

Electronic Supplementary Information

Conformational Dynamics of Di-(Perylene Bisimide Acrylate) and its Footprints in Steady-State, Time-Resolved, and Fluorescence- Correlation Spectroscopy

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1. Gel Permeation Chromatography (GPC)

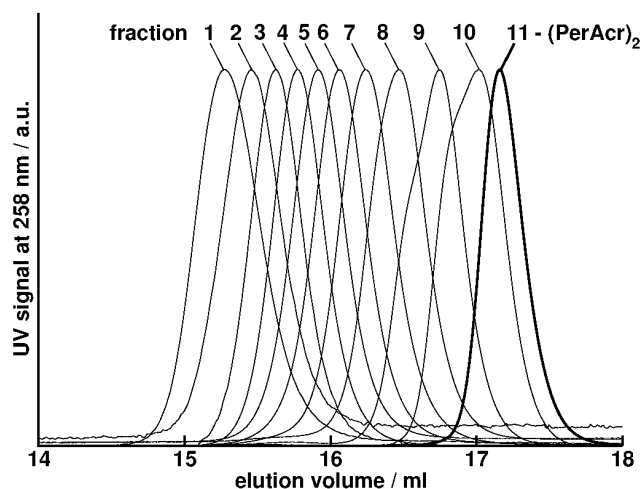


Figure SI-1. GPC traces of the fractionated PerAc oligomers (fraction 1 to 11; all curves are normalised to the maximum). The individual fractions were measured on an analytical GPC setup with THF as the eluent, a flow rate of 1 ml/min. Polystyrene standards were used for calibration and 1,2-dichlorobenzene as an internal standard. The last fraction (fraction 11, containing the lowest molecular weight oligomer; M_n : 1600g/mol) had a very low polydispersity index (PDI) of 1.01 comparable to monodisperse compounds and did not show any shoulders on either side. Since the monomer PerAc was already removed, we concluded that the last fraction contained dimer $(\text{PerAc})_2$.

2. Matrix-Assisted Laser Desorption Ionization - Time-of-Flight (MALDI-ToF) Mass Spectrometry

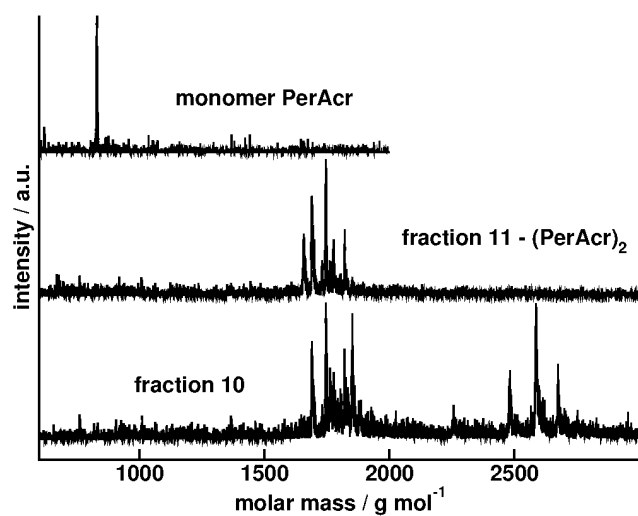


Figure SI-2. MALDI-ToF spectrum of the monomer PerAc (top, measured molar mass: 829.5 g/mol, calculated molar mass: 825.1/mol), fraction 11 (centre) and fraction 10 (bottom); all curves are normalised to the maximum and offset for clarity. Fraction 10 is a mixture of the dimer and the trimer. Although the baseline is of moderate quality, it can be clearly seen that fraction 11 does in fact only contain dimer and no residual monomer or trimer.

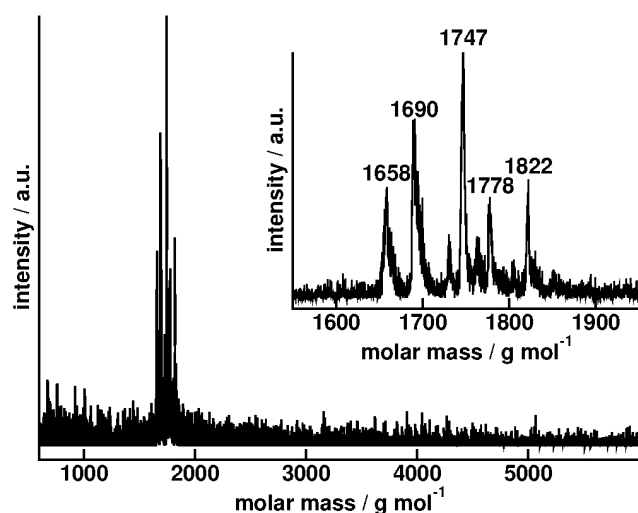


Figure SI-3. MALDI-ToF spectrum of fraction 11 (PerAcr)₂ with the inset showing dimer peaks with different end-groups. The observation that the (PerAcr)₂ produces several peaks can be explained by the polymerization method used. For nitroxide mediated polymerization (NMRP) of PerAcr chain transfer¹ is known, which leads to the initiation of new chains that do not carry the initiator group. Thus, for low degrees of polymerization, dimers can be formed without the typical end-groups usually observed in NMRP. In addition, the nitroxide end-group of regularly initiated chains can be cleaved off in MALDI-ToF², which causes additional signals. For instance, the mass peak at molar mass 1658 could be caused by chain transfer, which would give the dimerised product without the initiator (calculated 1650). Or, the most intense peak at 1747 could be the result of the regularly initiated dimer without the nitroxide (calculated $825,1 \cdot 2 + 325 - 220 = 1755$). While it is not the purpose of this study to identify all different end-groups involved, it is important to note that all species observed in the (PerAcr)₂ spectrum are indeed dimers in the sense that two perylene bisimide units are covalently connected.

¹ A. S. Lang, A. Neubig, M. Sommer, M. Thelakkat, *Macromolecules*, **2010**, *43*, 7001.

² M. Mazarin, M. Girod, S. Viel, T. N. T. Phan, S. R. A. Marque, S. Humbel, L. Charles, *Macromolecules*, **2009**, *42*, 1849.