Charge Separation in an Acceptor-Donor-Acceptor Triad Material with a Lamellar Structure

Electronic Supplementary Information

Damien Rolland,[1] Jan C. Brauer,[1] Lucia Hartmann,[1] Laure Biniek,[2] Martin Brinkmann,[2]

Natalie Banerji,[3] Holger Frauenrath[1],*

[1] Ecole Polytechnique Fédérale de Lausanne (EPFL)
Institute of Materials
Laboratory of Macromolecular and Organic Materials

EPFL – STI – IMX – LMOM, MXG 135, Station 12
1015 Lausanne, Switzerland

holger.frauenrath@epfl.ch

[2] CNRS – Université de Strasbourg, France
Institut Charles Sadron
France

[3] University of Fribourg
Department of Chemistry
Switzerland

Supplementary Figures
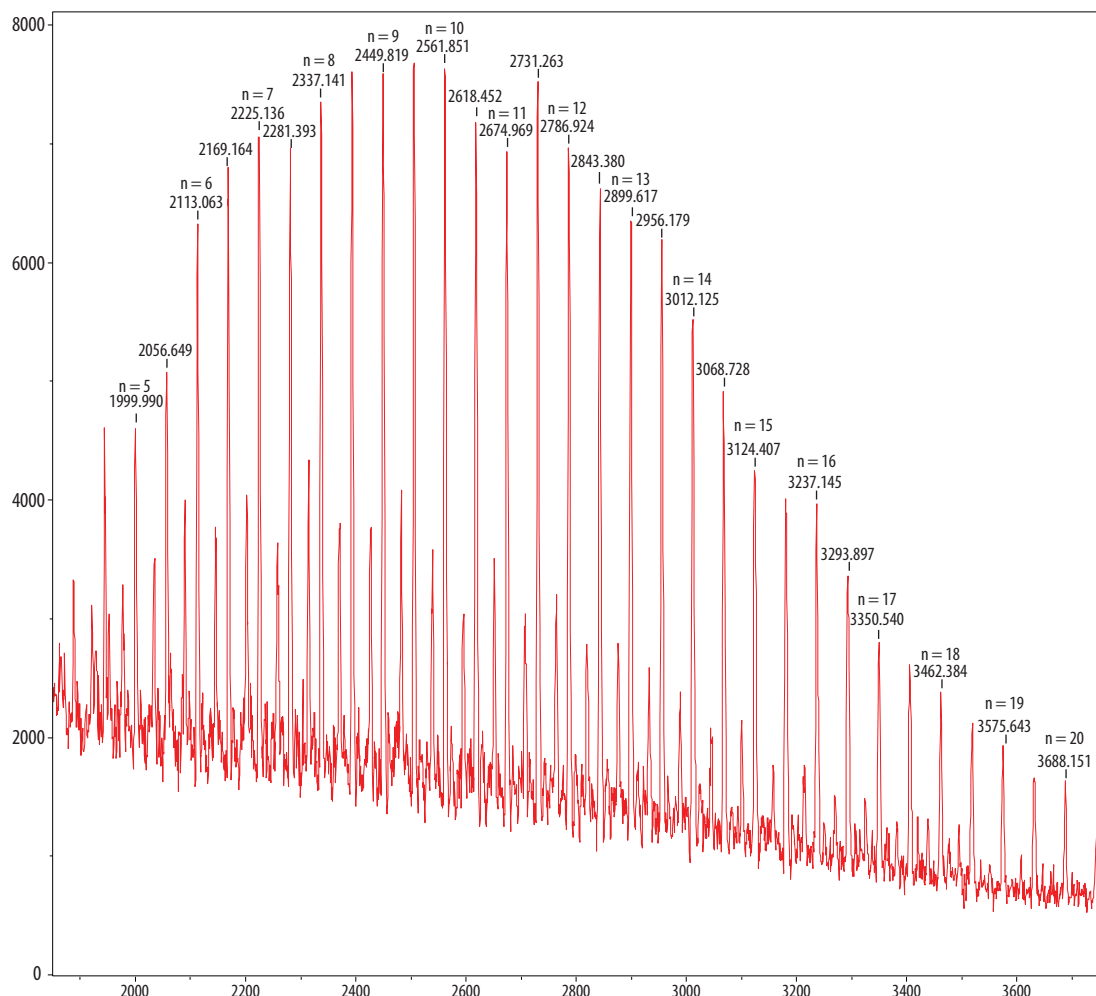
Supplementary Figure S1. MALDI mass spectrum of **PTP-9**. The mass spectrum shows a well-developed envelope for the molecular weight distribution with mass differences between the peaks corresponding to the molecular mass of the repeating units m/z = 56.06. Analysis of the spectrum with Bruker Polytools™ resulted in a molecular weight of M_n = 2.500 (which translates into a $P_n \approx$ 9–10 for each of the polyisobutylene substituents) and a dispersity $Đ$ = 1.02. As is typical for mass spectrometry, however, the dispersity probably underestimates the polydispersity of the sample which, according to GPC on the pure polymer substituent, should be on the order of $Đ$ = 1.2.
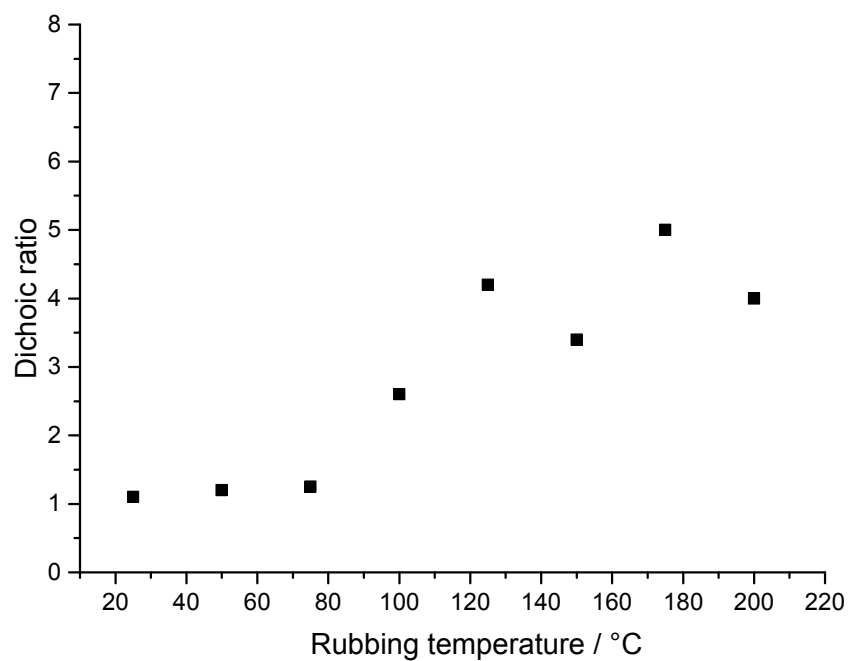
Supplementary Figure S2. Dependence of the dichroic ratio measured in films of **PTP-19** on the rubbing temperature.
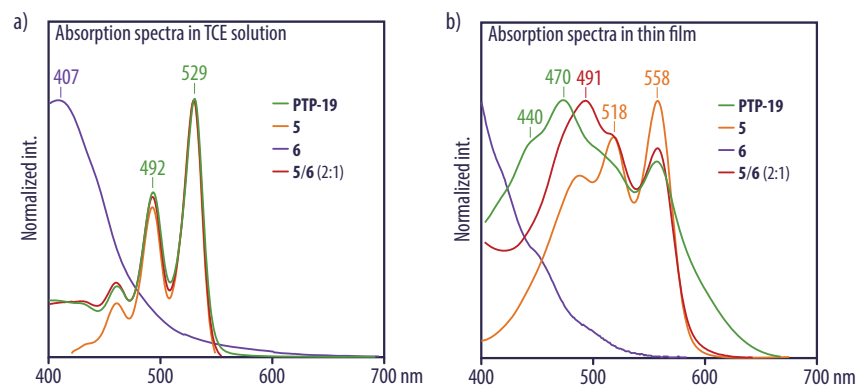
Supplementary Figure S3. Absorption spectra of the *a)* solution phase and *b)* thin film samples measured in transient absorption spectroscopy.
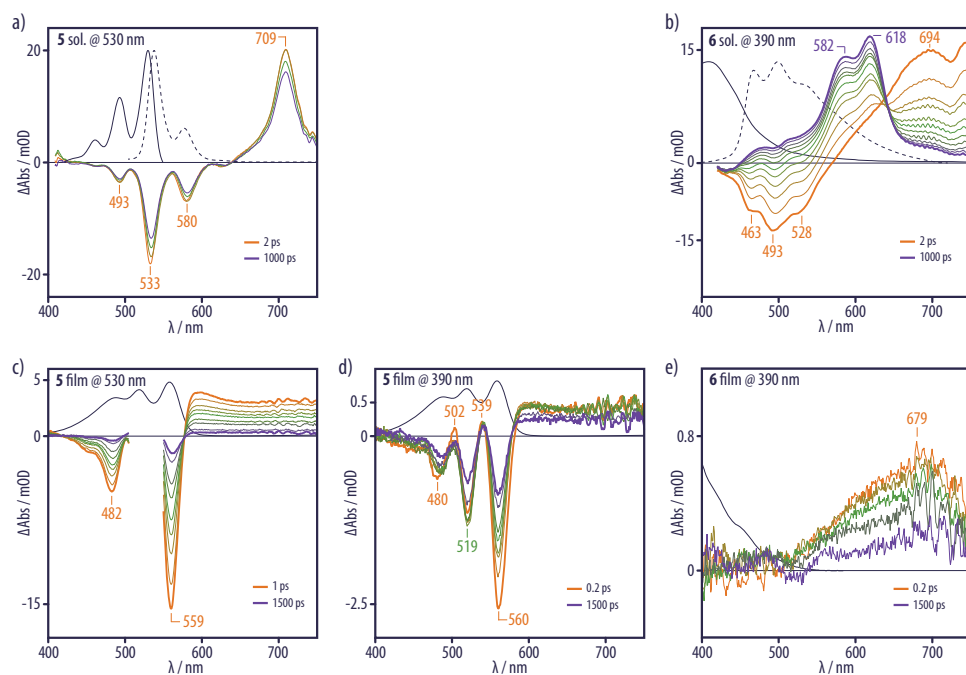
Supplementary Figure S4. *a)* TA spectra of the perylene bisimide **5** alone in solution excited at 530 nm. *b)* TA spectra of the quaterthiophene **6** alone in solution excited at 390 nm. *c)* TA spectra of the perylene bisimide **5** alone in thin film excited at 530 nm. *d)* TA spectra of the perylene bisimide **5** alone in thin film excited at 390 nm. *e)* TA spectra of the quaterthiophene **6** alone in thin film excited at 390 nm.

Multi-Exponential Global Analysis

Multi-exponential global analysis serves to simultaneously analyze the set of dynamics recorded during a white light transient absorption spectroscopy experiment. Dynamics corresponding to many different probe wavelengths were obtained by taking cross-sections through the chirp-corrected TA spectra recorded at about 350 different time delays in the range of –1 to 2 ns. The interpretation of such dynamics is not trivial, given the complexity of processes occurring in the samples. First, there are often overlapping broad spectral signatures, making assignment of the dynamics at a particular probe wavelength to a unique species or process difficult. Then, the time evolution of the TA signals can be influenced by multiple processes, for example the pure charge transfer dynamics might be entangled with spectral shifts due to relaxation. For all the above reasons, the analysis of a single-wavelength TA dynamics is typically not very meaningful. Therefore, we have opted for global analysis, i.e., for the simultaneous analysis of the TA dynamics taken every 5 nm throughout the spectrum. Apart from being more robust to noise-related artifacts encountered at a single wavelength, this method allows for correlating the evolution of different signatures in the TA spectrum, greatly facilitating the interpretation.

Given the complexity of the TA dynamics, it is challenging to devise a kinetic model that accurately and comprehensively describes all the dynamics. Therefore, we have performed data analysis without imposing any specific model to the results, but instead by globally fitting a convolution of a Gaussian and a sum of exponential functions to the dynamics. There is not always a direct physical meaning to using such exponential functions. We also note that a Gaussian distribution of time constants for highly multiphasic processes can crystallize into only a few average exponential time constants. Nevertheless, the multi-exponential analysis provides an excellent overview of the data and allows estimating the time scale on which processes are occurring. Most useful are also the pre-exponential factors associated with the exponential time constants and obtained at different wavelengths throughout the TA spectrum. The sign of the pre-exponential factor indicates whether the process associated with the time constant leads to a rise or a decay of the TA signal at a given probe wavelength. By plotting the pre-exponential factors as a function of probe wavelength (yielding decay associated amplitude spectra), concerted changes in different parts of the transient spectrum can be identified. This global appreciation of the evolution of several bands consolidates the assignment of the observed dynamics to physical processes.

3b

4b

PTP-19

8.76
8.69
7.08
6.94
6.00
4.60
4.31
3.38

16.00   5.23   1.73   3.72   3.83   3.66   358.45

10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.