Synthesis and Characterization of Conjugated Poly(diindenopyrazine)s

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Abstract

Organic light emitting diodes (OLEDs) are the subject of ongoing research due to their potential as active material of electroluminescent devices (e.g. for full-color displays).[1] Blue light emitting organic materials often show poor color purity, relatively low efficiency, and lifetimes of only 12000 h at 7 cd/A.[2] Due to this there is still much interest in developing new blue emitting organic materials with optimized optoelectronic properties. In 2009, Park *et al.* presented the synthesis of the tetraalkyldiindenopyrazine homopolymer poly[6,6,12,12-tetrakis(2-ethylhexyl)-6,12-dihydrodiindeno[1,2-*b*:1',2'-*e*]pyrazin-2,8-diyl] (**PEHIP**) that shows a photoluminescence (PL) maximum at 470 nm. This feature makes it a promising new blue emitting material for OLEDs.[3] We synthesized a series of poly(diindenopyrazine)s (**PIP**s) with different alkyl side chains (**PEHIP**, **PC8IP**, **PC12IP**, **PC15IP**) recently and investigated their optical properties such as absorption (UV/Vis) and PL spectra in solution and solid state. Protonation and complexation (with BF_3) of diindenopyrazine units of **PEHIP** regarding changes of the absorption and PL spectra were studied as well. Furthermore, we determined the photoluminescence quantum yields (PLQYs) and studied the photoluminescence quenching of **PEHIP** after interaction with CdSe quantum dots (QDs) in polymer/QD blends. Finally, a diindenopyrazine/dithienyl-benzothiadiazole based alternating copolymer (**PIPTBTT**) was synthesized.

Synthesis

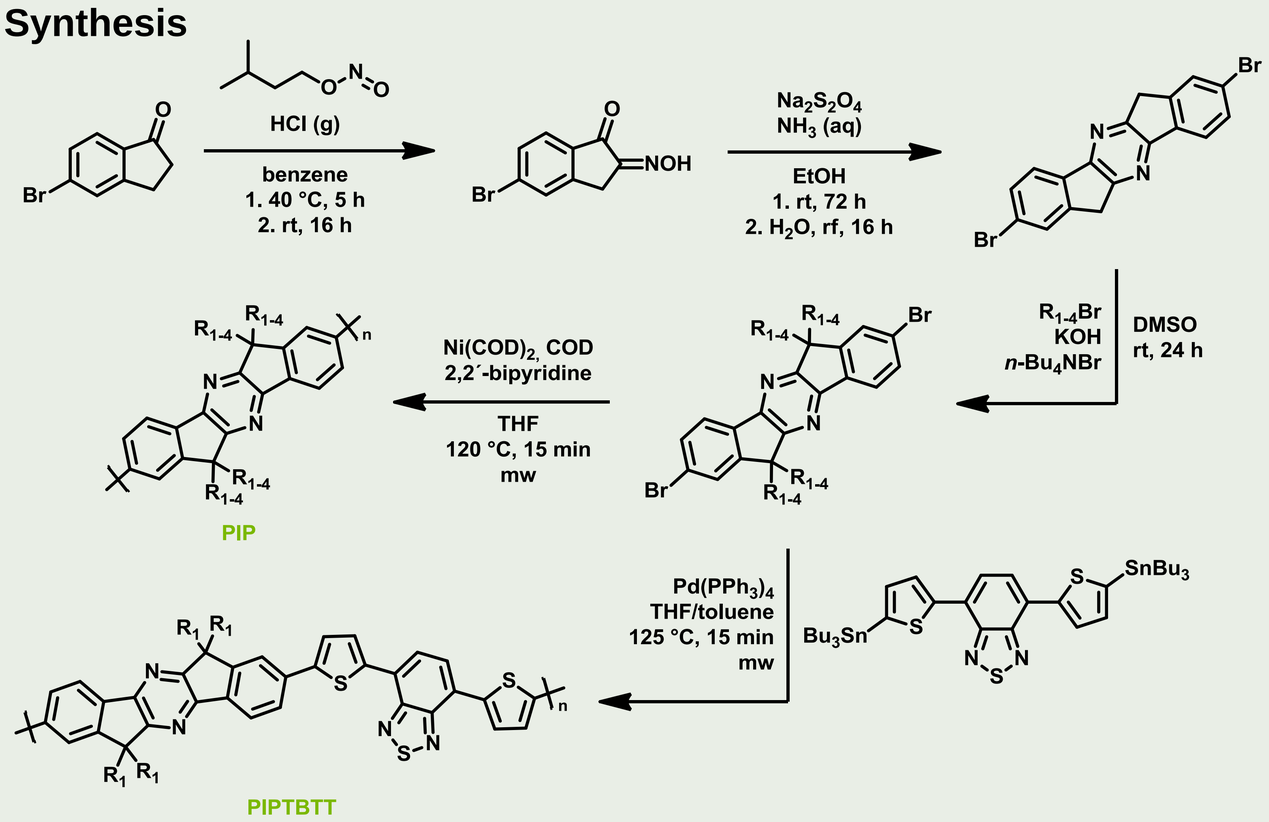


Figure 1: Synthesis of the homopolymeric **PIP**s (R_1 = -ethex (**PEHIP**), R_2 = -C_8H_{17} (**PC8IP**), R_3 = -$C_{12}H_{25}$ (**PC12IP**), R_4 = -$C_{15}H_{31}$ (**PC15IP**)) and the alternating copolymer **PIPTBTT**.

Changes in the Optical Properties of PEHIP

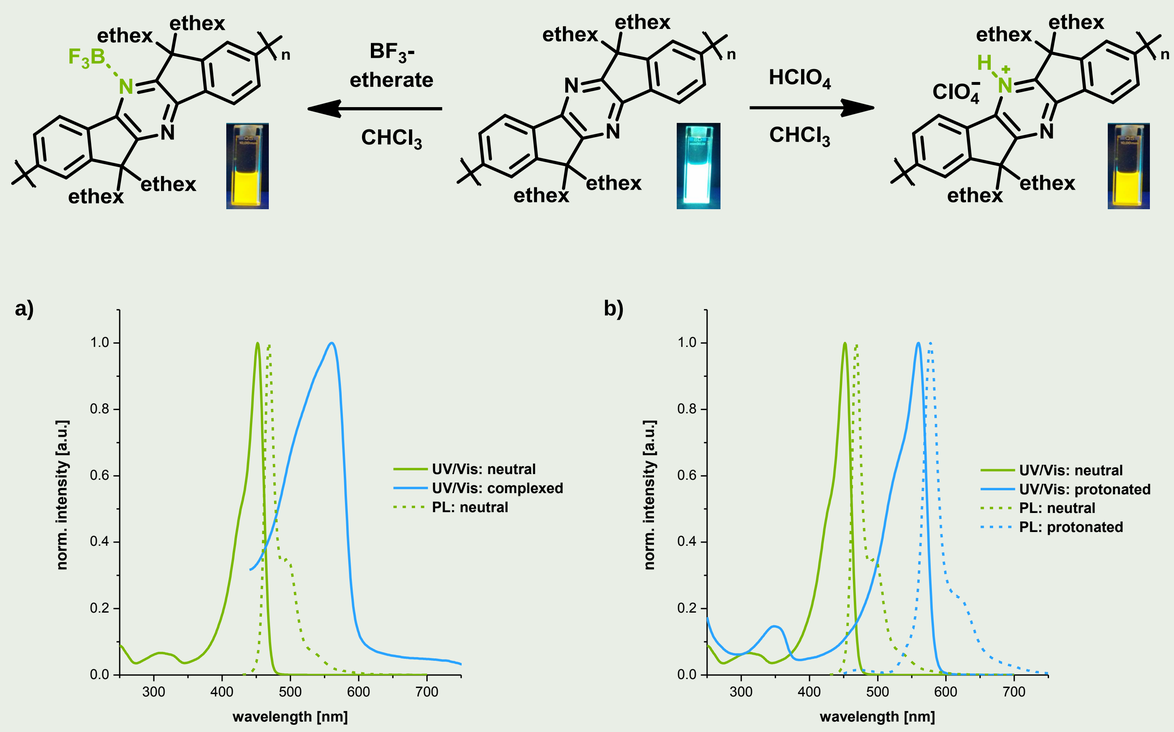
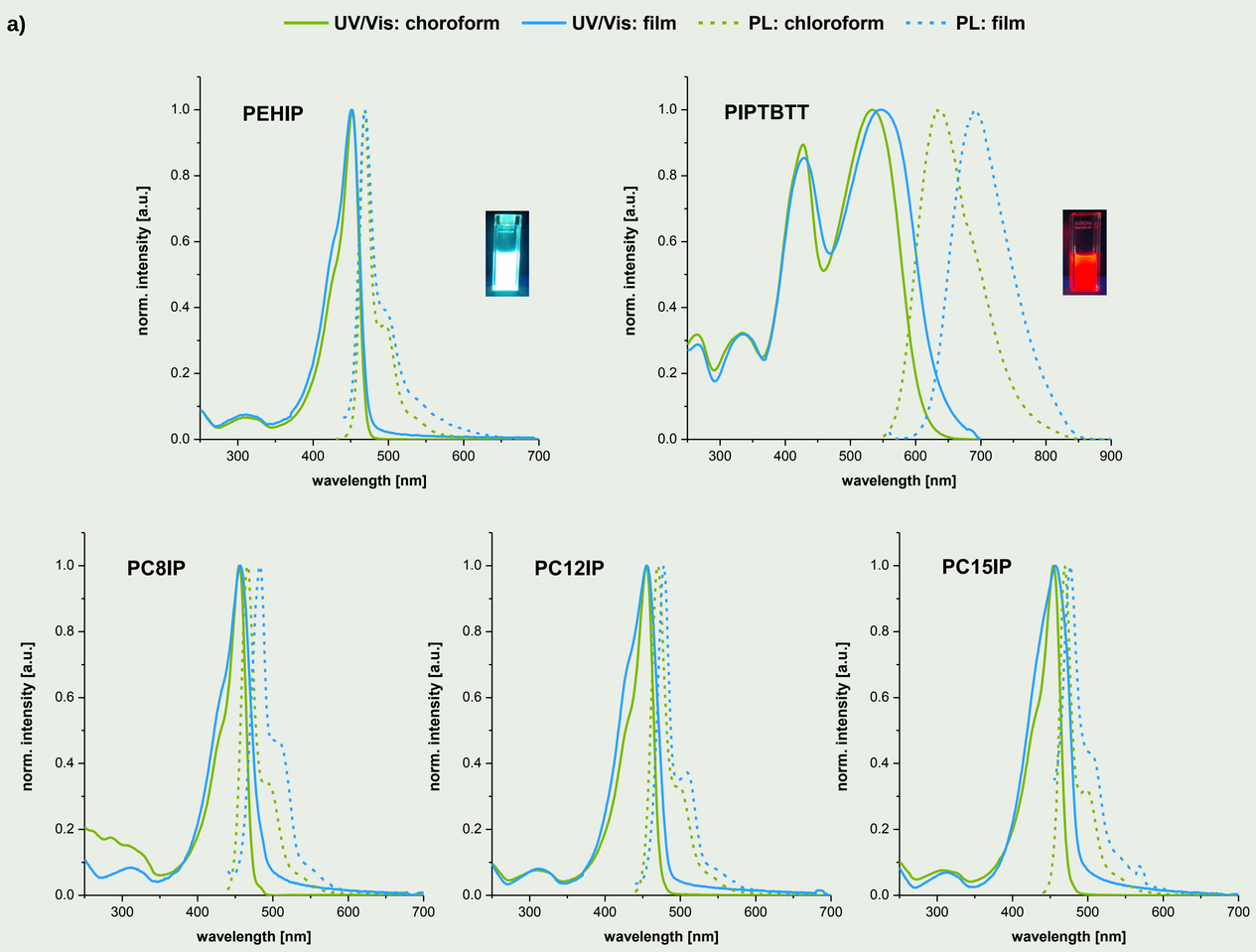


Figure 3: Changes in the optical properties of **PEHIP** due to a) complexation with BF_3 and b) protonation with $HClO_4$ ($\lambda_{ex.}$ = 420 nm).

Properties and Optical Spectra



b)

	fraction	M_n [g/mol]	M_w [g/mol]	PDI	$\lambda_{max.\ abs.}$ [nm] ($CHCl_3$/film)	$\lambda_{max.\ PL}$ [nm] ($CHCl_3$/film)	HOMO[a] [eV]	LUMO[b] [eV]	E_g [eV]
PEHIP	DCM	92000	288000	3,1	452/451	468/469	-5,96	-3,08	2,88
PC8IP	$CHCl_3$	46500[c]	1035000[c]	22,3[c]	455/457	466/482	-5,91	-3,08	2,83
PC12IP	$CHCl_3$	114000	286000	2,5	455/456	470/478	-5,93	-3,11	2,82
PC15IP	$CHCl_3$	232000	582000	2,5	454/457	469/477	-5,93	-3,11	2,82
PIPTBTT	$CHCl_3$	31600	63200	2,0	428,534/ 428,548	632/691	-5,59	-3,37	2,22

[a] HOMO was estimated by AC2 measurements
[b] LUMO was calculated from the optical bandgap E_g and the estimated HOMO
[c] due to solubility problems GPC was measured at high temperature (135 °C) using TCB as eluent

Figure 2: a) Comparison of the normalized UV/Vis and PL spectra for **PIP**s ($\lambda_{ex.}$ = 420 nm) and **PIPTBTT** ($\lambda_{ex.}$ = 520 nm); b) Summerized physical and optical properties of **PIP**s and the **PIPTBTT**.

PLQYs of PIPs and Interaction of PEHIP with CdSe Quantum Dots

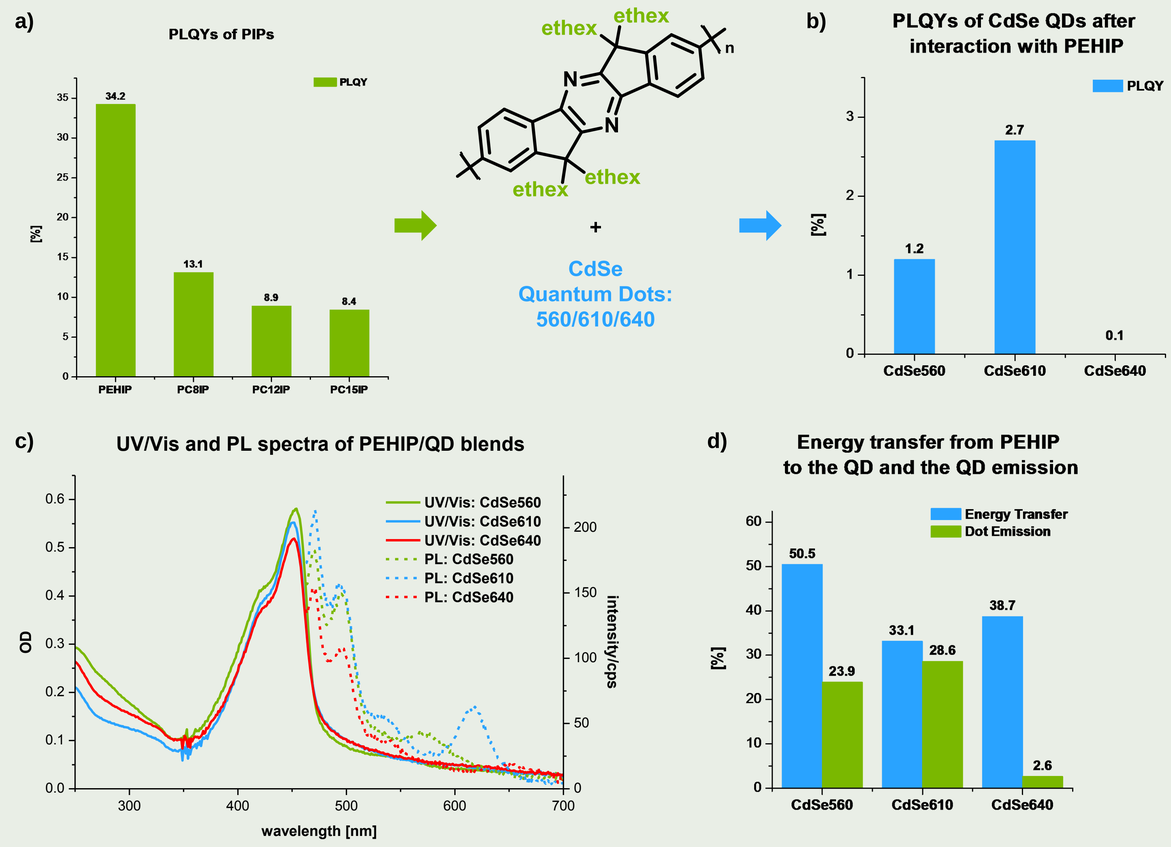


Figure 4: a) PLQYs of **PIP** films; b) PLQYs of the CdSe QDs after interaction with **PEHIP**; c) UV/Vis and PL spectra of the **PEHIP**/QD blends with different CdSe QDs: CdSe560, CdSe610, CdSe640 (concentration: 5 mg CdSe QD and 5 mg polymer/mL toluene; $\lambda_{ex.}$ = 452 nm); d) Percentage of the energy transfer from **PEHIP** to the QDs and percentage of the QD emission.

Conclusion

- Successful synthesis of different blue emitting **PIP**s and a red emitting **PIPTBTT**
- A red shift of the PL features for polymer films can be observed for the **PIP**s with unbranched alky side chains (e.g. **PC8IP**), probably caused by crystallization
- Protonation and complexation of **PEHIP** cause a strong bathochromic shift in the optical spectra
- **PEHIP** shows the best PLQY and was used for investigations of the energy transfer from the polymer to CdSe quantum dots

References

[1] D. Kumar, K. R. J. Thomas, Y.-L. Chen, Y.-C. Jou, J.-H. Jou, *Tetrahedron* **2013**, *69*, 2594-2602.
[2] Y.-I. Park, J.-H. Son, J.-S. Kang, S.-K. Kim, J.-H. Lee, J.-W. Park, *Chem. Commun.* **2008**, 2143-2145.
[3] J. S. Kang, S.-K. Kim, J.-Y. Jung, J.-H. Lee, J.-Y. Jaung, J.-W. Park, *Mol. Cryst. Liq. Cryst.* **2009**, *514*, 171-179.