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INTRODUCTION

In order to obtain chromophores which absorb light in the far red or even in the near infrared (NIR) region, increased efforts were put into the development of new molecular dye structures or into investigations of profound structure-property relationships. Intense absorption in the NIR is required for many technologies and applications, e.g. energy conversion in organic photovoltaic cells. Here, one prominent point in favor of NIR dyes is the improvement of the overall photoelectric conversion efficiency by coverage of the whole range of solar irradiation, including the visible and NIR light.

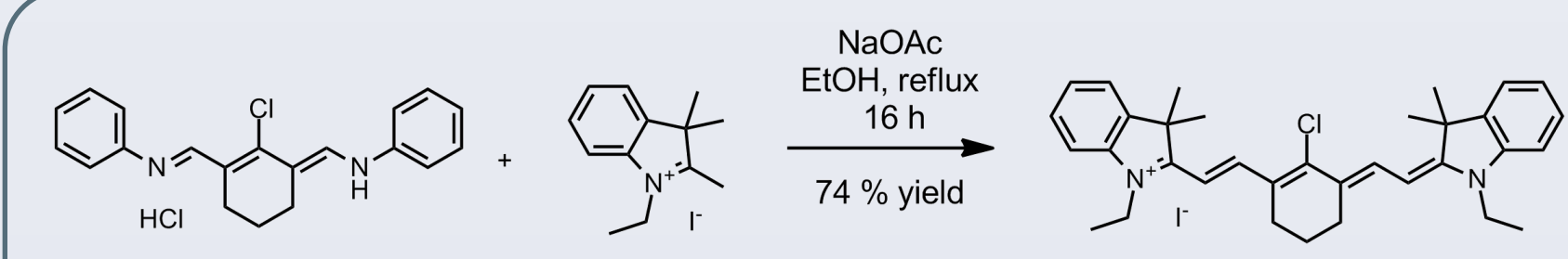
There are several dyes known that provide absorption from the visible to the NIR range, however the selective absorption of NIR light while maintaining efficient energy conversion is still an issue. Only few dye classes are known to be strong NIR absorbers with a single absorption maximum that lies above 750 nm. Among them are polymethine dyes, naphthalo- or phthalocyanine dyes, croconic and squaraine dyes, diketopyrrolopyrrole or perylene derivatives.

Our goal is the development of heptamethine dyes with tailor-made counter ions and the utilization of their outstanding photophysical properties for energy conversion in the NIR region. Heptamethine dyes have the distinction of being achievable via straightforward and cost-effective synthesis in high yields. The properties can be tuned by molecular design of the terminal heterocyclic moieties or by choice of the counterion. In combination with C60 or PCBM heptamethine dyes can operate as a donor in bilayer or bulk heterojunction (BHJ) solar cells. By optimizing the layer structure and thicknesses the heptamethine dyes also offer the possibility of realizing transparent and colorless organic solar cell devices.

This study focuses on the influence of the counterion (Δ -TRISPHAT or hexafluorophosphate) of two cationic cyanine dyes (a heptamethine as the NIR dye, and a trimethine for comparison) on their optical and electrochemical properties in solution, as well as their optical properties in thin films. First results of applications in organic bilayer solar cells with C60 as the acceptor are shown as a proof of principle.

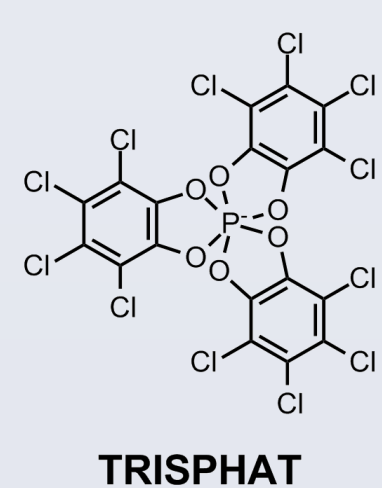
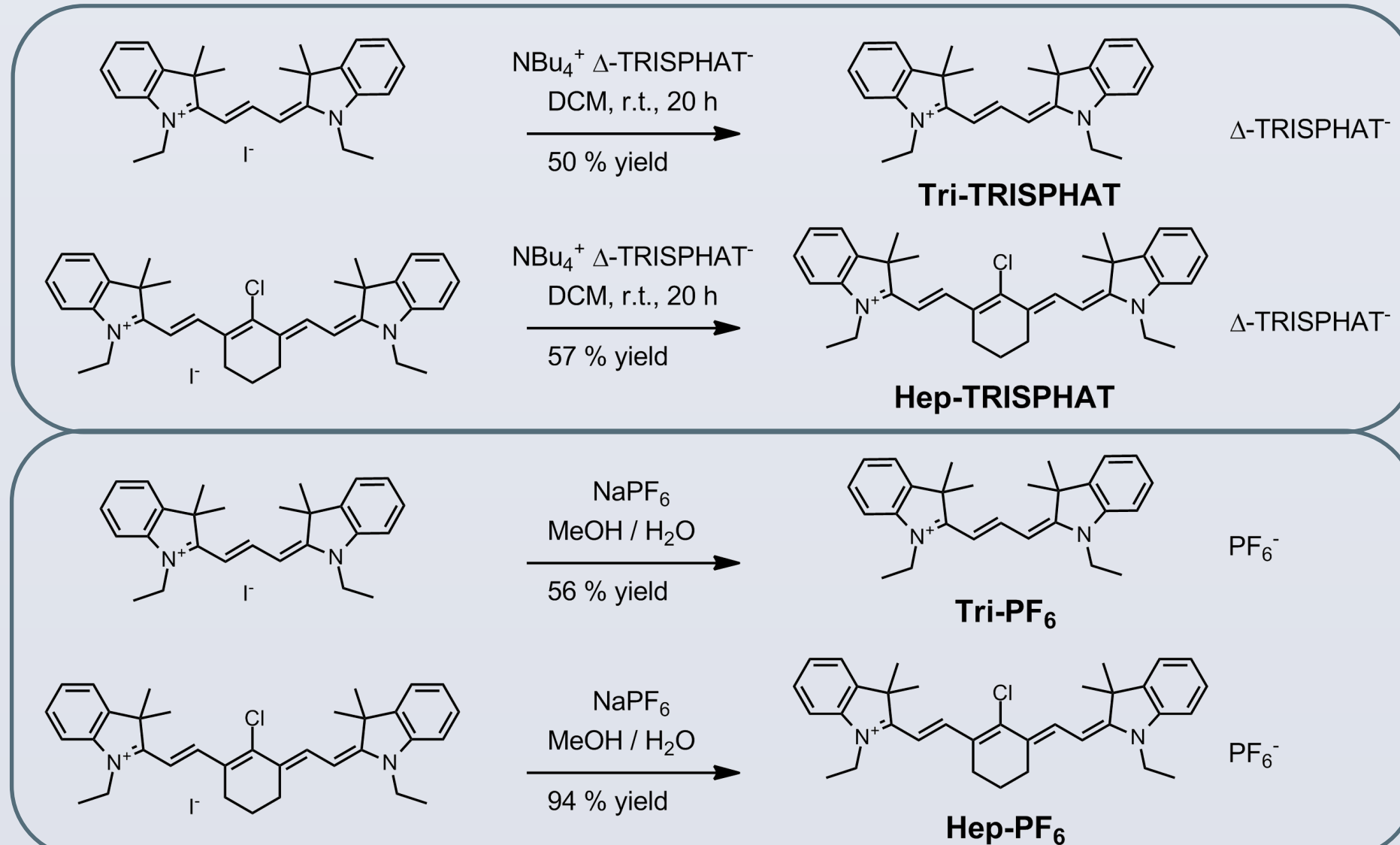
SYNTHESIS AND COUNTER ION EXCHANGE

Synthesis of Heptamethine Iodide (Hep-I)



- Hep-I was prepared using the straightforward synthetic procedure for heptamethine cyanine dyes [2].

Ion Exchange from Iodide to Δ -TRISPHAT and Hexafluorophosphate (PF₆)



- Ion exchange to Δ -TRISPHAT was achieved by stirring the corresponding iodide salts and Δ -TRISPHAT tetrabutylammonium salt in DCM for 20 h.
- Tri-PF₆ and Hep-PF₆ were obtained from the corresponding iodide salts by precipitation with NaPF₆ in methanol [3].

OPTICAL ANALYSIS IN SOLUTION

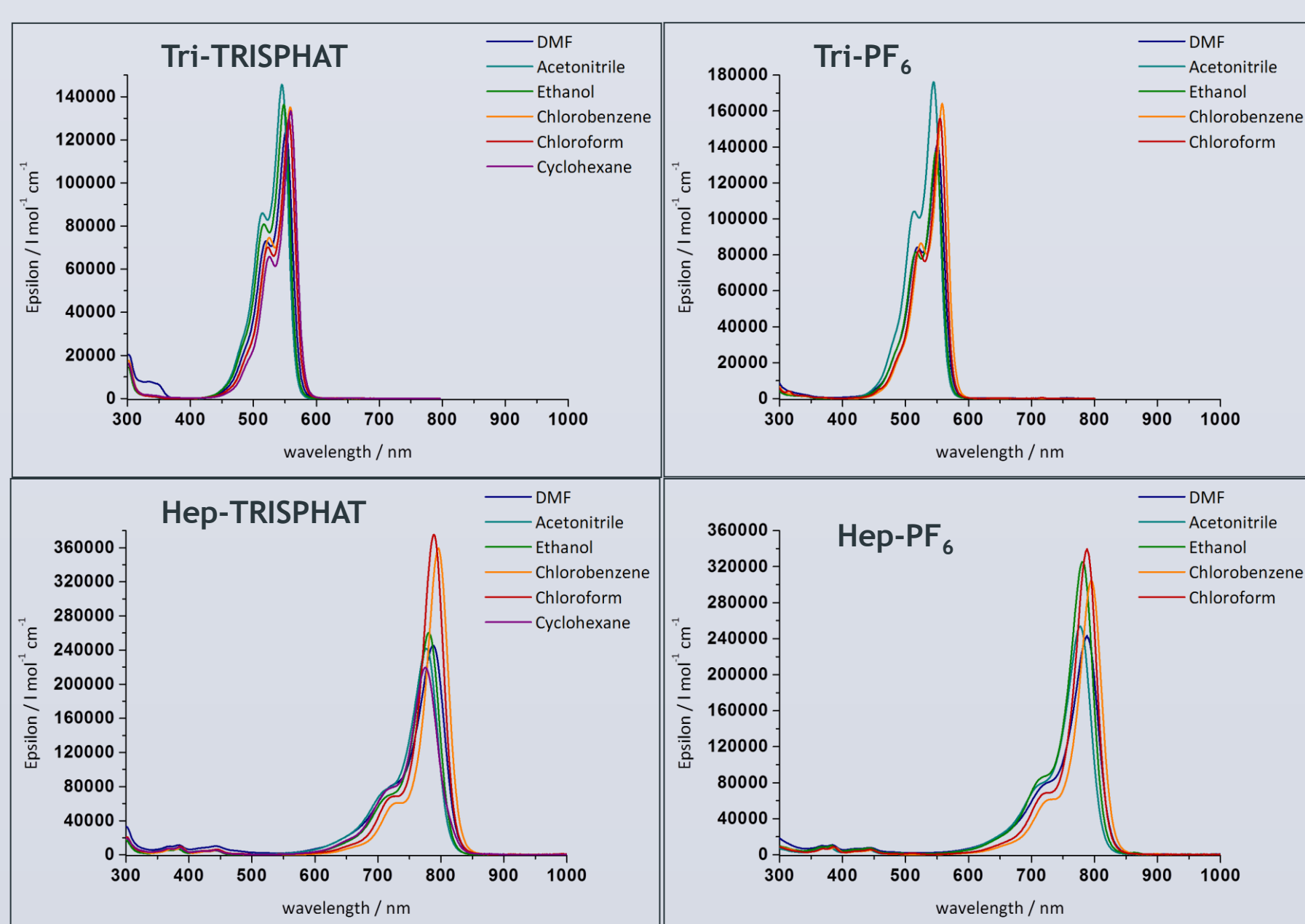


Figure 1: absorption spectra of cyanine dyes in solvents of different polarities.

- The counter ion seems to have no influence on λ_{max} .
- λ_{max} is only shifted by a few nm when the solvent is changed.
- ϵ and IAC^a show that the dyes are strong absorbers. The PF₆ salts give higher values than the TRISPHAT salts.
- The oscillator strength indicates 1-electron transitions for trimethines and >1-electron transitions for heptamethines.

Dye	Solvent	$\lambda_{max}(abs)$ nm	ϵ (λ_{max}) L mol ⁻¹ cm ⁻¹	log ϵ	IAC ^a $\times 10^{18}$ L mol ⁻¹ cm ⁻¹ s ⁻¹	f ^b	$\lambda_{max}(em)$ nm	λ_s ^c nm
Tri-TRISPHAT	DMF	550	124'000	5.09	6.87	0.99	567	17
	Acetonitrile	544	146'000	5.16	7.96	1.15	559	15
	Ethanol	548	136'000	5.13	7.50	1.08	564	16
	Chlorobenzene	557	135'000	5.13	7.01	1.01	574	17
	Chloroform	555	129'000	5.11	6.65	0.95	570	15
Tri-PF ₆	Cyclohexane	558	133'000	5.13	6.34	0.91	572	14
	DMF	550	141'000	5.15	8.06	1.16	567	17
	Acetonitrile	544	176'000	5.25	9.80	1.40	560	16
	Ethanol	548	137'000	5.14	7.60	1.09	563	15
	Chlorobenzene	558	164'000	5.22	8.11	1.16	571	13
Hep-TRISPHAT	Chloroform	555	156'000	5.19	7.75	1.11	567	12
	DMF	787	245'000	5.39	10.30	1.47	813	26
	Acetonitrile	777	242'000	5.38	9.74	1.40	795	18
	Ethanol	781	260'000	5.42	9.07	1.31	799	18
	Chlorobenzene	796	360'000	5.56	9.83	1.41	809	13
Hep-PF ₆	Chloroform	789	375'000	5.57	10.80	1.55	808	19
	Cyclohexane	775	219'000	5.34	8.88	1.27	799	24
	DMF	788	243'000	5.39	10.10	1.46	806	18
	Acetonitrile	777	254'000	5.40	10.00	1.44	796	19
	Ethanol	781	325'000	5.51	11.50	1.66	798	17
	Chlorobenzene	795	305'000	5.48	9.16	1.32	811	16
	Chloroform	788	340'000	5.53	10.30	1.48	803	15

Table 1: Experimental and calculated optical properties of cyanine dyes in different solvents.

^a integrated absorption coefficient, ^b oscillator strength $f = 4.31 \times 10^{-9} \cdot \int \epsilon(\nu) d\nu$, ^c Stokes shift
PF₆ dyes were not soluble in cyclohexane.

ELECTROCHEMICAL ANALYSIS

Oxidation and reduction potentials (E^0_{ox} and E^0_{red}) have been calculated from cyclic voltammograms measured in DMF or TFE (2,2,2-trifluoroethanol) and are visualized in **Figure 2**. It could be shown that the oxidation and reduction potentials of the dyes in solution are hardly influenced by the counter ion. This observation meets the expectation that the chosen counter ions are not redox active in the potential window used in solar cells. Furthermore, we can deduce from the obtained redox level, that the dyes are suitable as electron donor materials in solar cells with PCBM or C₆₀ as the acceptor.

Cyanine dye	E^0_{ox} vs. NHE (V)	E^0_{red} vs. NHE (V)	E^0_{ox} (eV)	E^0_{red} (eV)
TRI-TRISPHAT	1.41*	-0.72	-5.91*	-3.78
TRI-PF ₆	1.41*	-0.72	-5.91*	-3.78
Hep-TRISPHAT	0.87	-0.30	-5.37	-4.20
Hep-PF ₆	0.87	-0.30	-5.37	-4.20

Table 2: Summary of electrochemical data

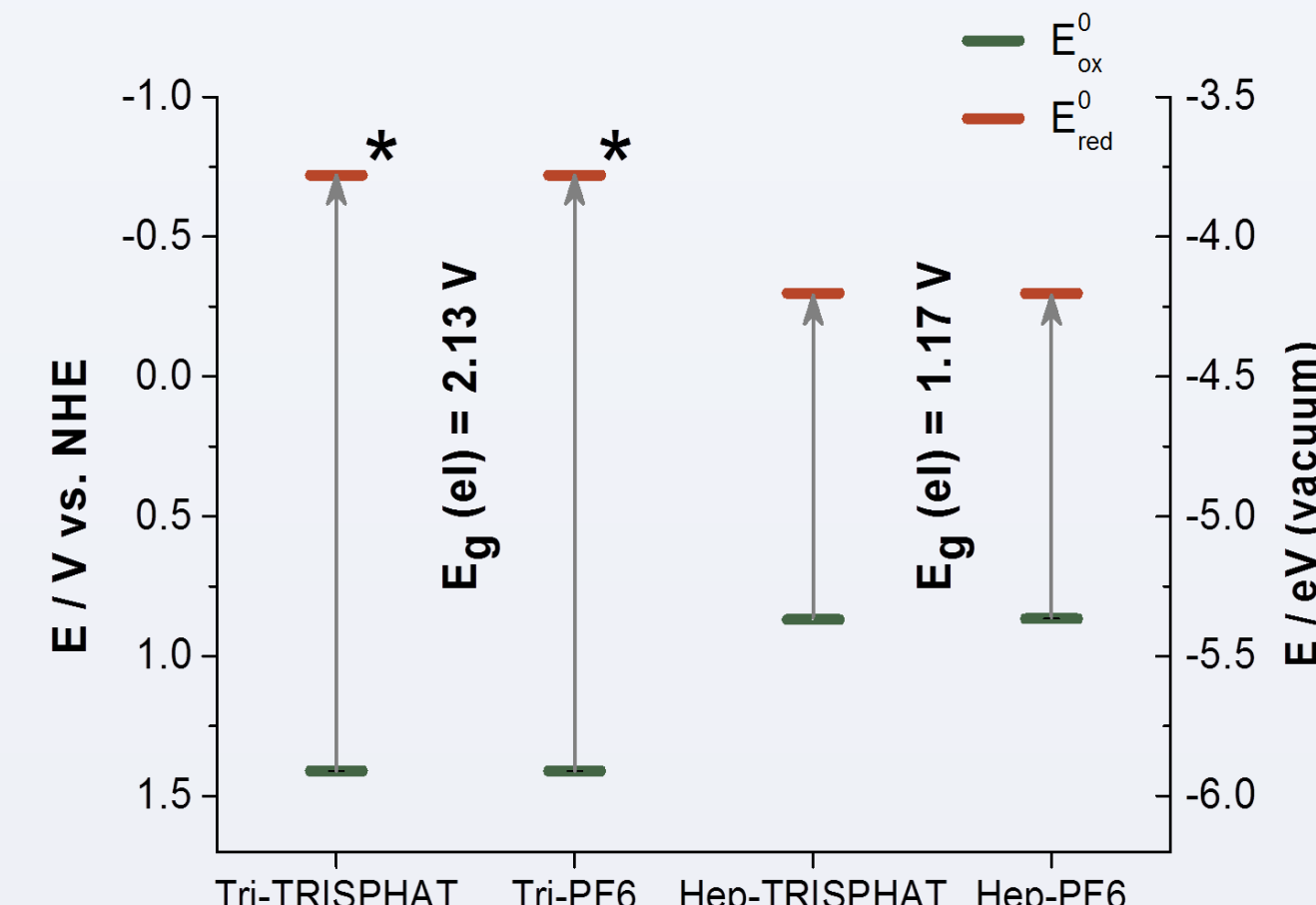
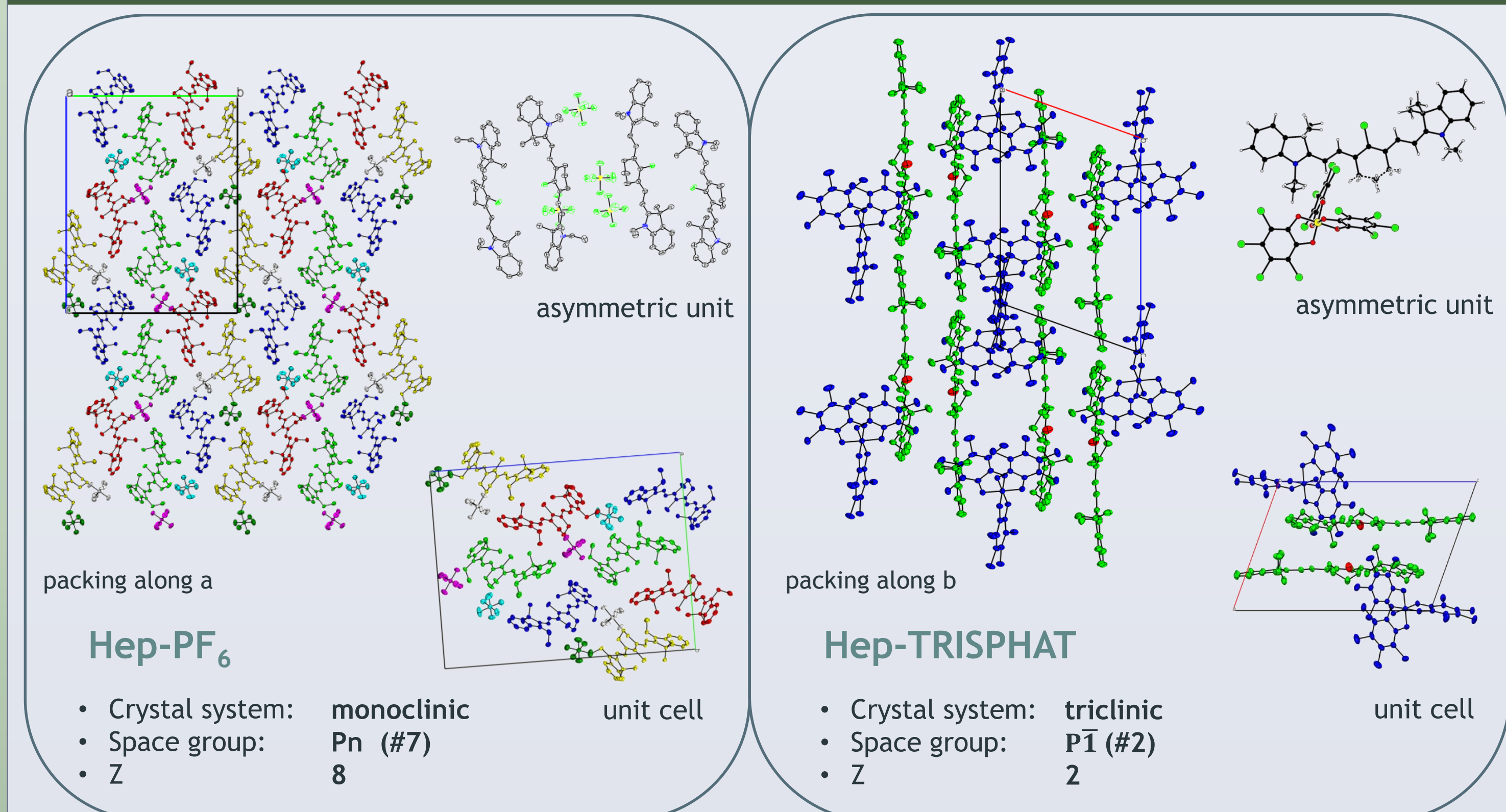


Figure 2: comparison of E^0_{ox} and E^0_{red} of heptamethine and trimethine dyes with different counter ions.

* = these values are derived from measurements in TFE, because oxidation of trimethine dyes is not reversible in DMF. All other values from DMF.

It can be seen that the elongation of the polymethine chain from trimethine to heptamethine leads to a higher E^0_{ox} and a lower E^0_{red} and thus a lower bandgap.

X-RAY CRYSTAL STRUCTURES OF HEPTAMETHINES



FURTHER ANALYSIS AND SOLAR CELLS

	X-Ray crystal structure	Thermal Behavior	Thin Film Absorption
Hep-TRISPHAT	more order on short range	only one symmetry for cyanine cation	melting point at 182 °C, crystallization upon cooling
Hep-PF₆	less order on short range	four different symmetries for cyanine cation	no melting point, decomposition at 273 °C

Bilayer solar cells*

	V_{oc} V	J_{sc} mA cm ⁻²	FF %	η %
Hep-T	0.63	7.1	52.3	2.3
Hep-P	0.38	5.7	64.3	1.4

ITO/MoO₃(5nm)/Dye/C₆₀/Alq₃(2nm)/Ag(80nm)

* Data from Hui Zhang

- V_{oc} with TRISPHAT much higher than with PF₆ (not expected from redox levels in solution)
- better solar cell performance might be related to more ordered solid state structure
- more analysis of the thin films of the dyes with different counterions is required.

CONCLUSIONS & OUTLOOK

- The presented cyanine dyes are easily synthesized in very high purity and have promising optical and electrochemical properties for the application in organic solar cells.
- Single crystals suitable for X-ray crystal structure determination were obtained and the crystal structure Hep-TRISPHAT counterion is highly ordered compared to the salt Hep-PF₆.
- Hep-TRISPHAT gives higher performance in solar cells than Hep-PF₆, possibly due to a more regular solid state structure, which might be beneficial for charge transport
- Thin films spin-coated from different solvents will be analyzed
- Connection between X-ray crystal structure and thin films?
- Further analysis methods of films?
- Studies of Bulk heterojunction blend films together with PCBM are ongoing
- Synthesis of new cyanine dye structures with absorption above 750 nm is ongoing



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