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Benzo[rst]pentaphene derivatives as building blocks for 2D material with intense ECL emission

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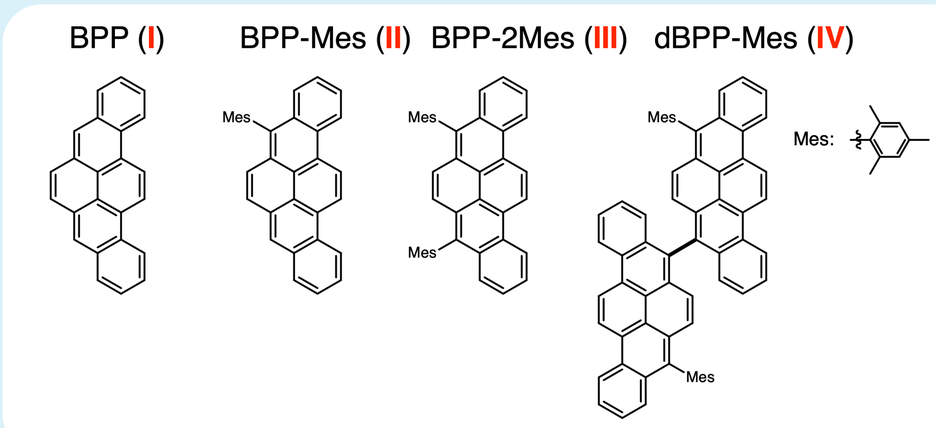
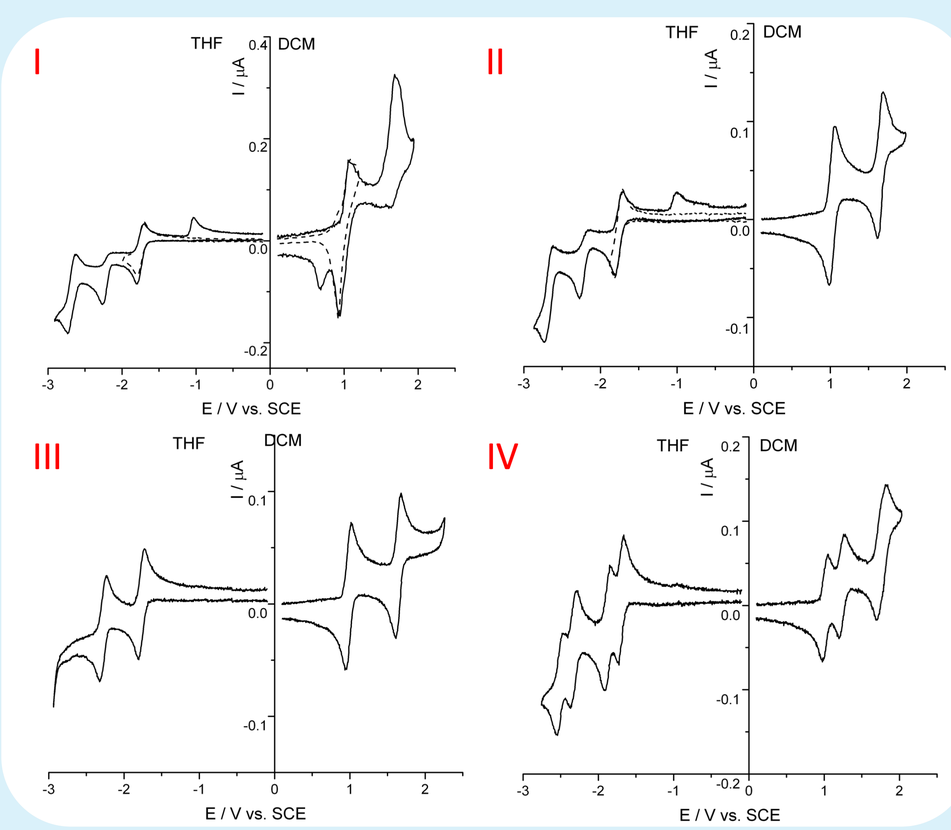
Introduction

- Polycyclic aromatic hydrocarbons *(PAHs)* constitute a large class of organic molecules with extended π-molecular orbitals. Although PAHs are currently considered as pollutants, mainly due to incomplete combustion by-product of organic matter, there is an extensive, very active and challenging research on PAHs to exploit these molecules in designing optoelectronic devices *[1]* and energy-storage applications *[2]*.
- In this work, we report the electrochemical characterization and electrochemiluminescence *(ECL)* in solution of a family of pristine and mesitylen-substituted mono and dimeric benzo*[rst]*pentaphene *(BPP)*.



Electrochemical characterization

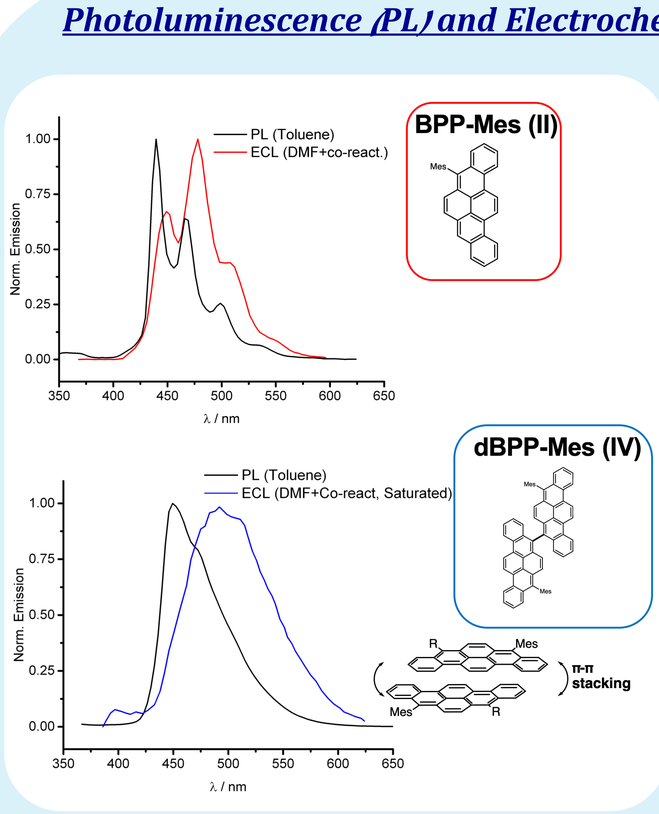


- Mesitylene substitution, as a bulky side-group, provides a more stable electrochemical behaviour than pristine BPP.
- The two BPP subunits of dBPP-Mes *(IV)* are partially interacting due to the observed *180-190* mV difference between consecutive $E_{1/2}$ *[3]*.

	Oxid.[a] $E_{1/2}$ / V vs. SCE			Red.[b] $E_{1/2}$ / V vs. SCE			
species	I	II	III	I	II	III	IV
I	*+1.07**	*+1.70**		*-1.75*	*-2.26**	*-2.68*	
II	*+1.03*	*+1.66*		*-1.76*	*-2.28**	*-2.68*	
III	*+0.98*	*+1.64*		*-1.77*	*-2.28*		
IV	*+1.01*	*+1.23*	*+1.76*	*-1.70*	*-1.88*	*-2.33*	*-2.51*

(a) Tetrabutylammonium hexafluorophosphate(TBAH)/DCM, (b)TBAH/THF,* Peak potential for irreversible processes

Photoluminescence (PL) and Electrochemiluminescence (ECL)

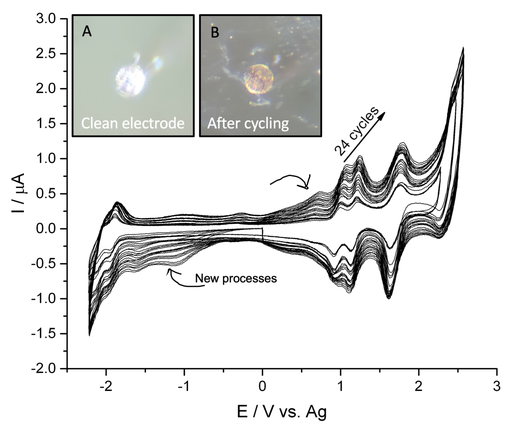


	Emission spectra	
species	PL (λ_1) /nm	ECL (λ_1) /nm
I	*435*	*/*
II	*440*	*449*
III	*443*	*444*
IV	*450*	*495*

- ECL is generated through the benzyl-peroxide *(BPO)* co-reactant method by the simultaneous reduction of BPO and the species in DMF. The ECL spectrum of species II and IV is compared with the corresponding photoluminescence *(PL)* one.
- BPP-Mes *(II)* emission shows different relative intensities, related to the vibrational structure, between PL and ECL.

The maximum of ECL emission for dBPP-Mes *(IV)* shows an unexpected red shift, of about *45* nm, compared with the photoluminescence spectrum. As this compound is poorly soluble in DMF, which has resulted in a saturated solution, a plausible hypothesis is that the lowering of the emitting energy state is due to a π-π stacking interaction occurring in the current experimental conditions. Further experiments are in progress to confirm such a hypothesis.

Film growth during CV of dBPP-Mes (IV)



- Cycling repeatedly the potential scan up to about *2.5* V, a stepwise increase of the current is observed.
- New electrochemical processes develop..
- After cycling, the Platinum electrode showed a deposited brownish film.

Summary and future prospective

- We reported the electrochemical characterization and ECL of a family of benzo*[rst]*pentaphene derivatives, we observed that bulky side-groups help to stabilize the radical ions generated at the electrode and redshift the emission wavelength.
- Our next aim will be to further investigate the spectroscopic properties of these molecules and to characterize thoroughly the film observed during the oxidation of dBPP-Mes.

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REFERENCES

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[3] A.J. Bard and L.R. Faulkner, Electrochemical Methods: Fundamentals and application, Wiley

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