

***In Situ* Characterization of Self-Assembled Monolayers of Amphiphilic Push-Pull-Thiazoles *via* Photothermal Deflection Spectroscopy**

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METHODS

Quartz glass substrates were treated 15min with acetone and iso-propanol in the ultrasonic bath for each solvent three times and the substrates were stored in isopropanol. The purified substrates were immersed in silanization solution I (Sigma Aldrich) for 24h for hydrophobisation and then shortly rinsed with hexane.

Photothermal Deflection Spectroscopy

The photothermal deflection spectroscopy¹⁻⁹ (PDS) setup used here consists of a light source (LOT-QD; 1000W Xe high pressure lamp and a 260mm monochromator optimized for a maximum intensity of 200nm to 2500nm). The light is modulated by a chopper (Thorlabs) with a frequency of 5Hz and focused on a spot size of 3x6mm on the sample through a f=75mm lens. The intensity of the incident light(2.05mW at 430nm in the focal spot) is monitored using a quartz glass plate as a beam splitter placed between the focusing lens and the sample, and a trans-impedance amplified silicon detector (Thorlabs). The deflection of a 0.5mW HeNe laser is measured with a lateral effect sensor (Thorlabs PDA90). The deflection and reference signals were read out using two lock-in amplifiers (Stanford Research Systems SRS-830). The whole system is controlled by a self-written Labview program, which collects all data and also corrects the PDS signal according to the incident light intensity. A 5mm · 30mm glassy carbon sample was used as a reference sample.

Concentrations

In the self-assembly experiments we ensured constant dye concentrations in the solutions by using saturated solutions and small amounts of precipitates. The dye concentration of the saturated solutions is determined from their UV-vis absorption spectra as follows: **1**: 1.06 μM (octane); 3.35 μM (hexane); 5.14 μM (heptane); **5**: 0.39 μM (octane); 0.4 μM (hexane); 1.37 μM (heptane); **10**: 0.46 μM (octane); 0.5 μM (hexane); 1.43 μM (heptane).

The absorbance of the solution should be less than 0.2 to ensure that sufficient light intensity reaches the surface of the SAM after passing through the saturated solution. Dye concentrations that are too high will cause heating of the solution upon absorption of light, resulting in a low signal-to-noise ratio. Too low dye concentrations cause might be insufficient for self-assembly and thus can cause low signal-to-noise ratios, too.

UV-vis Transmission Spectroscopy

The absorption spectroscopic measurements we used a UV-vis (Varian: Cary 5000) spectrometer in transmission mode.

λ_{max} [nm] $\Delta\tilde{\nu}$ [cm^{-1}] ^a	1			5			10		
	Sol.	SAM		Sol.	SAM		Sol.	SAM	
		Phil.	Phob.		Phil.	Phob.		Phil.	Phob.
isooctane	419	418 (475) -292	418 -145	432	439 1413	/ /	422	436 1526	/ /
hexane	413	450 2303	410 (488) -295	429	/ /	/ /	432	429 -597	/ /
heptane	420	452 1930	416 (478) 2662	432	444 1242	/ /	432	448 1760	/ /

Table SI 1: Absorption maxima of the saturated solutions (sol.) measured *via* UV-vis transmission - and self-assembled monolayers (SAMs at hydrophilic (Phil.) and hydrophobic (Phob.) surfaces) *via* photothermal deflection spectroscopy of the amphiphilic push-pull thiazoles **1**, **5** and **10** in isooctane, hexane, and heptane. ^aSpectral shift with respect to solution (Sol.), measured at the low-energy edge at half of the maximum absorbance

PDS ABSORBANCE MEASUREMENTS OF SAMS WITH RAW DATA

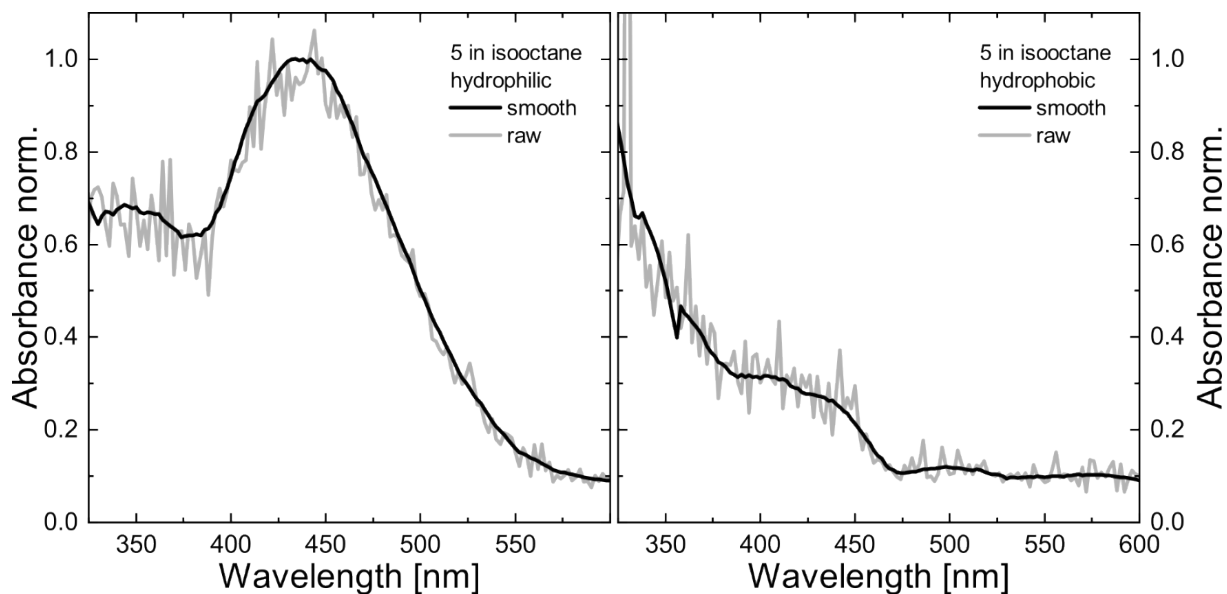


Figure SI 1: Normalized raw and smoothed absorption spectra of self-assembled monolayer of the amphiphilic push-pull-thiazoles **5** in saturated solutions of isooctane on hydrophilic (left) and hydrophobized (right) quartz-glass substrate

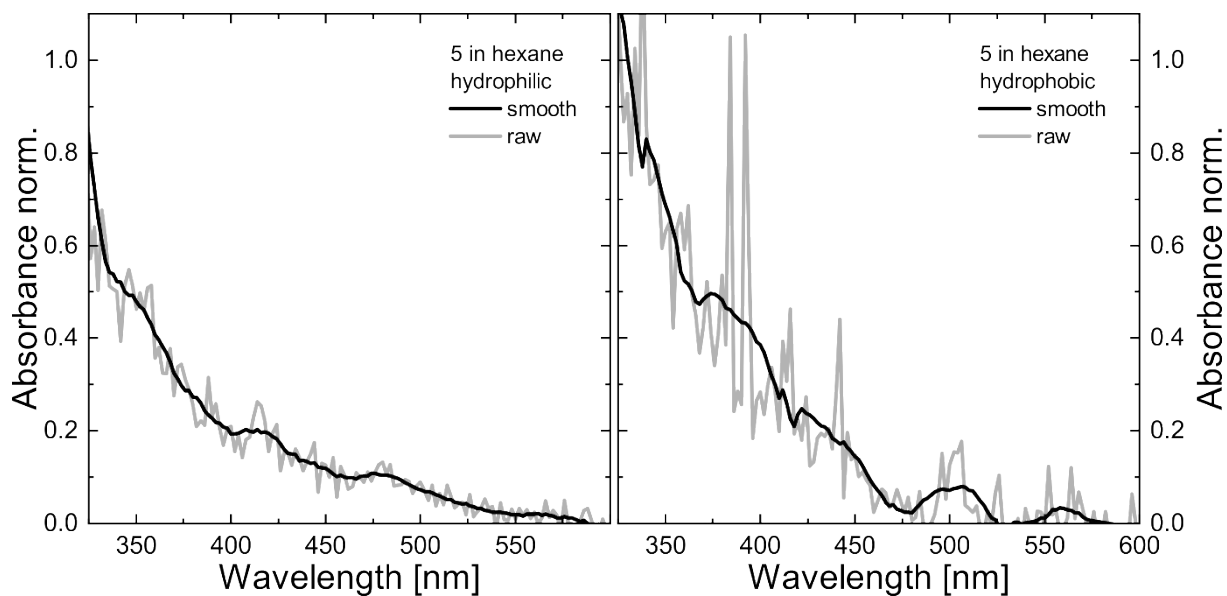


Figure SI 2: Normalized raw and smoothed absorption spectra of self-assembled monolayer of the amphiphilic push-pull-thiazoles **5** in saturated solutions of n-hexane on hydrophilic (left) and hydrophobized (right) quartz-glass substrate

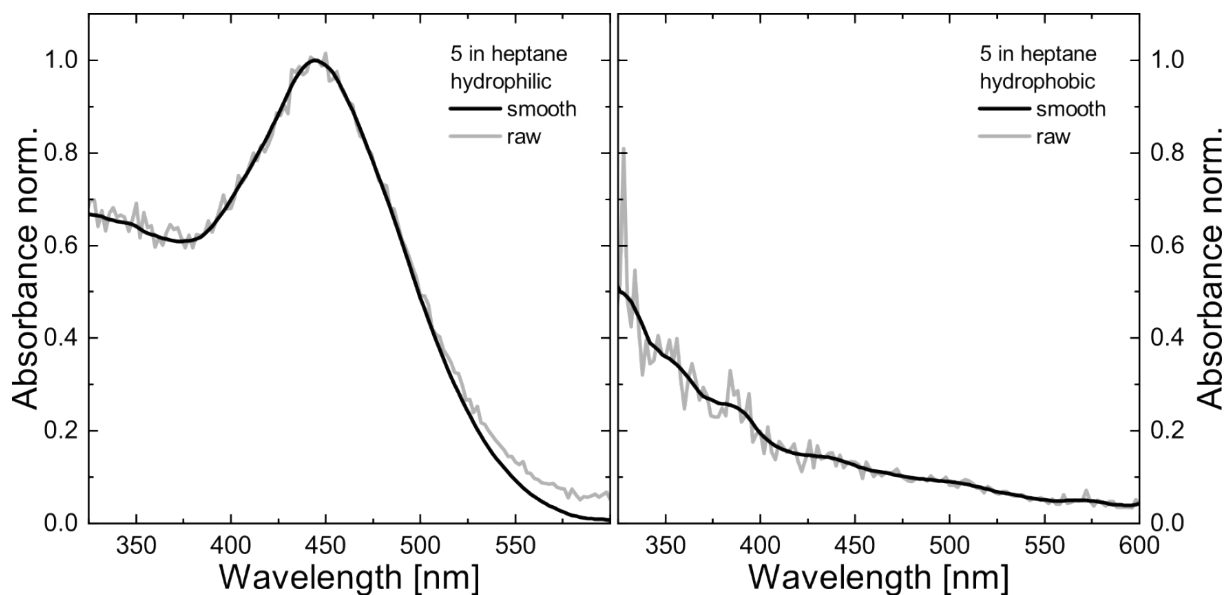


Figure SI 3: Normalized raw and smoothed absorption spectra of self-assembled monolayer of the amphiphilic push-pull-thiazoles **5** in saturated solutions of n-heptane on hydrophilic (left) and hydrophobized (right) quartz-glass substrate

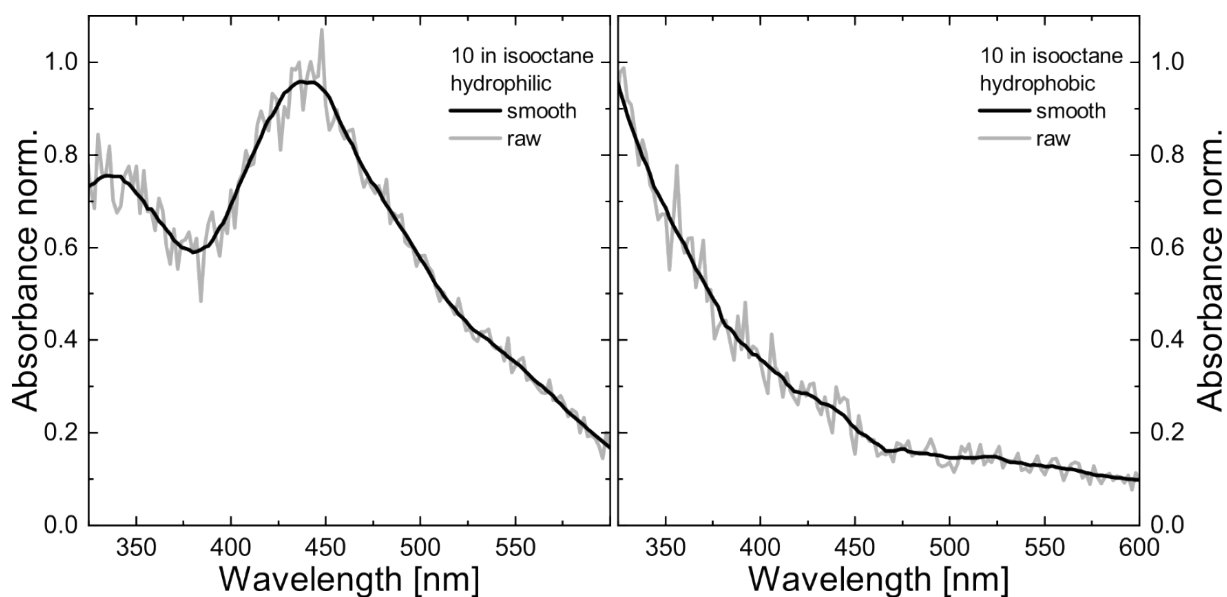


Figure SI 4: Normalized raw and smoothed absorption spectra of self-assembled monolayer of the amphiphilic push-pull-thiazoles **10** in saturated solutions of isooctane on hydrophilic (left) and hydrophobized (right) quartz-glass substrate

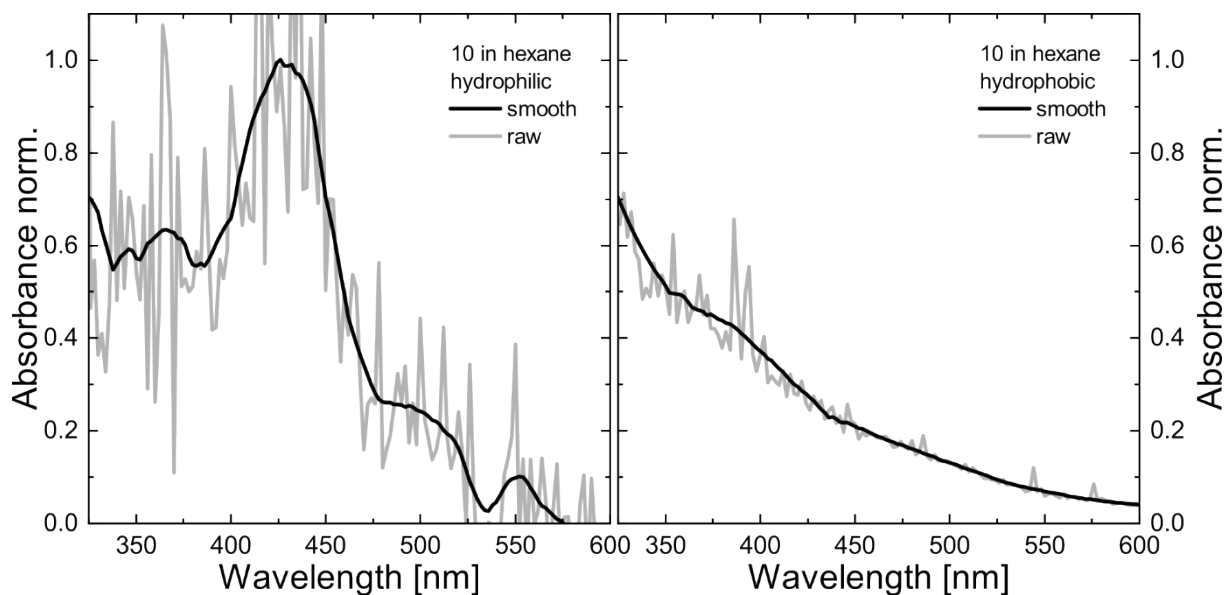


Figure SI 5: Normalized raw and smoothed absorption spectra of self-assembled monolayer of the amphiphilic push-pull-thiazoles **10** in saturated solutions of n-hexane on hydrophilic (left) and hydrophobized (right) quartz-glass substrate

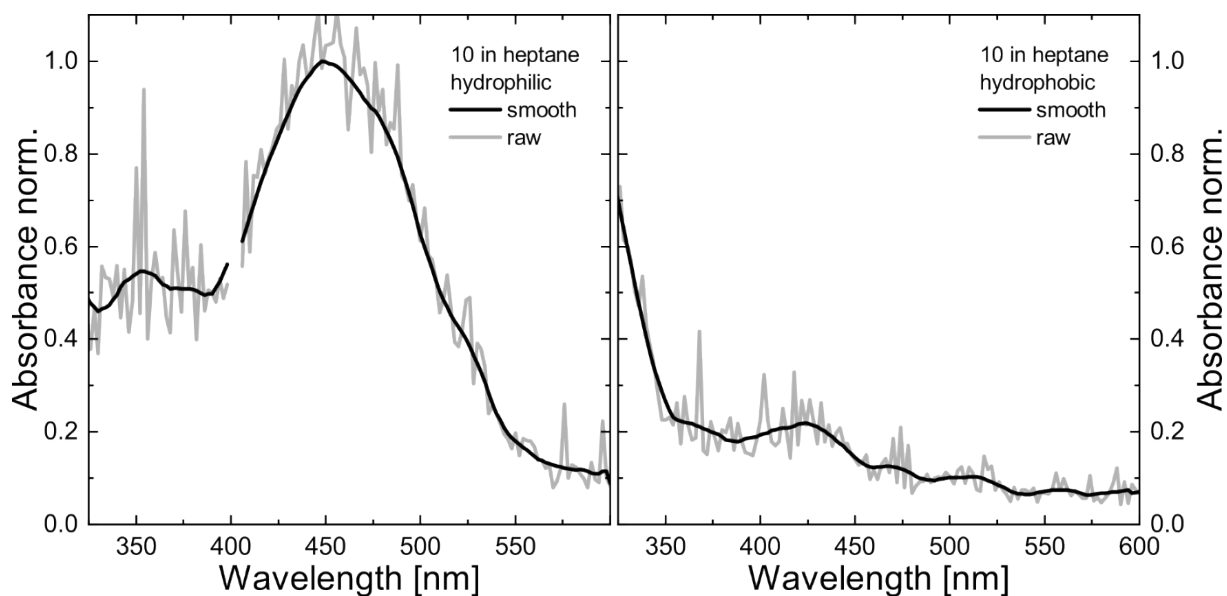


Figure SI 6: Normalized raw and smoothed absorption spectra of self-assembled monolayer of the amphiphilic push-pull-thiazoles **10** in saturated solutions of n-heptane on hydrophilic (left) and hydrophobized (right) quartz-glass substrate

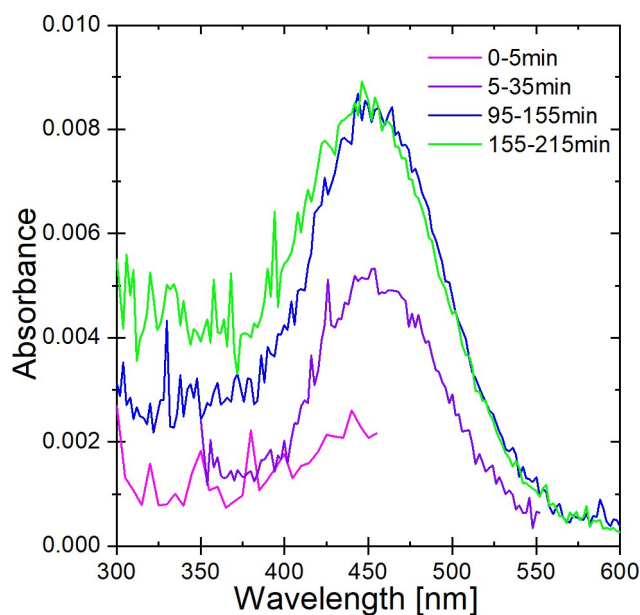


Figure SI 7: Raw absorption spectra of self-assembled monolayer of the amphiphilic push-pull-thiazole **1** in saturated solutions of n-heptane on hydrophilic quartz-glass substrate. Spectra are measured in between 0-5min (pink), 5-35min (purple), 95-155min (blue), 155-215min (green).

The spectra in Figure SI 7 show the evolution of absorption spectra and thus of the surface coverage of the self-assembled monolayer. The assembly is influenced by the measurement time and the heat input during the measurement, thus the complete surface coverage is reached faster than in previous publications¹⁰, where adsorption kinetics have been determined at individual wavelengths (causing very fast measurements in the range of few minutes) instead of measuring UV-vis absorbance spectra in a broad range.

To investigate the influence of fluorescence on the shape of the PDS absorption spectra, we applied the formula provided by Couch et al.¹¹ :

$$A^{PDS}(\lambda) = \left(1 - \Phi_F \frac{\lambda}{\bar{\lambda}}\right) A(\lambda)$$

where Φ_F is the fluorescence quantum yield, $A(\lambda)$ is the absorbance spectrum, $\bar{\lambda}$ is the average wavelengths of the fluorescence spectrum (estimated from LB fluorescence spectra to be 580nm)¹².

In Figure SI 8, the PDS spectrum of **5** adsorbed onto hydrophilic glass from a saturated heptane solution and UV-vis absorbance spectra determined from transmission spectra are shown. The absorbance spectra have been calculated for Φ_F ranging from 0 to 1. Hence, at $\Phi_F = 0$ the calculated absorbance spectrum is identical to the one of the solution. At increasing fluorescence quantum yields the long wavelengths spectral part is reduced stronger than the short-wavelengths part, thus causing an apparent blue-shift in the normalized spectra.

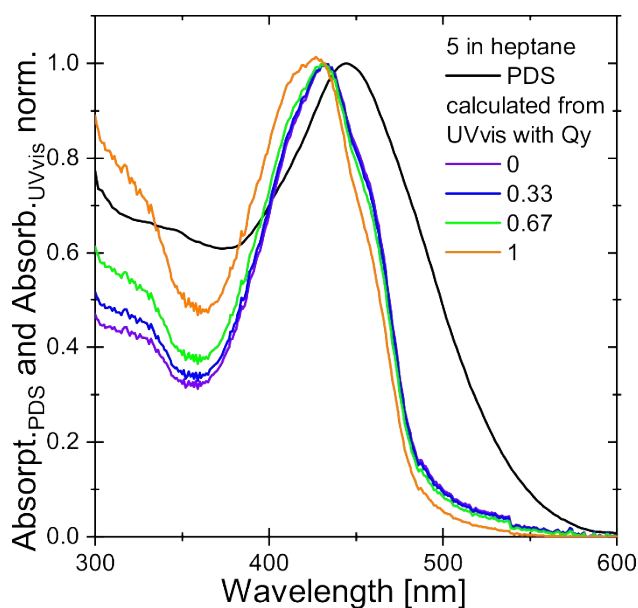


Figure SI 8: PDS Absorbance spectra of 5 from a saturated solution in heptane. Calculated absorption spectra from a saturated solution of 5 in heptane with fluorescence quantum yield (Q_y) of 0 (violet), 0.33 (blue), 0.67 (green) and 1 (orange)

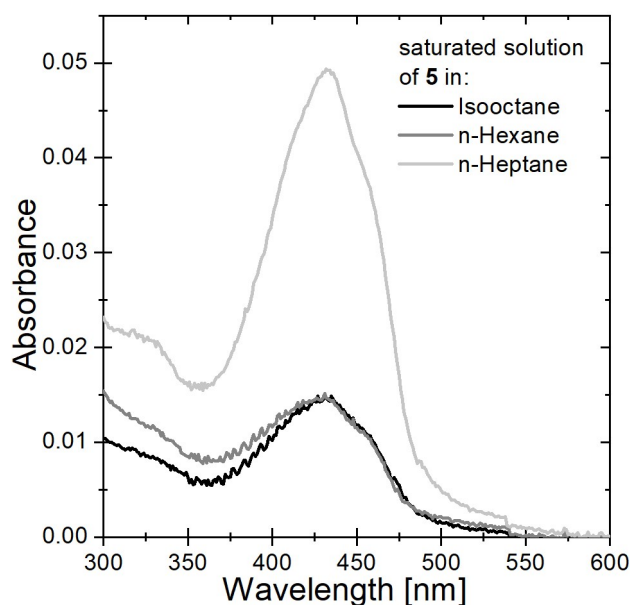


Figure SI 9: UVvis absorbance spectra of 5 in isooctane, hexane and heptane

REFERENCES

1. W. B. Jackson, N. M. Amer, A. C. Boccara and D. Fournier, *Appl. Opt.*, 1981, **20**, 1333-1344.
2. M. Presselt, M. Bärenklau, R. Rösch, W. J. D. Beenken, E. Runge, S. Shokhovets, H. Hoppe and G. Gobsch, *Applied Physics Letters*, 2010, **97**, 253302.
3. L. Goris, K. Haenen, M. Nesládek, P. Wagner, D. Vanderzande, L. De Schepper, J. D'haen, L. Lutsen and J. V. Manca, *Journal of Materials Science*, 2005, **40**, 1413-1418.
4. F. Herrmann, S. Engmann, M. Presselt, H. Hoppe, S. Shokhovets and G. Gobsch, *Applied Physics Letters*, 2012, **100**, 153301-153301 - 153303.
5. M. Presselt, F. Herrmann, H. Hoppe, S. Shokhovets, E. Runge and G. Gobsch, *Advanced Energy Materials*, 2012, **2**, 999-1003.

6. A. Asano and M. Stutzmann, *Journal of Non-Crystalline Solids*, 1991, **137-138**, 623-626.
7. M. Presselt, F. Herrmann, S. Shokhovets, H. Hoppe, E. Runge and G. Gobsch, *Chem. Phys. Lett.*, 2012, **542**, 70-73.
8. S. Nonomura, T. Nishiwaki and S. Nitta, *Philosophical Magazine B*, 1994, **69**, 335-348.
9. F. Herrmann, B. Muhsin, C. R. Singh, S. Shokhovets, G. Gobsch, H. Hoppe and M. Presselt, *The Journal of Physical Chemistry C*, 2015, **119**, 9036-9040.
10. M. L. Hupfer, F. Herrmann-Westendorf, M. Kaufmann, D. Weiss, R. Beckert, B. Dietzek and M. Presselt, *Chemistry*, 2019, **25**, 8630-8634.
11. B. Couch, A. Meyer, B. Heller and S. L. Johnson, *Methods Appl Fluoresc*, 2018, **7**, 015004.
12. M. L. Hupfer, M. Kaufmann, J. Preiss, D. Weiss, R. Beckert, B. Dietzek and M. Presselt, *Langmuir*, 2019, **35**, 2587-2600.