Synthesis and Characterization of Phenoxy-substituted Poly(phenylene vinylene)s

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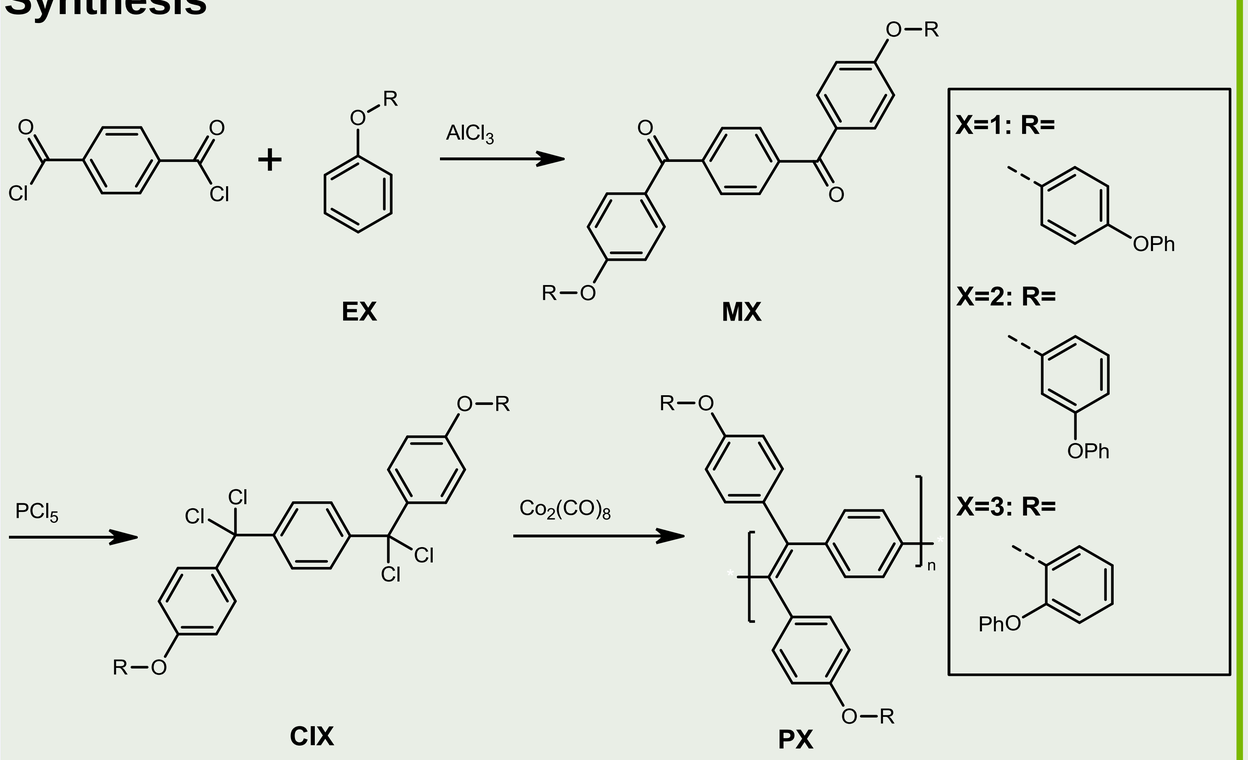
Introduction

Materials with aggregation-induced emission (AIE), so-called AIEgens, have attracted much academic and industrial attention, because of their high application potential in fluorescence biosensors and optoelectronic devices. AIEgens show a weak photoluminescence in dilute solutions, but become highly emissive upon aggregation, through a restriction of intramolecular motions.[1] In contrast, the commonly observed aggregation-caused quenching often limits an application in concentrated solution or solid phase.[1] Tetraphenylethylene and corresponding polymers are well-known representatives of AIE-active materials. In previous work of our group, phenoxy side groups were introduced into a poly(tetraphenylethylene) backbone, resulting in a remarkable increase of the solid state photoluminescence quantum yield from 37% to 73%.[2] Now, the effect of an elongation of the phenoxy into bis(phenoxy) side chains was studied. Three regioisomers were synthesized by reductive polyolefination reaction, their optical properties were investigated and compared, regarding their AIE characteristics.

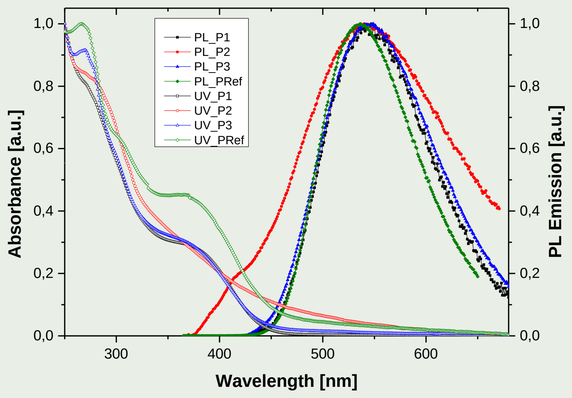
Synthesis

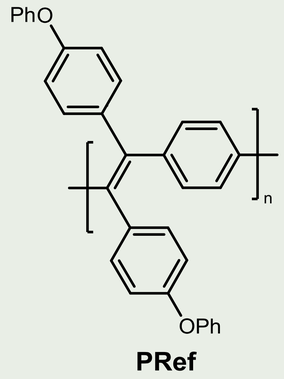


GPC Results

Polymer	M_n [g/mol]	M_w [g/mol]	PDI	DP
P1	14000	23600	1.69	22
P2	6230	16500	2.64	10
P3	7060	11900	1.68	11

Absorption and Photoluminescence properties





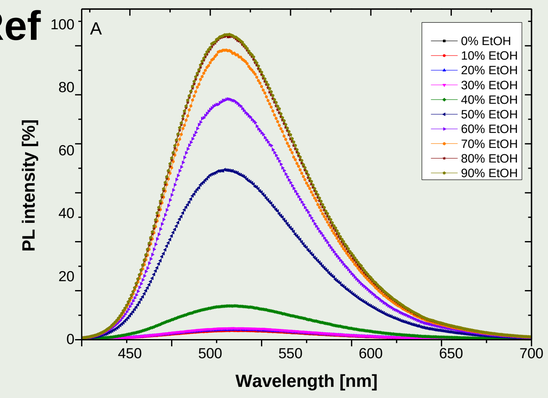
PRef

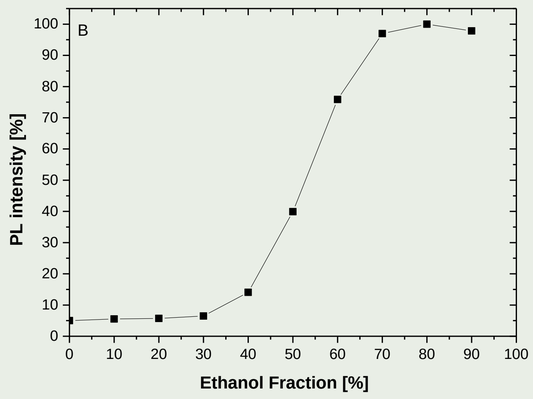
Normalized absorbance and photoluminescence spectra of polymers **P1-P3** and **PRef**[2] in chloroform.

Polymer	UV/VIS λ_{max} [nm]	PL λ_{max} [nm]	PLQY solution [%]	PLQY solid [%]
PRef[2]	364	534	2.0	73
P1	360	547	2.8	2.5
P2	NA	540	0.2	NA
P3	355	549	1.7	0.6

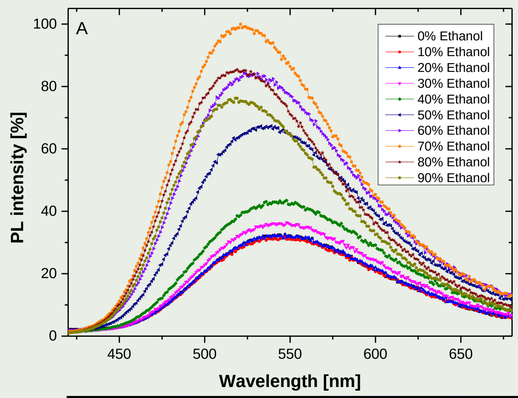
AIE/ACQ characteristics

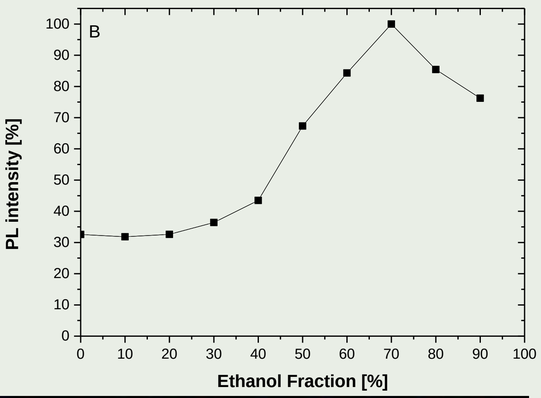
PRef



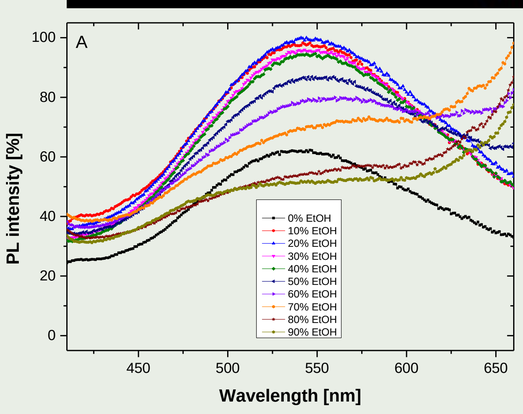


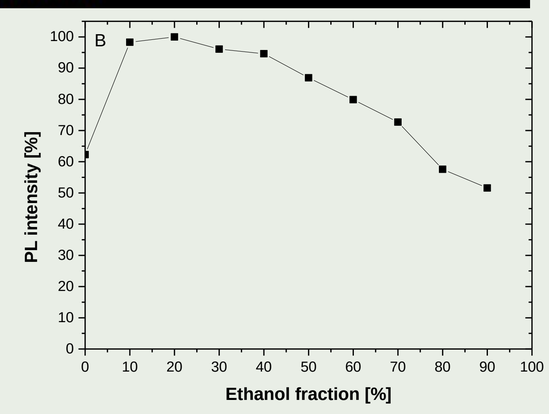
P1



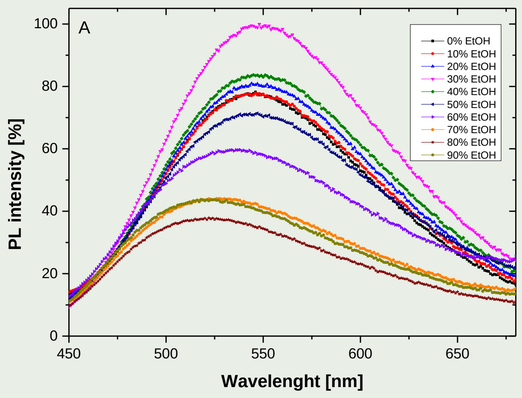


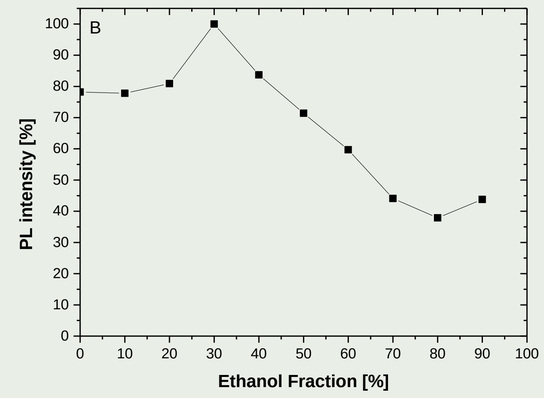
P2





P3





PL intensity of Polymers **P1**-**P3** and **PRef** in different $CHCl_3$/ethanol mixtures (polymer concentration 10^{-5} M).

Conclusion

- Three novel polymers **P1**-**P3** have been successfully synthesized via reductive polyolefination.
- Introduction of additional phenoxy groups increases the Stokes shift but decreases the photoluminescence of the solid polymers.
- ACQ effect of polymers **P1**-**P3** outweighs the AIE effect at some concentration of the poor solvent (ethanol) in chloroform/ethanol mixtures.
- Comparison of the regioisomeric polymers indicates that an angular arrangement at the diphenoxybenzene unit increases the ACQ effect in comparison to a linear arrangement.

Quellen

[1] Y. Hong, J. W. Y. Lam, B. Z. Tang, *Chem. Commun*. **2009**, 4332-4353.

[2] S. Baysec, E. Preis, S. Allard, U. Scherf, *Macromol. Rapid Commun.* **2016**, *37*, 1802-1806.