in the organic and hybrid materials.



**Figure 1.** (a) The layout of the experimental PPP setup; (b) PPP time-resolved data showing the effect of polymer-fullerene blend composition and morphology on charge dynamics in the organic solar cell devices.

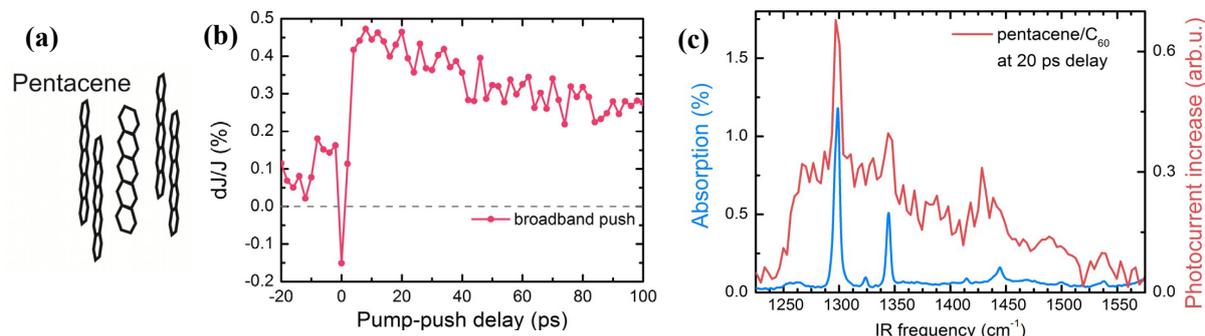
Our main experimental tool is visible-pump – IR-push – photocurrent-probe spectroscopy (PPP), outlined in figure 1a. First, a 100-fs visible pump pulse illuminates the active layer of optoelectronic device introducing a population of charge carriers. The dynamics of carriers is then ‘controlled’ by an interferometer-controlled sequence of two 40-fs IR push pulses. Depending on the IR frequency, the push pulse can excite electronic transitions between localized and delocalized states, charges in low-energy ‘trapping’ states or molecular vibrations. The molecular-scale effect of IR excitation on the charge dynamics is observed through the corresponding change in the macroscopic photocurrent ( $\delta PC$ ) as a function of the delay between ‘pump’ and push. A positive  $\delta PC$  value in such measurements is associated with the immobilized charge carriers, which can be made mobile again by the modification of the vibronic state of the molecular system.

In a broad range of organic systems we observed [1] that promotion of localized polaron states to delocalised band states is critical for long-range charge separation in OPV devices. The study of the material composition effect (fig. 1b) on the charge separation dynamics indicates that it is the resonant coupling of photogenerated singlet excitons to a high-energy manifold of fullerene electronic states that enables efficient charge generation, bypassing localized charge-transfer states. These findings suggest that fullerene cluster size, concentration, and dimensionality are major factors in determining charge generation efficiency. [3]



**Figure 2.** (a) Energy diagram for the PPP experiment on the hybrid material; PPP time-resolved data showing the dynamics of immobile carriers in the quantum-dot (b) and polymer/oxide hybrid (c) solar cell devices.

PPP experiments on colloidal quantum dots (fig. 2a) and polymer-oxide hybrid materials reveal the presence of bound charges (fig. 2b) or charge-transfer excitons (fig. 2c) at the organic-inorganic interfaces and demonstrate their detrimental effect on the charge separation and transport.[4,5] We show that the efficiency of exciton harvesting and dissociation to free charge carriers strongly depends on the properties of the interface, and can be substantially enhanced by the improved passivation of the inorganic surface.



**Figure 3.** (a) Pentacene molecular crystal; PPP time-resolved (b) and push-frequency resolve (c) data showing the effect of vibrational and electronic excitation on the conductivity in the pentacene molecular crystal device.

Finally, we demonstrate that the effect of vibronic coupling [6] in pentacene (fig. 3a) can be used to optically control the conductivity in molecular crystal-based devices. The IR-push excitation of the aromatic C=C stretching mode at  $1440\text{ cm}^{-1}$  induced the modulation of the nuclear coordinates, which appears to be favorable for the intermolecular charge transport (fig. 3b,c). This observation opens the road for direct optical observation and utilization of nonadiabatic effects, which until now have been addressed mostly theoretically.

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