

Session : 1

EPREUVE
Electrochimie Moléculaire
Calculatrice non autorisée
Durée : 01h00

A – 1. Soit la réaction redox $Ox + e^- \rightleftharpoons R$ se caractérisant par une cinétique de transfert électronique rapide (limitation de courant par le transfert de masse).

2 a) Représenter l'allure du voltammogramme cyclique d'une solution de Ox seul.

1 + 2 b) Comment qualifier la réponse du couple Ox/R. Quelles en sont les valeurs caractéristiques qui peuvent être extraites de l'enregistrement voltammétrique ?

2. Envisageons maintenant que R soit le siège d'une réaction irréversible de vitesse finie.

1 a) A quel grand type appartient le mécanisme ?

2 b) Représenter et décrire l'évolution du voltammogramme cyclique sur une gamme très large de vitesse de balayage, en précisant le paramètre dictant cette évolution

1 3. a) Définir le mécanisme $E_r C_{cat}$.

2 b) Même question qu'en 2. b).

B – Analyse de la publication *Journal of Organic Chemistry* 2012, 77, 143

2 1. Dire brièvement en quoi consiste(nt) la(les) réaction(s) représentée(s) sur le schéma réactionnel, colonne de gauche.

2 2. a) Décrire la variation de E_{ox} et E_{red} dans la série $2 \rightarrow 2m \rightarrow 2d$.

2 b) Interpréter ces variations du point de vue des niveaux d'orbitales frontière.

2 3.a) Dans quelles conditions expérimentales sont obtenues les voltammogrammes cycliques ?

1 b) Le « redox potential » mentionné dans l'article désigne en réalité le *potentiel de demi-vague*, $E_{1/2}$, qui permet d'approcher le potentiel standard, E° . Sachant que l'oxydation et la réduction d'intérêt sont réversibles, quelle est la façon pertinente d'obtenir le $E_{1/2}$ à partir du voltammogramme cyclique ?

Porphyrins Fused with Unactivated Polycyclic Aromatic Hydrocarbons

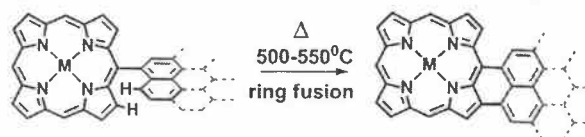
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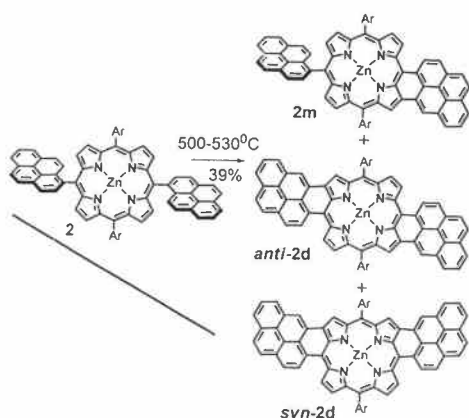
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Supporting Information

ABSTRACT: A systematic study of the preparation of porphyrins with extended conjugation by *meso*, β -fusion with polycyclic aromatic hydrocarbons (PAHs) is reported. The *meso*-positions of 5,15-unsubstituted porphyrins were readily functionalized with PAHs. Ring fusion using standard Scholl reaction conditions (FeCl₃, dichloromethane) occurs for



perylene-substituted porphyrins to give a porphyrin β ,*meso* annulated with perylene rings (0.7:1 ratio of *syn* and *anti* isomers). The naphthalene, pyrene, and coronene derivatives do not react under Scholl conditions but are fused using thermal cyclodehydrogenation at high temperatures, giving mixtures of *syn* and *anti* isomers of the *meso*, β -fused porphyrins. For pyrenyl-substituted porphyrins, a thermal method gives synthetically acceptable yields (>30%). Absorption spectra of the fused porphyrins undergo a progressive bathochromic shift in a series of naphthyl ($\lambda_{\text{max}} = 730$ nm), coronenyl ($\lambda_{\text{max}} = 780$ nm), pyrenyl ($\lambda_{\text{max}} = 815$ nm), and perylenyl ($\lambda_{\text{max}} = 900$ nm) annulated porphyrins. Despite being conjugated with unsubstituted fused PAHs, the β ,*meso*-fused porphyrins are more soluble and processable than the parent nonfused precursors. Pyrenyl-fused porphyrins exhibit strong fluorescence in the near-infrared (NIR) spectral region, with a progressive improvement in luminescent efficiency (up to 13% with $\lambda_{\text{max}} = 829$ nm) with increasing degree of fusion. Fused pyrenyl-porphyrins have been used as broadband absorption donor materials in photovoltaic cells, leading to devices that show comparatively high photovoltaic efficiencies.



Ar = 3,5-di-*tert*-butylphenyl

Electrochemical and Theoretical Characterization. The electrochemical properties of zinc porphyrins 2, 2m and 2d (*syn/anti* mixture) were analyzed using cyclic voltammetry (Table 1).

Table 1. Electrochemical Potentials for the HOMO and LUMO Energies of Pyrene-functionalized Porphyrins 2, 2m and 2d^a

compound	E^{ox}	E^{red}	$\Delta E^{\text{ox-red}}$
2	0.41	-1.92	2.33
2m	0.18	-1.52	1.70
2d	0.01	-1.44	1.45

^aPotentials were determined by cyclic voltammetry referenced to an internal ferrocenium/ferrocene potential. Each compound shows two oxidations and two reductions, but only the first oxidation and reduction values are listed.

EXPERIMENTAL SECTION

Redox potentials were measured by the cyclic voltammetry method.

0.1 M *n*-Bu₄NPF₆ in CH₂Cl₂ was used as the supporting electrolyte (degassed with nitrogen), a Pt wire was employed as the counter electrode, an Ag wire used as the pseudoreference electrode and a glassy carbon electrode was used as the working electrode. Ferrocene (Fc) or decamethylferrocene (dmfc) was added as an internal reference, and the potentials were measured relative to the Fc/Fc⁺ couple. CV was used to determine electrochemical reversibility, redox potentials were found using CV.