New perylene derivatives for LSC

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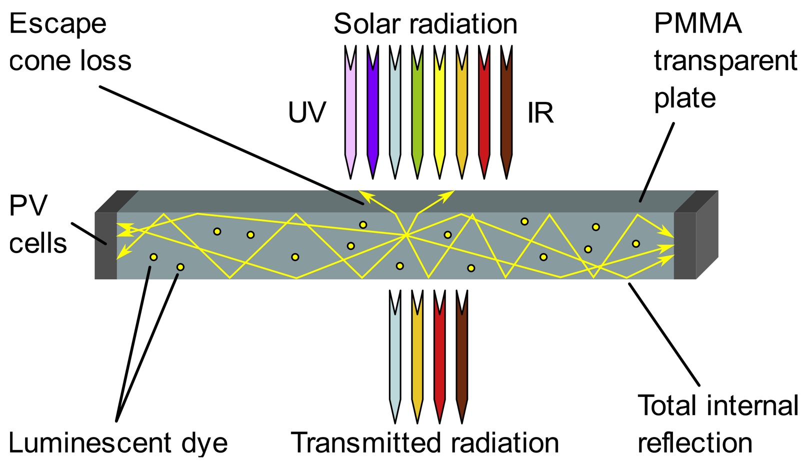
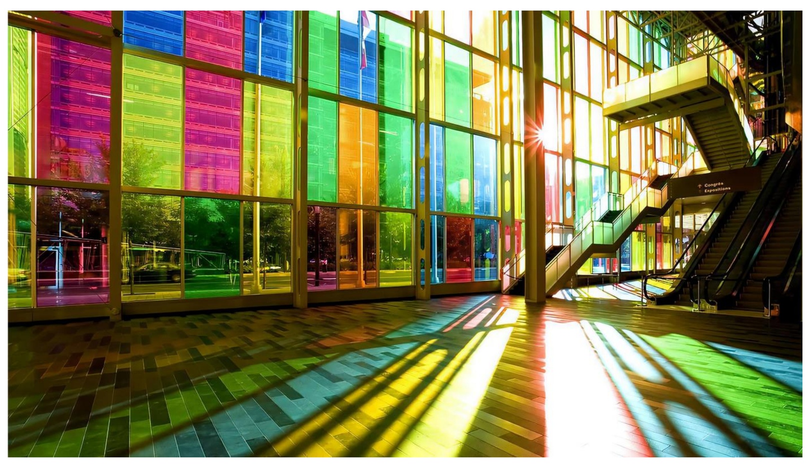


Simplified scheme of a LSC: part of the solar radiation is absorbed by the dye, re-emitted, and concentrated at the edges, where is converted into electricity by photovoltaic (PV) cells.

Introduction

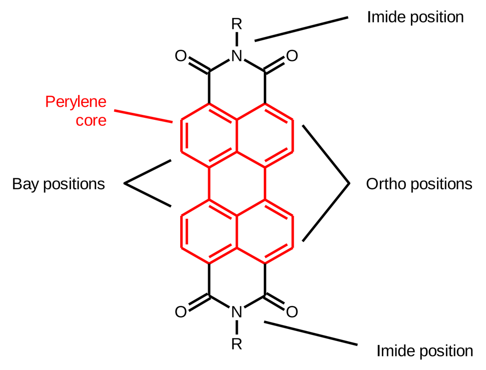
The rapid world population growth and the ever-decreasing amount of fossil fuels are leading to the search for **alternative energy sources** to meet the changed **energy demand**, standing around **15 TW**[1]. The **Sun** provides more than **50 TW** of power - much more than the estimated demand - but the solar cells used to convert sunlight into electricity can collect only incident photons and are also rather expensive. **Luminescent Solar Concentrators** (**LSC**) instead allow to collect even the **diffused sunlight** and to **reduce the cost** of the energy conversion. Such devices consist in a **slab of a polymeric material** in which a highly **luminescent dye** is dispersed. Sunlight is absorbed by the dye, re-emitted, and **concentrated at the edges** thanks to total internal reflection, where **small solar cells** are placed. LSC devices are **transparent** and can be used as structural elements (e.g. windows)[2].



Palais des Congrès de Montréal, Canada: Luminescent Solar Concentrators are used both as power conversion devices and structural elements (windows).

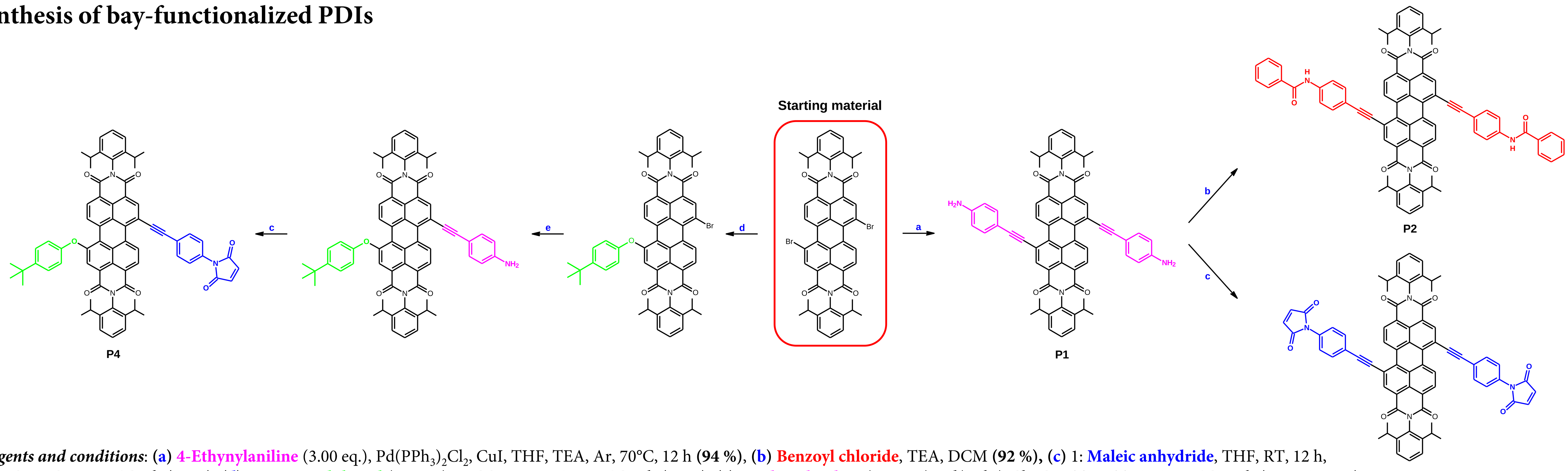
Perylene diimide dyes (PDI)

Perylene diimides showed interesting properties, such as quite **broad** absorption and emission **spectra**, **high quantum yields**, and the **ease** with which they can be **functionalized**[3]. The starting material can be decorated with a variety of substituents in three different positions, **ortho, bay, and imide**, to improve the **solubility** and modulate the **emissive properties**.



Different substitution positions of a PDI molecule: imide, ortho, and bay. The perylene core is highlighted in red.

Synthesis of bay-functionalized PDIs



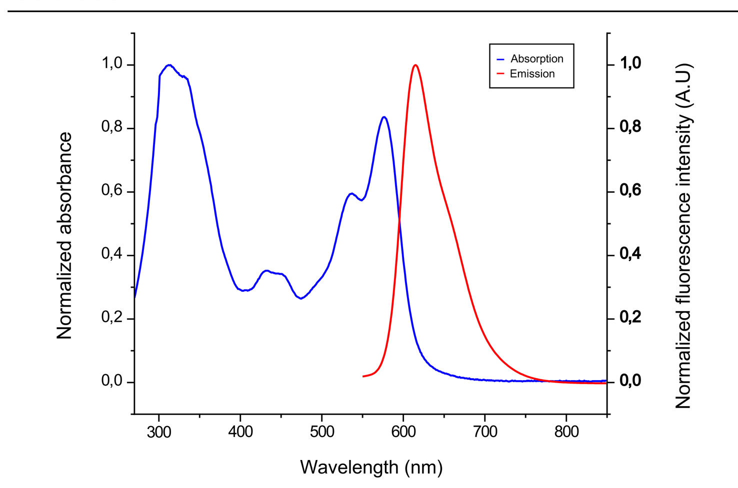
Reagents and conditions: (**a**) **4-Ethynylaniline** (3.00 eq.), $Pd(PPh_3)_2Cl_2$, CuI, THF, TEA, Ar, 70°C, 12 h **(94 %)**, (**b**) **Benzoyl chloride**, TEA, DCM **(92 %)**, (**c**) 1: **Maleic anhydride**, THF, RT, 12 h, 2: Ac_2O, AcONa, 100°C,1 h **(60 %)**, **(d)** ***4-tert*-Butylphenol** (1.00 eq), K_2CO_3, NMP, Ar, 100°C, 4 h **(50 %)**, (**e**) **4-Ethynylaniline** (1.50 eq.), $Pd(PPh_3)_2Cl_2$, CuI, THF, TEA, Ar, 70°C, 12 h (**quantitative**).

Spectroscopic characterization

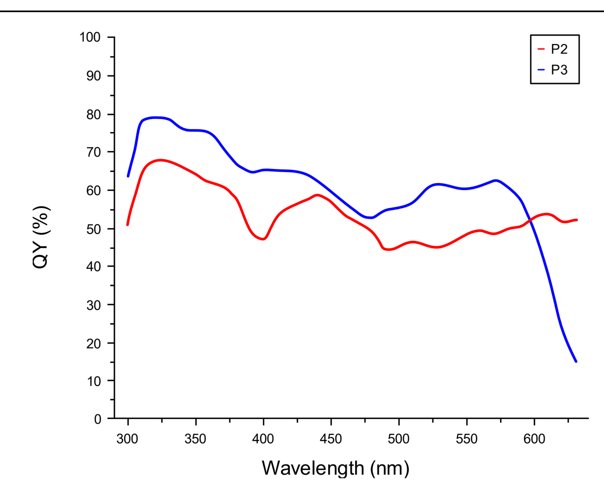
Compound	Solvent	Absorption spectra λ_{abs} (nm)	ε (M^{-1} cm^{-1})
P1	CH_2Cl_2	333	44732
		474	19093
		609	20969
P2	CH_2Cl_2/MeOH 1:1	227	87814
		320	37682
		456	12867
		577	26234
P3	CH_2Cl_2	226	38506
		318	24346
		589	12722

Fluorescence quantum yield (QY)

λ_{exc} (nm)	QY (%) P1	QY (%) P2	QY (%) P3
310-370	< 1	65.0	74.8
410-470	< 1	55.4	61.0
530-600	< 1	48.9	59.2



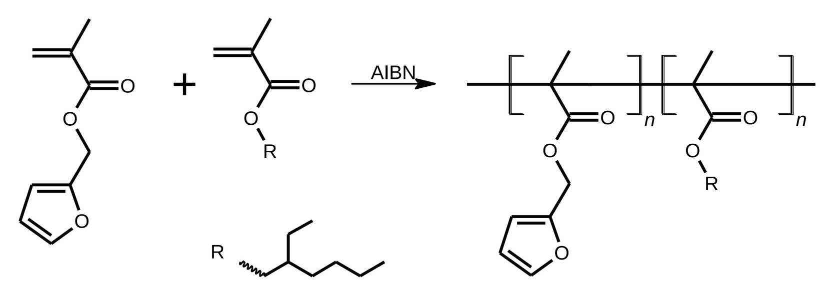
Absorption and emission spectra of P3 in $CHCl_3$: the absorption spectra is broad, but the Stokes' shift is quite small.



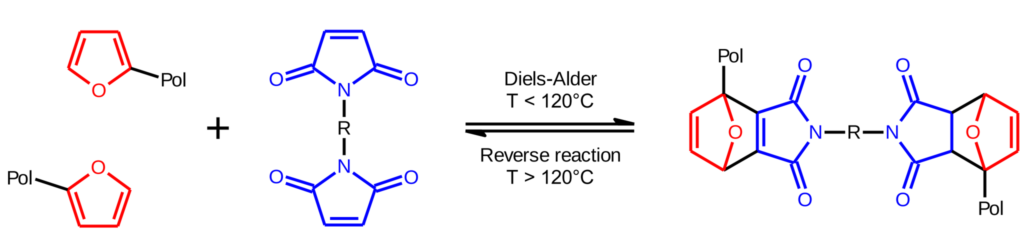
Comparison between the QY of P2 and P3: **P3** has stronger electron-withdrawing groups, hence a higher QY than **P2**.

Diels-Alder matrices

P3 and **P4** have been synthesized in order to take advantage of the maleimide moiety and perform **Diels-Alder** (DA) reactions in presence of furan-containing polymer matrices[4]. Perylene is **covalently linked** to the polymeric **matrix** and the overall performances of the LSC device are enhanced. Moreover, the Diels-Alder reaction is **reversible**, and it is possible to **repair** the sheet **simply heating** it above 120°C.



DA matrix precursor: furfuryl-ethylhexyl methacrylate copolymer.



Thermoreversible crosslinked DA matrix: the reactants are maleimide (dienophile) and furan (diene) rings. The reverse reaction is favoured at high temperature.

	Optical efficiency, η_{opt} (%)	Electrical efficiency, η_{el} (%)
PMMA-P3	0.61 ± 0.06	1.62 ± 0.03
DA30%-P3	0.59 ± 0.08	1.58 ± 0.04

Experimental setups for testing the optical and electrical **efficiencies** of LSC devices.

Conclusions

The functionalization of the **bay positions** causes a strong **variation** of the **optical properties** of the PDI. Strong electron-donor groups as $-NH_2$ are detrimental for the emission properties, whereas increasing the electron-withdrawing character raises the quantum yield.

Diels-Alder matrices have proved to be an **excellent alternative** to conventional **PMMA** matrices. The two are comparable in terms of efficiency but the former's **thermoreversibility** allows to easily repair the sheet, ensuring a **longer service life** and a **more stable performance over time**.

Compound **P4** has been recently synthesized and it has **not been tested yet**. Anyway, the maleimide will be used to link the dye molecule to the polymeric matrix, while the **phenoxy** group should **red-shift** the absorption and the emission **spectra**, and slightly **increase the Stokes' shift**.

References

[1] *Science* 13 Aug **2010**: Vol. 329, Issue 5993, pp. 786-787
[2] *Appl. Opt.* **15**(10) 2299-2300 (1976)
[3] *Chem. Mater.* **2017**, 29, 8395−8403
[4] *Macromol. Mater. Eng.* **2020**, 1900652