Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information

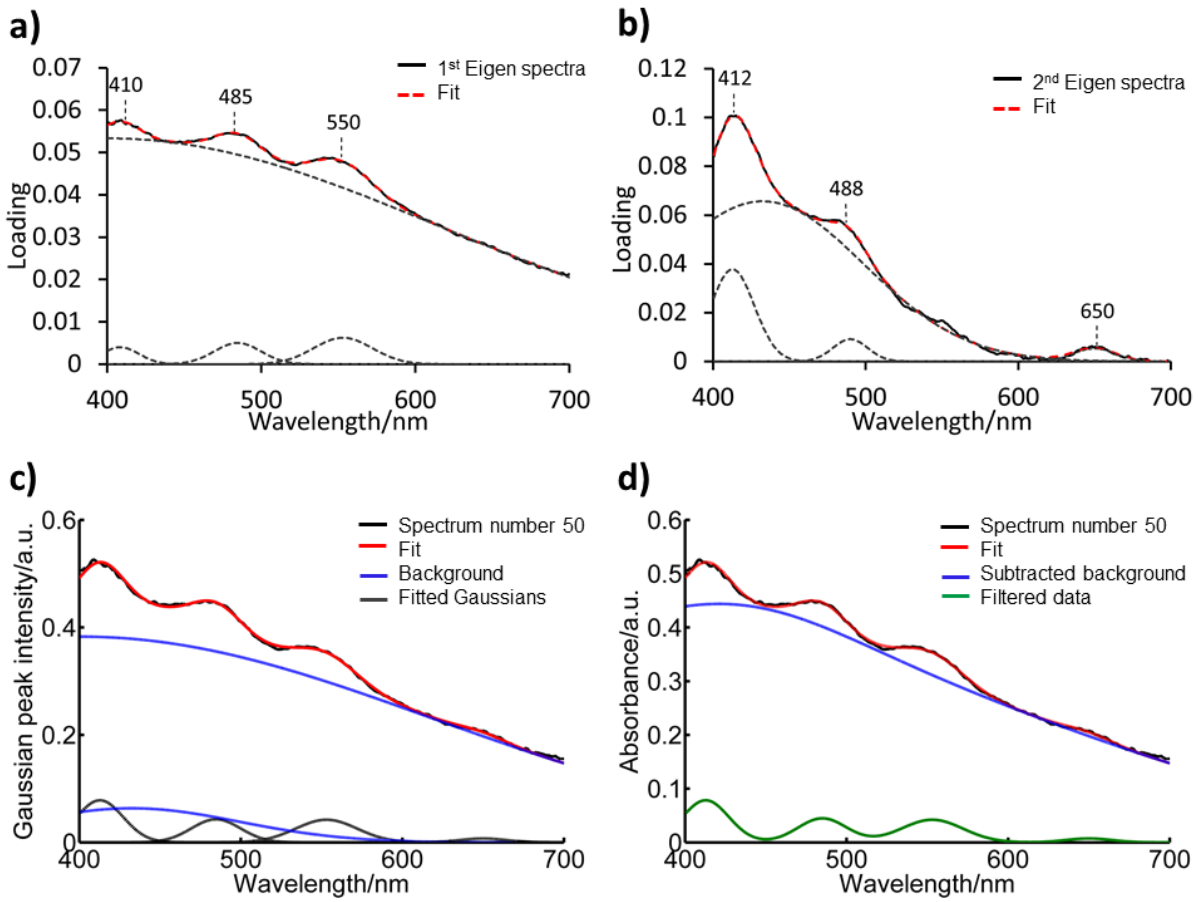


Fig. S1: a) First and b) second Eigen spectra obtained from NMF analysis of time series optical spectra of Na-100 (Fig. 2) during thiophene oligomerization. Eigen spectra fitted with the minimum number of Gaussians, creating a model which is applied to fit each individual optical spectra in the time series. c) Example of spectra number 50 fitted with the fitted Gaussian model and the corresponding bands and background present. d) Selective removal of the Gaussians corresponding to the background in the model and its application to each individual spectra (example given at spectra number 50).

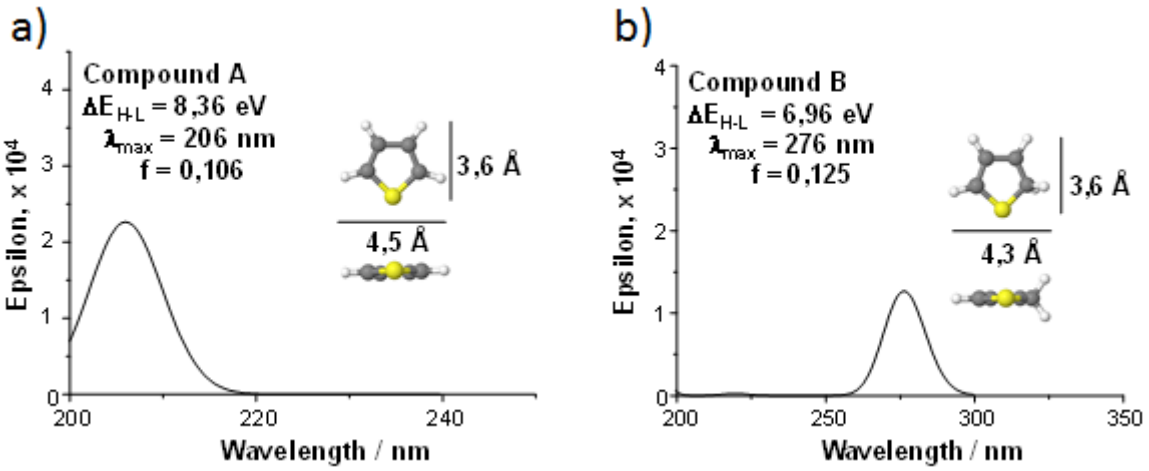


Fig. S2: Optimized geometries, molecular size, HOMO-LUMO gap (ΔE_{H-L}), wavelength of the π-π^* electronic transition (λ_{max}), oscillator strength (f) and simulated absorption spectra for: a) a thiophene monomer and: b) an adsorbed thiophene monomer; during oligomerization at M06-2X/6-31+G(d,p) level.

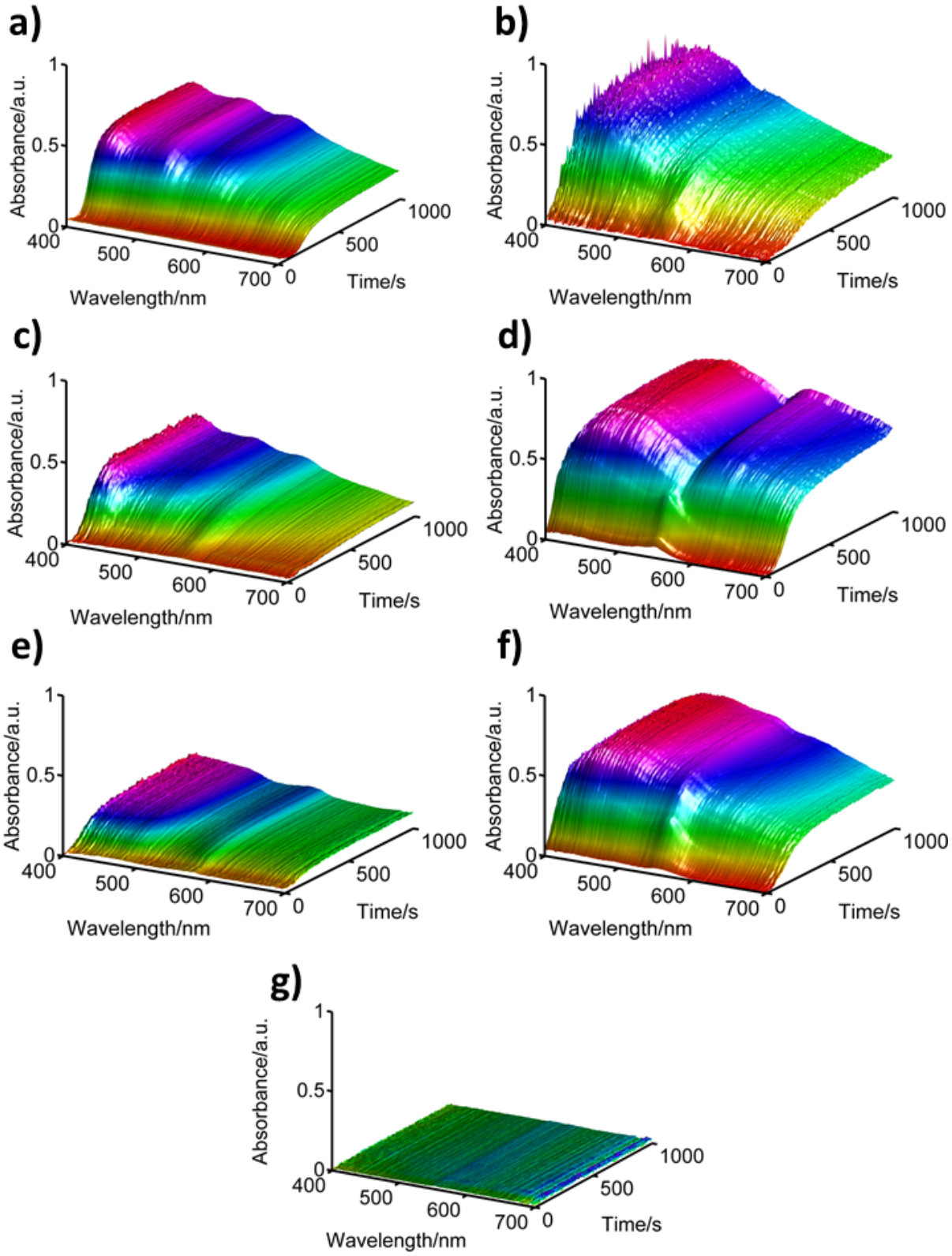


Fig. S3: Raw *in situ* optical absorption time series spectra recorded during thiophene oligomerization over a) Na-100 b) H-100 c) Na-80 d) H-80 e) Na-20 f) H-20, g) blank SiO_2 extrudate. Samples impregnated at 303 K before ramping (at 30 K min $^{-1}$) to 393 K, recording spectra every 10 s for a total of 1000 s.

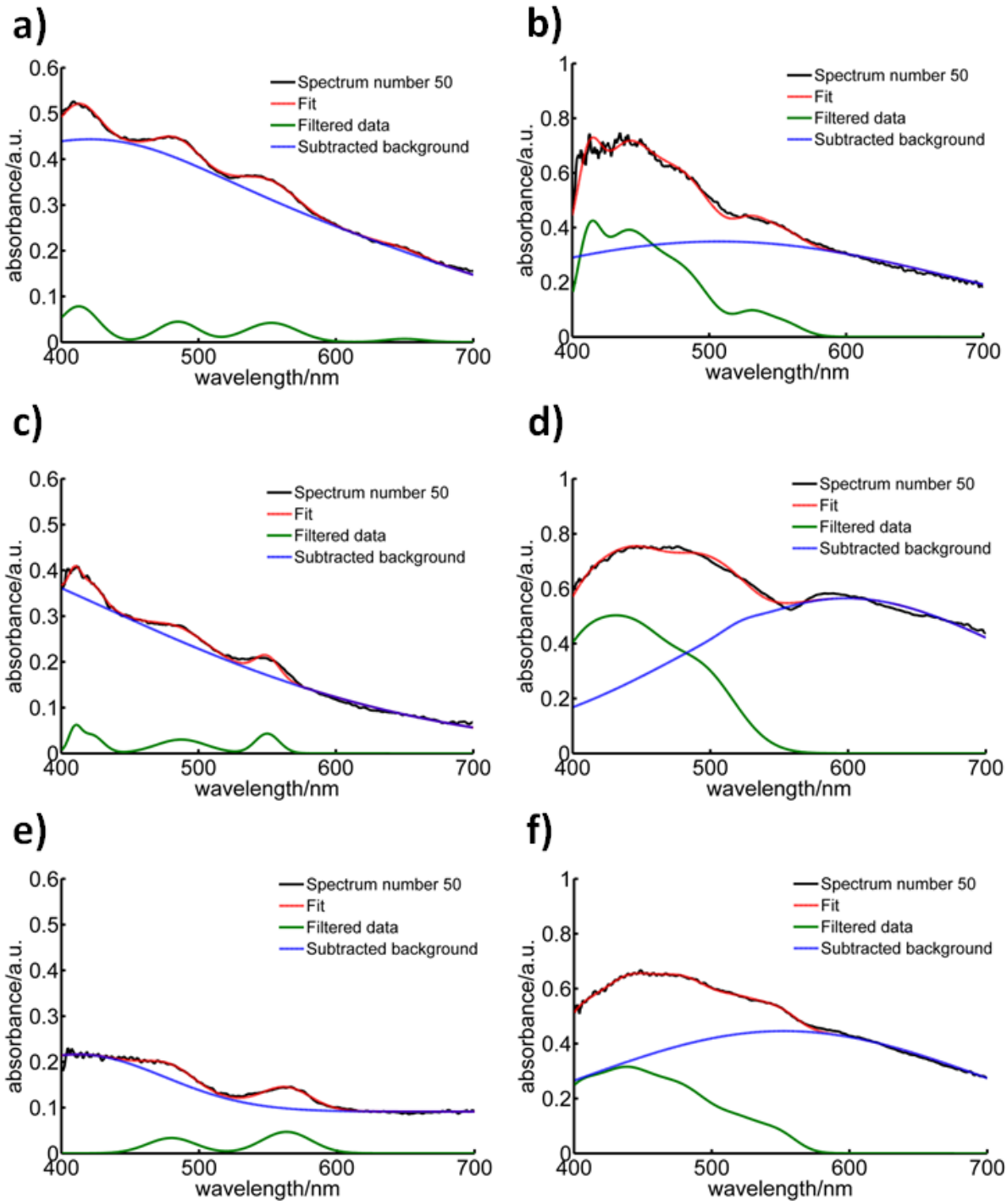
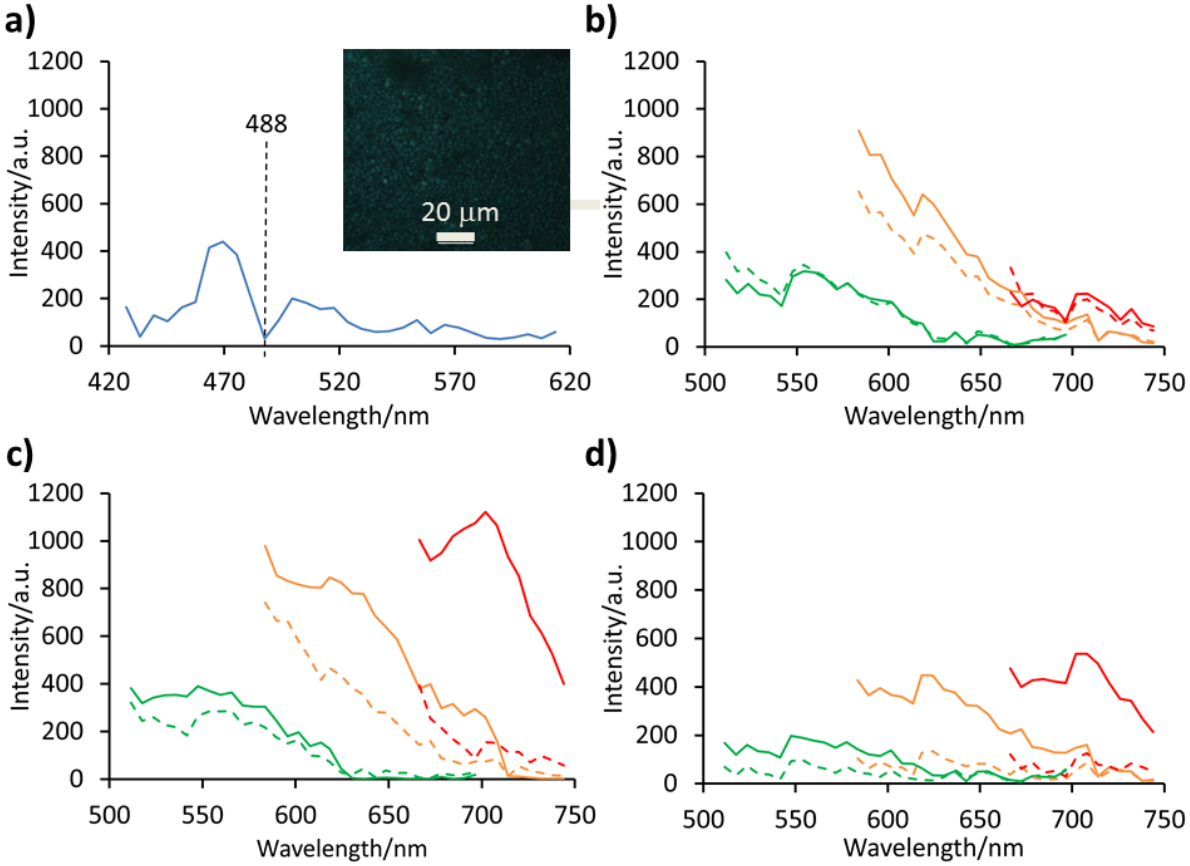


Fig. S4: Fitted and subtracted Gaussians of the created model (from NMF analysis and Eigen spectra fitting) applied to each individual raw optical absorption spectra in the time series during thiophene oligomerization of a) Na-100, b) H-100, c) Na-80, d) H-80, e) Na-20, f) H-20. (Example given at spectrum number 50 in each case).



S5: Fluorescence spectra recorded after thiophene oligomerization reaction at 393 K over samples: a) Na-100 excited with 404 nm laser. Black dotted line depicts dichroic mirror placement at 488 nm, leading to loss of main fluorescence band of excited oligomer species. Inset: 2D top view confocal fluorescence image of Na-100 excited with a 404 nm laser; b) Na-100 and H-100; c) Na-80 and H-80; d) Na-20 and H-20. **Legend for each image:** Dashed lines: Na-100, Na-80, Na-20; Solid lines: H-100, H-80, H-20. Green: 488 nm laser excitation; Orange: 561 nm laser excitation; Red: 642 nm laser excitation.

S6: Reference [34]

[34]: Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.