Development of molecular cassettes for the excitation energy transfer in the red region of the spectrum

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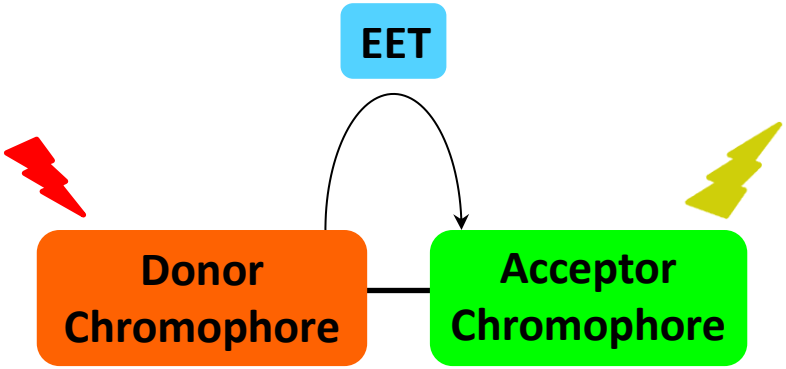
Introduction and background



Excitation Energy Transfer (EET) Cassettes

Advanced materials for photonic technologies:

- Solar harvesting
- Fluorescence microscopy
- Biomolecular probing

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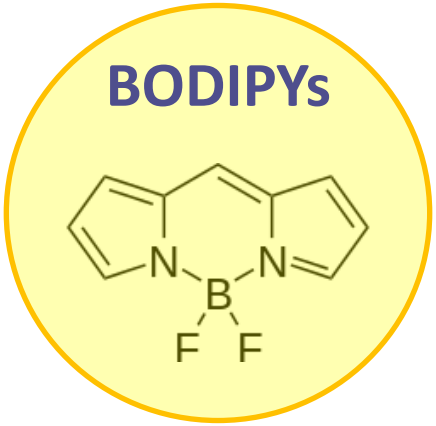
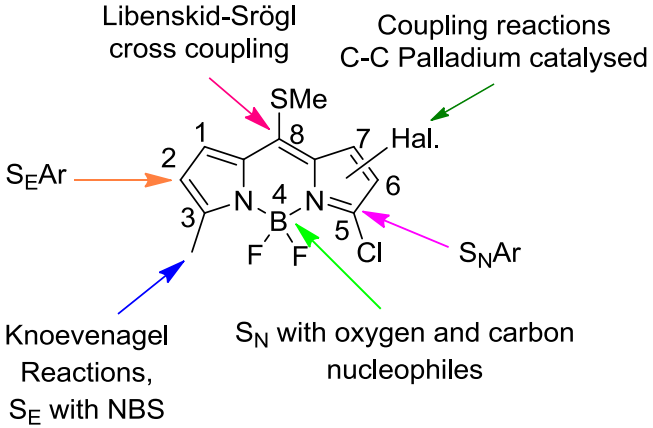
Introduction and background

Modulable organic fluorophores

- High molar absorption coefficients (ε)
- High fluorescence quantum yields (ϕ)
- Sharp fluorescence peaks



Easily derivatizable



APPLICATIONS

Development of photonic tools:
- bioimaging
- chemosensing
- lasing

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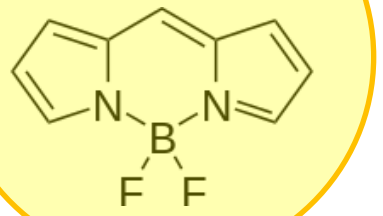
Introduction and background

Small Stokes shifts →
- Reabsorption of emitted light
- Effects from excitation light scattering

BODIPYs



Development of Energy Transfer Cassettes with large pseudo-Stokes shifts

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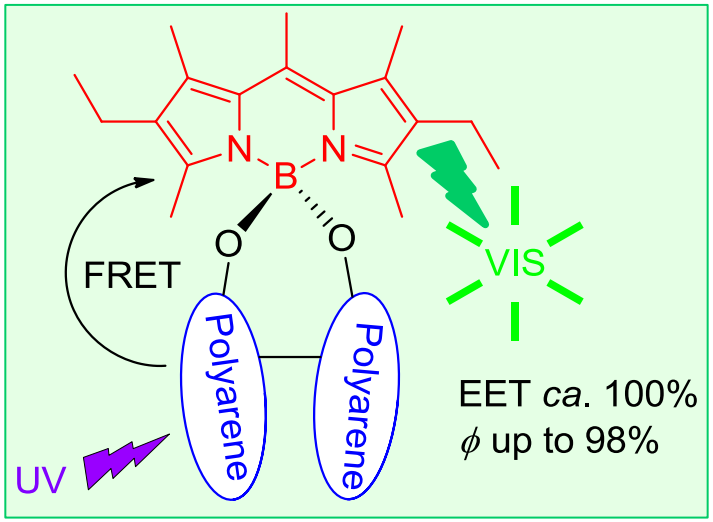
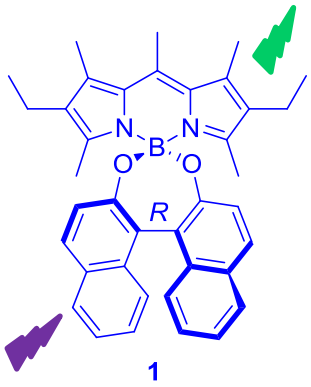
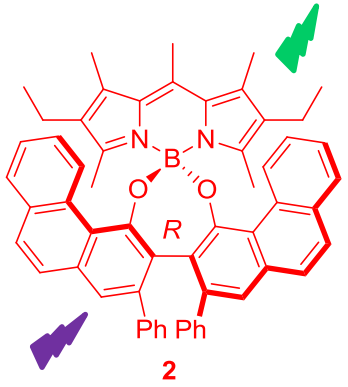
Introduction and background

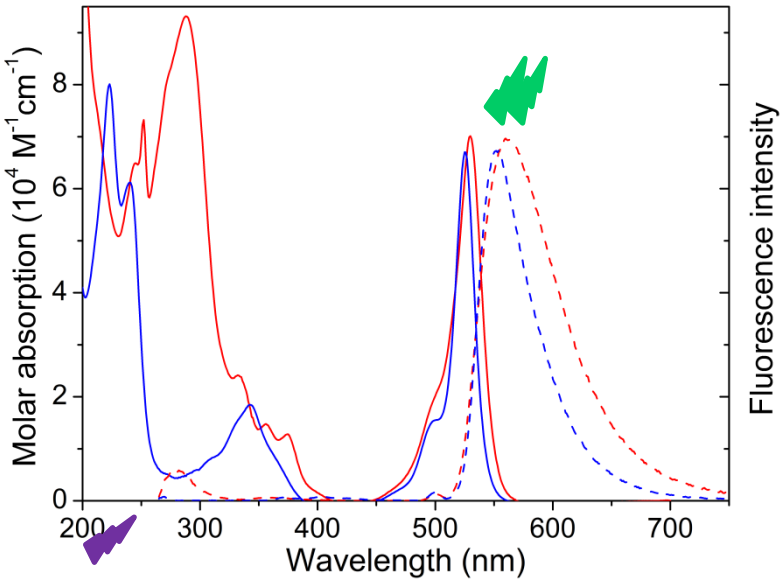






BODIPY	λ_{exc} (nm)	λ_{flu} (nm)	ϕ (%)	$\Delta\nu_{St}$ (cm^{-1})
1	470	546	89	800
	250	546	89	26130
2	470	552	94	750
	250	552	94	9970
		404	0,6	16600

n-hexane



Sánchez-Carnerero, E. M.; Gartzia Rivero, L.; Moreno, F.; Maroto, B. L.; Agarrabeitia, A. R.; Ortiz, M. J.; Bañuelos, J.; López-Arbeloa, I.; de la Moya, S. *Chem. Commun*. **2014**, *50*, 12765.

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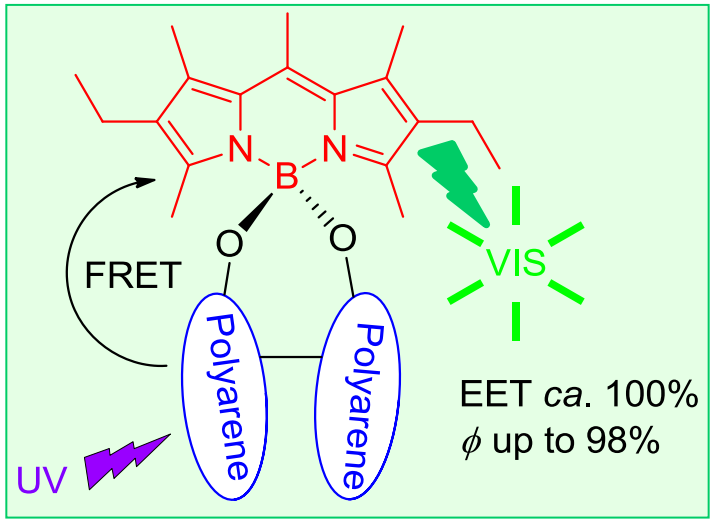
Objectives



Fluorophores with medical applications

red/NIR region

biological window (650 -1000 nm):

- Minimize autofluorescence
- Minimize absorption by water, tissues and cells
- Less light scattering

Deeper penetration by incident light

?

Red emission

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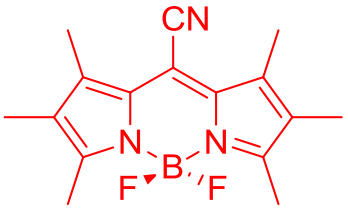
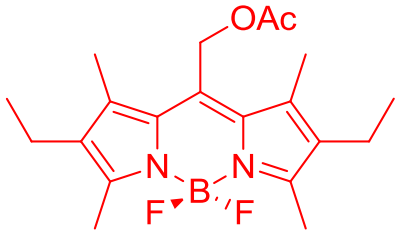
Objectives



PM650

λ_{flu} (hexane) = 599.5
ϕ (hexane) = 0.36

red emission

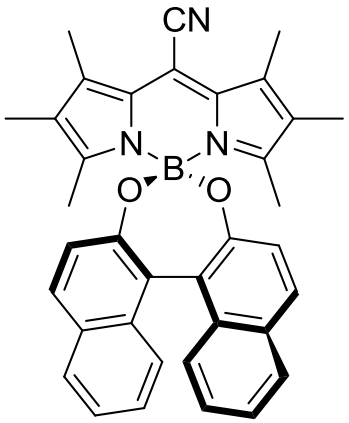


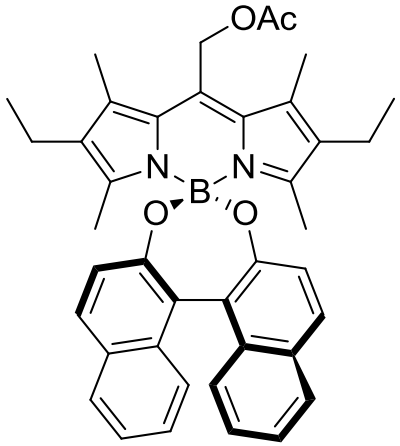
PM605

λ_{flu} (hexane) = 561.5
ϕ (hexane) = 0.74

red emission

Cassette?



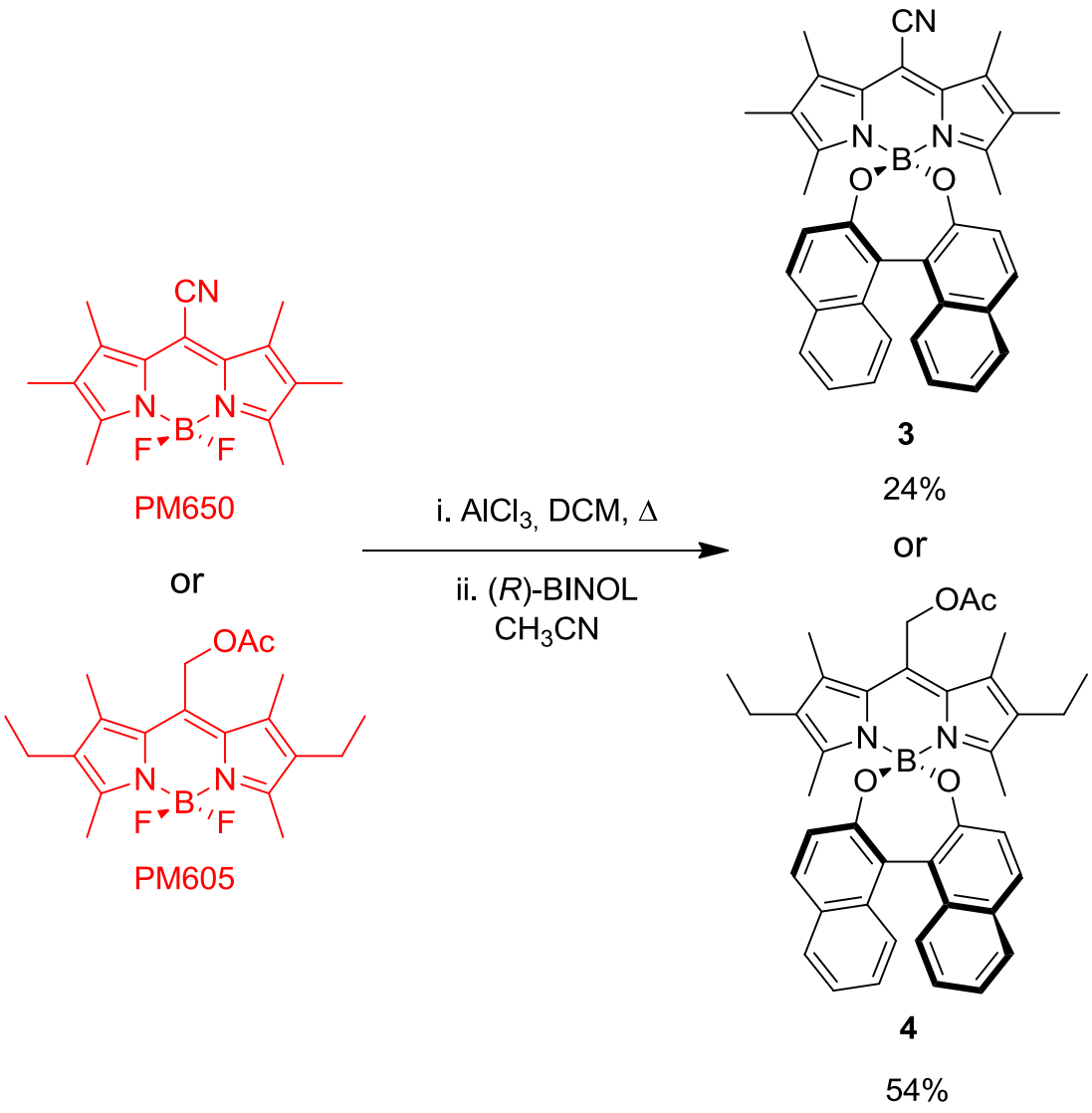


Cassette?

Development of molecular cassettes for the excitation energy transfer in the red region of the spectrum

Results

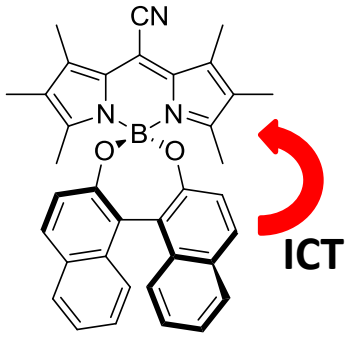
Synthesis



Development of molecular cassettes for the excitation energy transfer in the red region of the spectrum

Results

Photophysical properties



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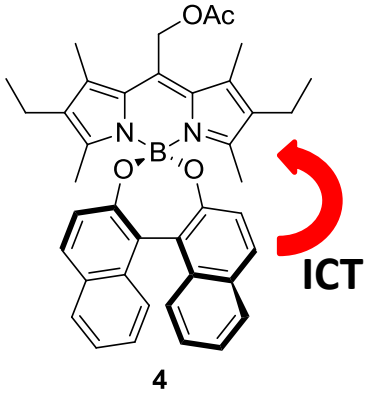

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BODIPY	solvent	λ_{ab} (nm)	$\varepsilon_{max}\cdot10^{-4}$ (M^{-1} cm^{-1})	λ_{fl} (nm)	$\Delta\nu_{St}$ (cm^{-1})	Φ
PM650	*c*-hexane	589.5	5.3	599.5	285	0.36*
	acetone	588.0	3.5	606.0	505	0.11*
3	*n*-hexane	587.0	3.6	**	**	**
	acetone	587.5	3.1	**	**	**
PM605	*n*-hexane	547.5	8.3	561.5	455	0.74
	acetone	542.0	7.1	559.0	560	0.70
4	*n*-hexane	549.5	5.6	579.5	940	0.13
	acetone	545.5	5.3	563.5	585	0.011

*Fluorescence deactivation by ICT due to the strongly electron-withdrawing cyano group.
**No signal was detected.

High deactivation of the fluorescence!!

Problem

Intramolecular Charge Transfer (ICT):
From electron rich *O*-BINOL to electron poor BODIPY

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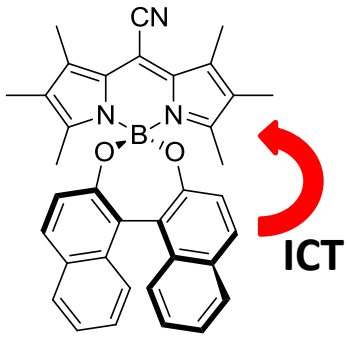
Results

Photophysical properties

Solution: ICT ↓ → ϕ ↑

Less electron-donor *O*-BINOL



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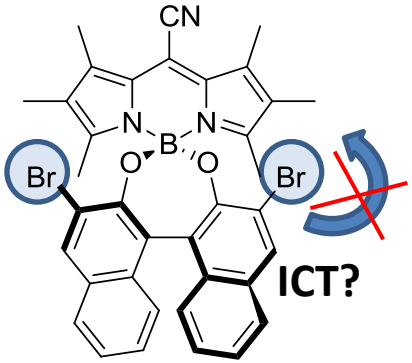

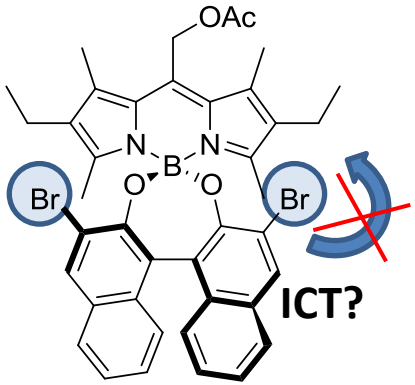

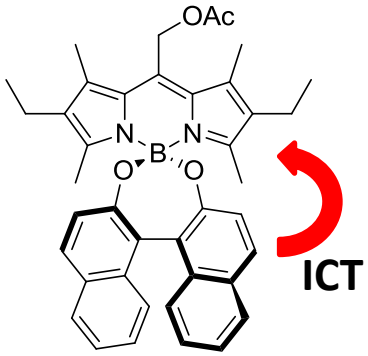

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High deactivation of the fluorescence!!

Problem

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From electron rich *O*-BINOL to electron poor BODIPY

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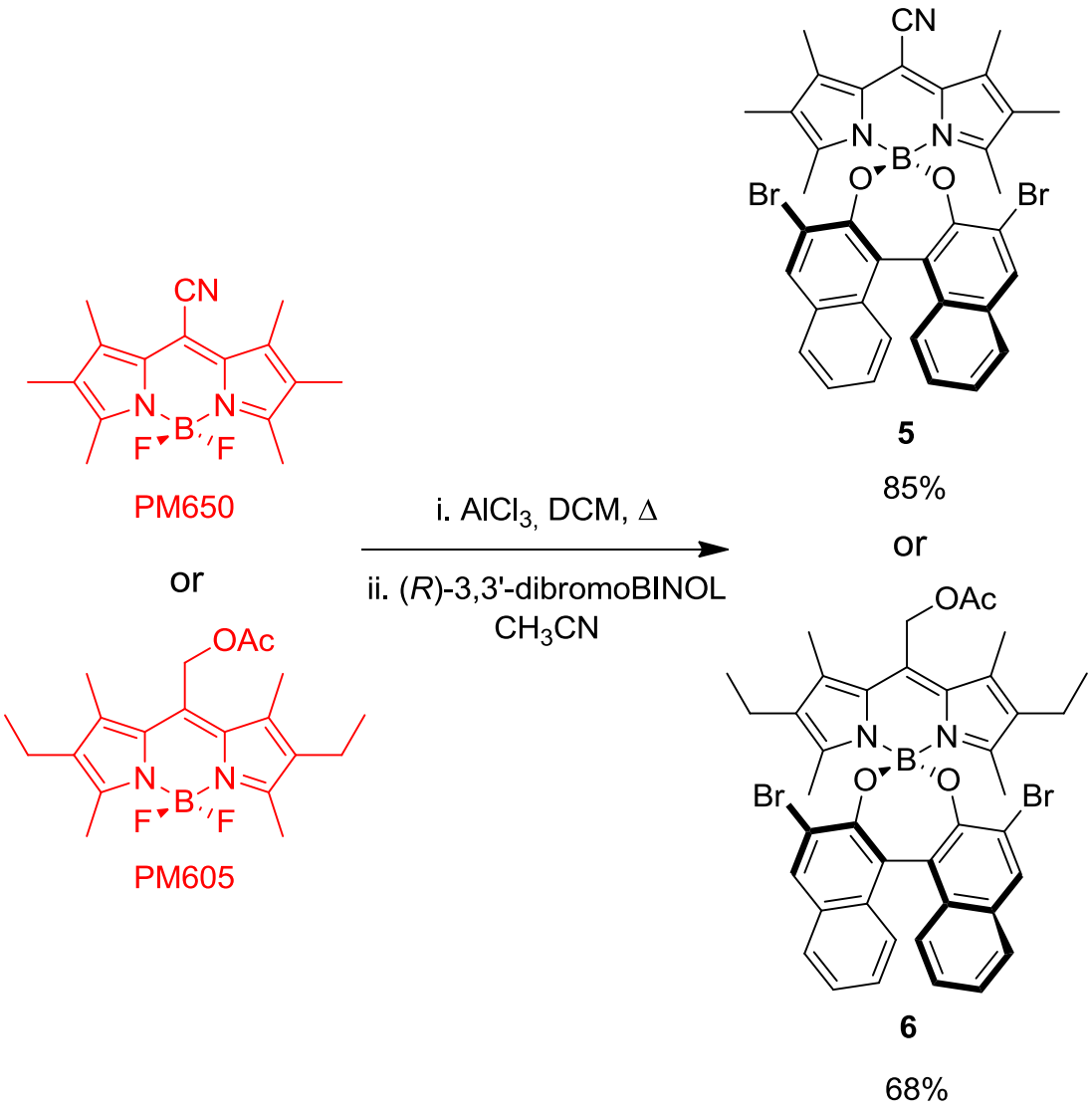
Results

Synthesis



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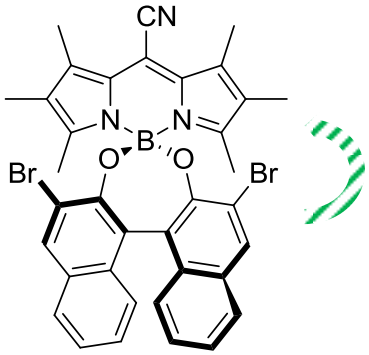
Results

Photophysical properties



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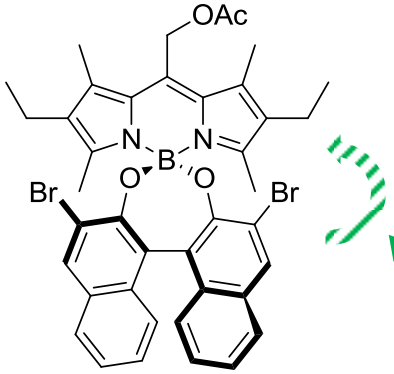

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3	*n*-hexane	587.0	3.6	-	-	-
	acetone	587.5	3.1	-	-	-
5	*n*-hexane	589.5	4.9	603.5	395	0.25
	acetone	591.0	4.4	619.0	765	0.02
PM605	*n*-hexane	547.5	8.3	561.5	455	0.74
	acetone	542.0	7.1	559.0	560	0.70
4	*n*-hexane	549.5	5.6	579.5	940	0.13
	acetone	545.5	5.3	563.5	585	0.011
6	*n*-hexane	552.5	6.1	575.0	710	0.60
	acetone	549.0	6.0	572.0	730	0.45

High improvement of the fluorescence!!

Less deactivation by ICT

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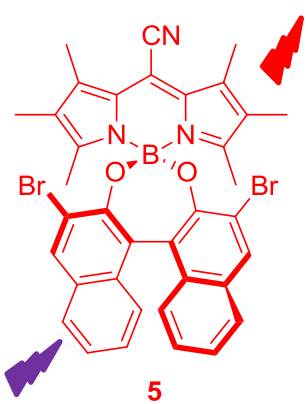
Results

EET behaviour



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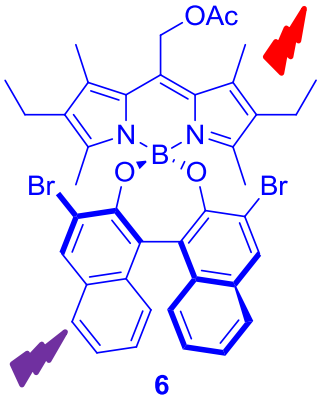

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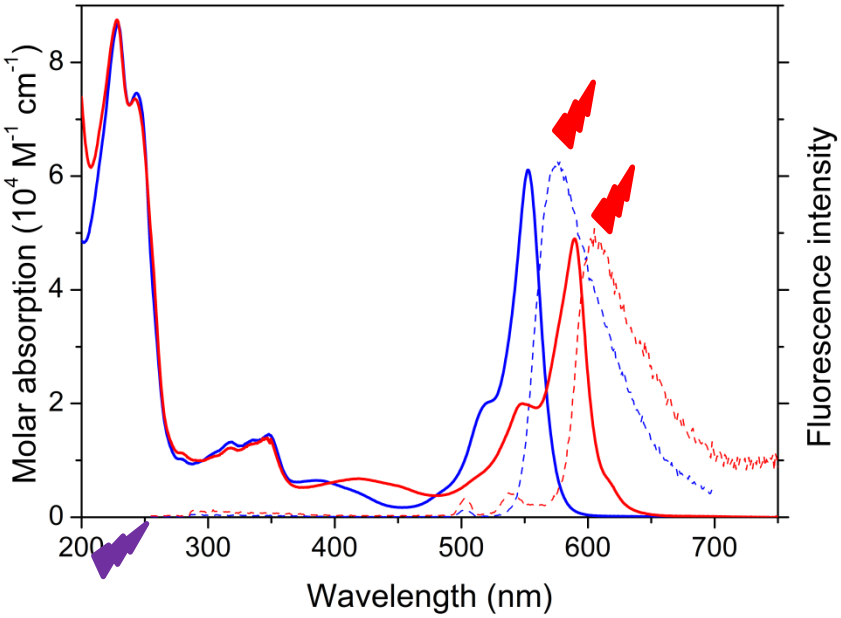

BODIPY	λ_{exc} (nm)	λ_{flu} (nm)	ϕ (%)	$\Delta\nu_{St}$ (cm^{-1})
5	570	604	0.25	395
	250	604	0.25	27900
6	510	575	0.60	710
	250	575	0.60	27050

n-hexane

EET 100%, large pseudo-Stokes shift, red emission

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Conclusions

Effcient EET cassette with red emission