

## Electronic Supplementary Information

# Bis-porphyrin copolymers covalently linked by pyridinium spacers obtained by electropolymerization from $\beta$ -octaethylporphyrins and pyridyl-substituted porphyrins

Yun Xia,<sup>a</sup> Delphine Schaming,<sup>a</sup> Rana Farha,<sup>b,c</sup> Michel Goldmann<sup>b,d</sup> and Laurent Ruhlmann\*<sup>a,e</sup>

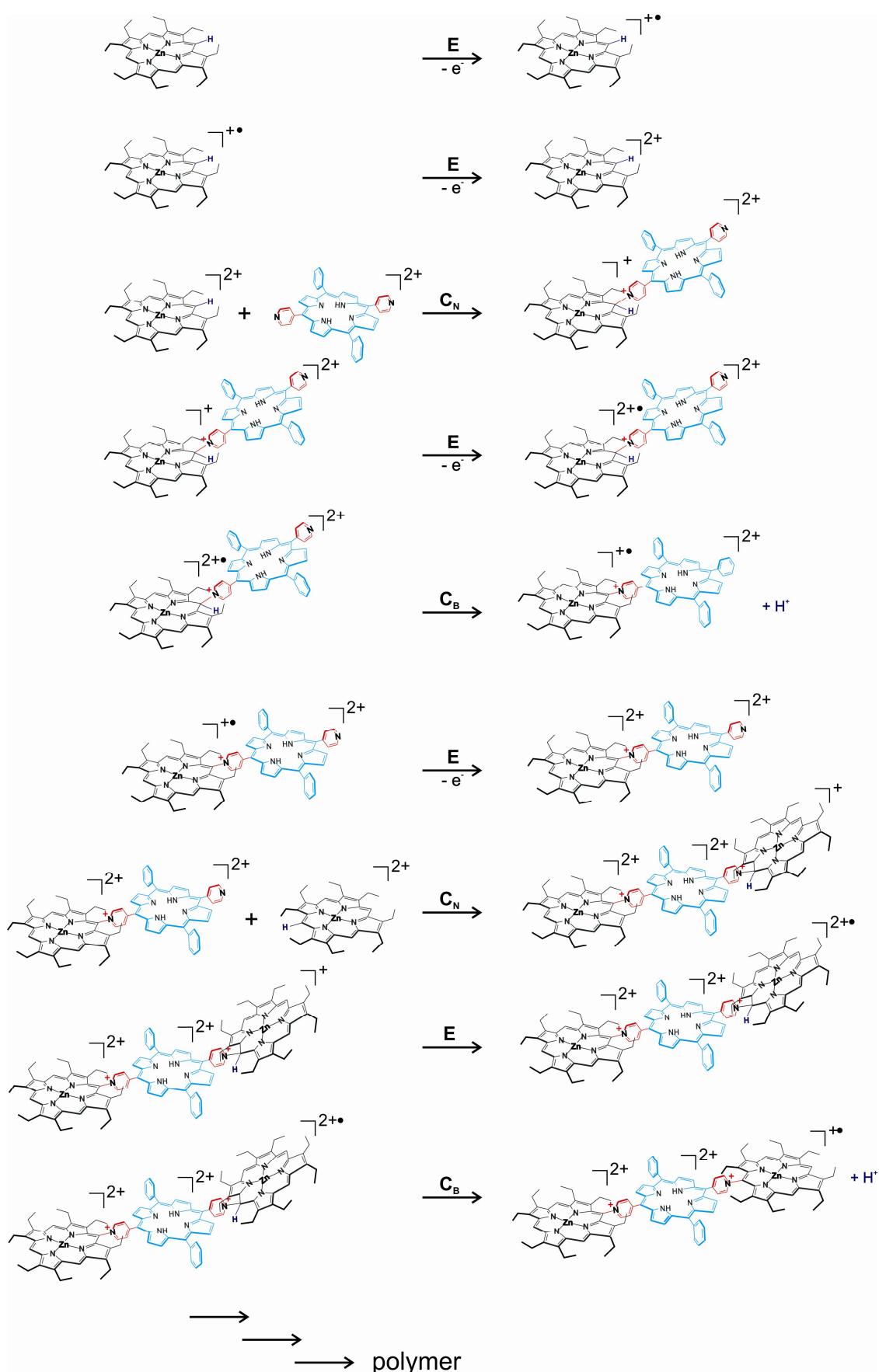
<sup>a</sup> Laboratoire de Chimie Physique, UMR 8000 CNRS/Université Paris-Sud 11, Faculté des Sciences d'Orsay, Bâtiment 349, 91405 Orsay, France.

<sup>b</sup> Institut des NanoSciences de Paris, UMR 7588 CNRS/Université Paris 6, 4 place Jussieu, boîte courrier 840, 75252 Paris, France.

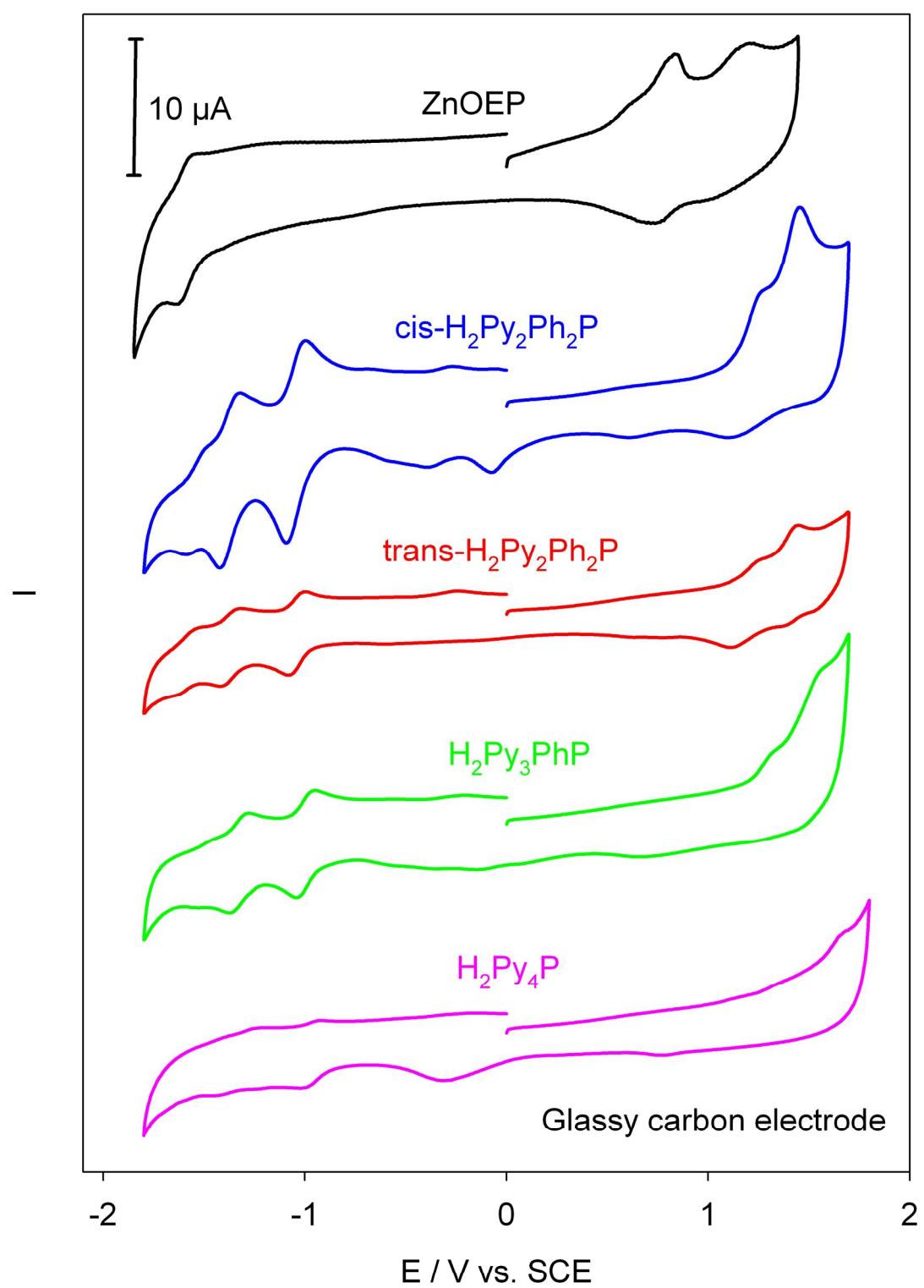
<sup>c</sup> Laboratoire d'Analyse et Contrôle des Systèmes Complexes, ECE Paris Ecole d'Ingénieurs, 37 quai de Grenelle, 75015 Paris, France.

<sup>d</sup> Université Paris Descartes, 45 rue des Saint Pères, 75006 Paris, France.

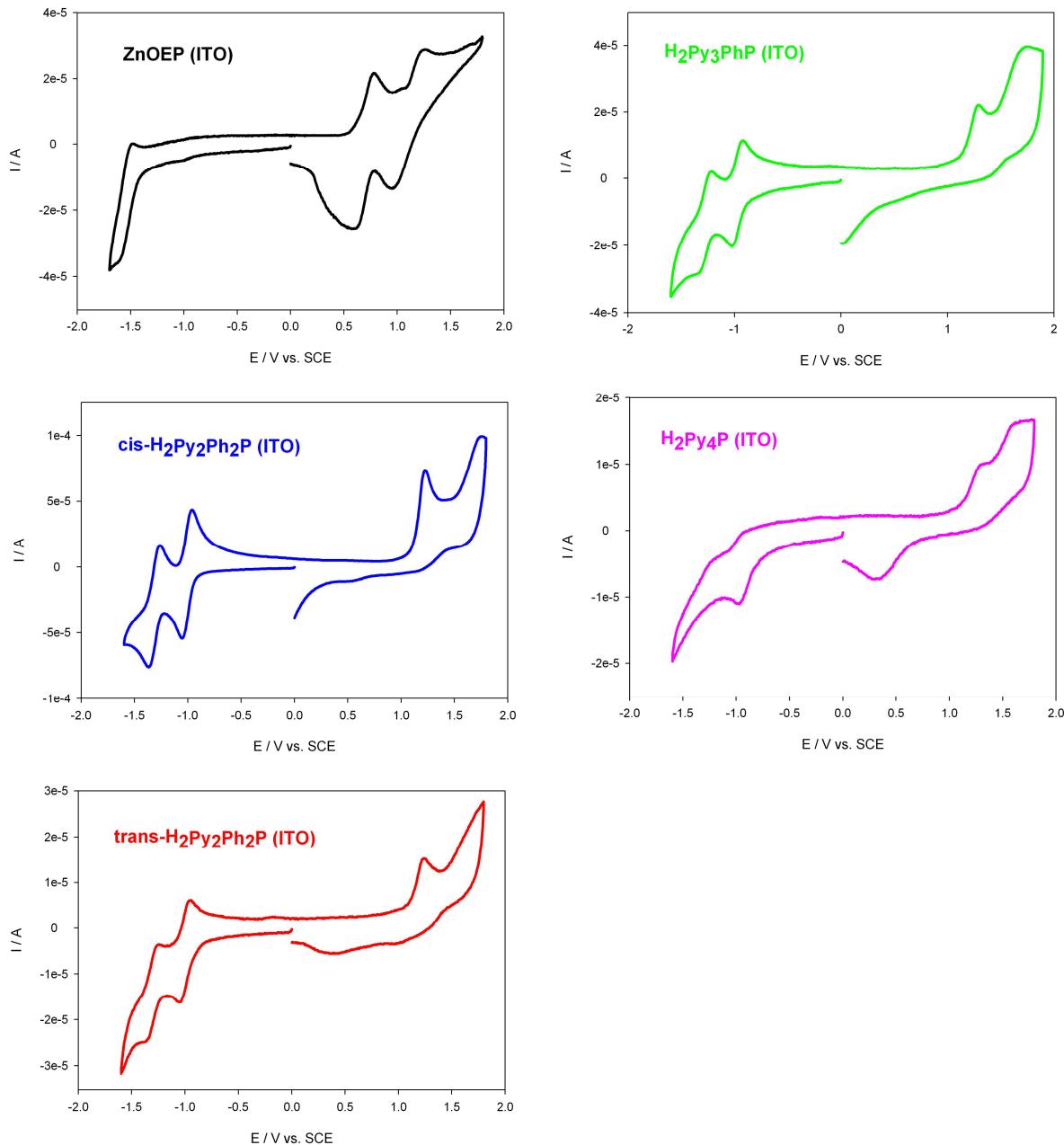
<sup>e</sup> Laboratoire d'Electrochimie et de Chimie-Physique du Corps Solide, UMR 7177 CNRS/Université de Strasbourg, 4 rue Blaise Pascal, 67081 Strasbourg, France.



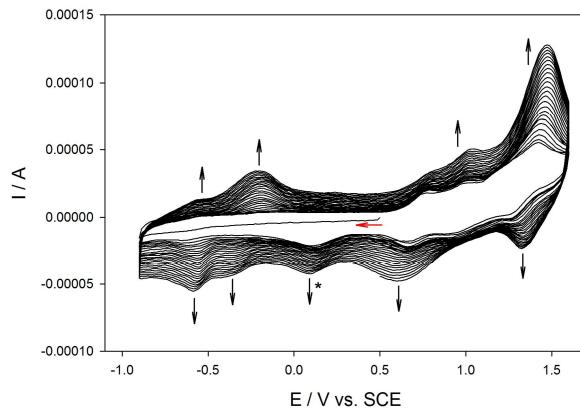
**Scheme S1.**  $E(EC_NEC_B)_nE$  mechanism proposed for the electropolymerization of ZnOEP with trans-H<sub>2</sub>Py<sub>2</sub>Ph<sub>2</sub>P.



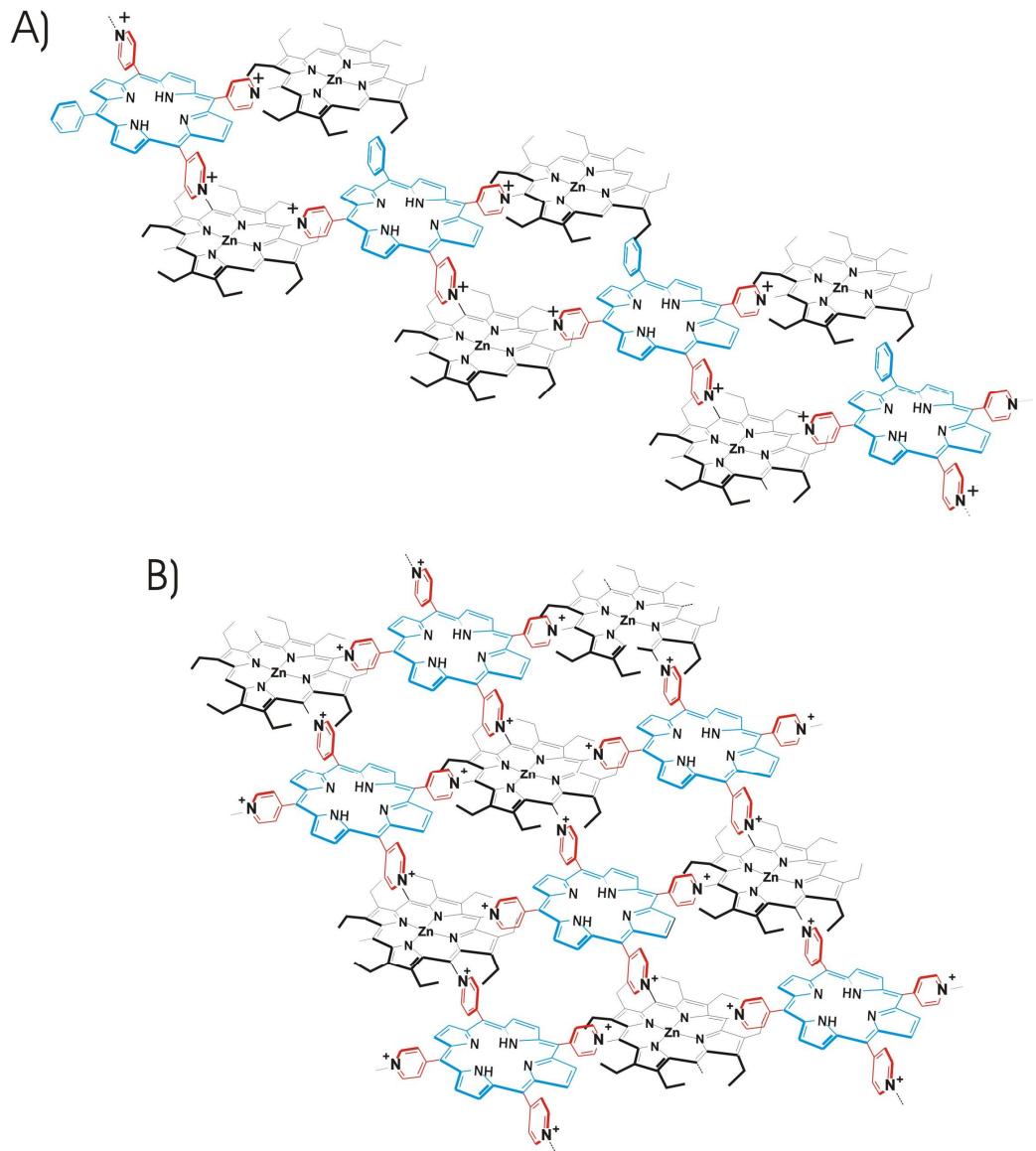
**Figure S1.** Cyclic voltammograms of ZnOEP, cis- $H_2Py_2Ph_2P$ , trans- $H_2Py_2Ph_2P$ ,  $H_2Py_3PhP$  and  $H_2Py_4P$  in  $CH_3CN/1,2-C_2H_4Cl_2$  (1:4) with 0.1 M  $NEt_4PF_6$ .  $c = 0.25$  mM. Working electrode: glassy carbon; scan rate:  $0.1 V s^{-1}$ .



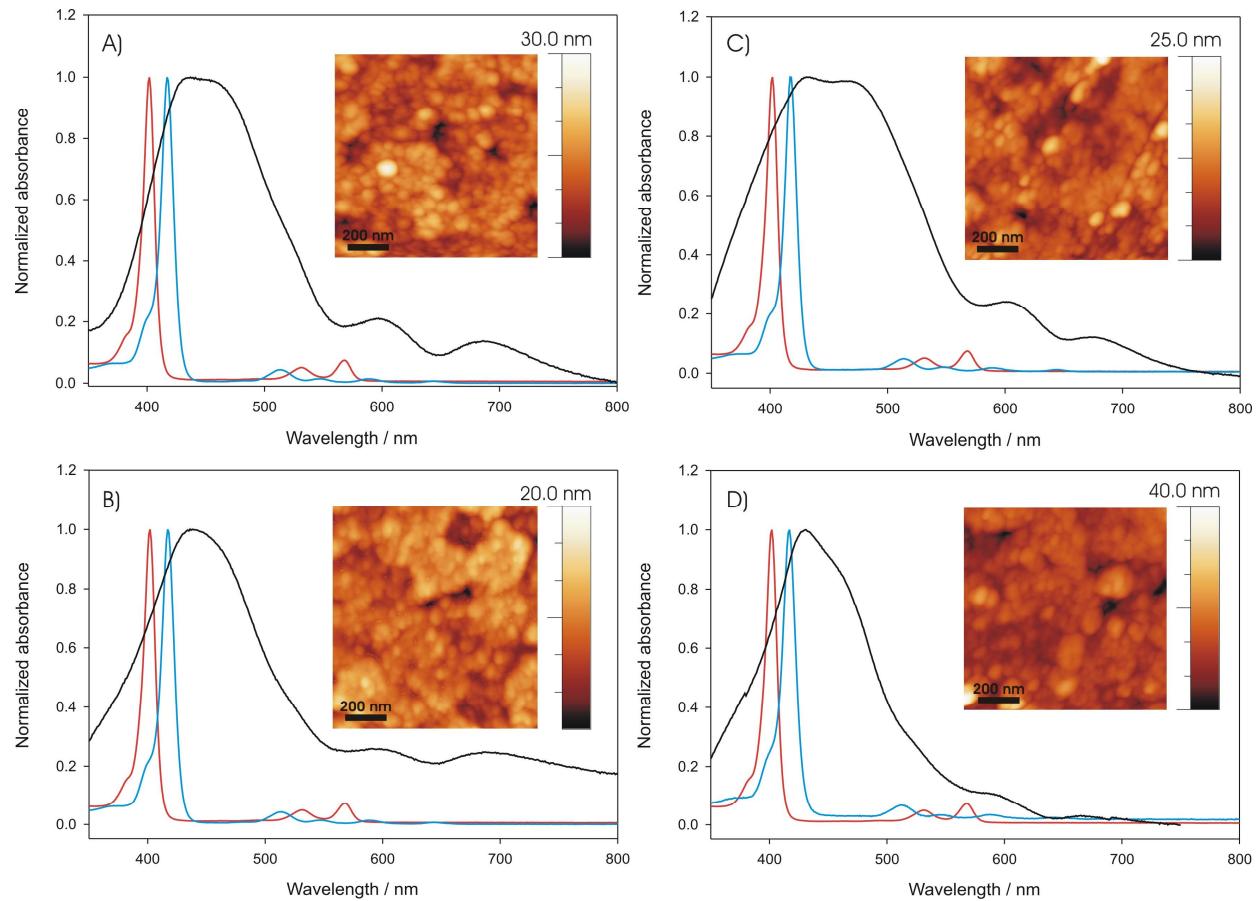
**Figure S2.** Cyclic voltammograms of ZnOEP, cis- $H_2Py_2Ph_2P$ , trans- $H_2Py_2Ph_2P$ ,  $H_2Py_3PhP$  and  $H_2Py_4P$  in  $\text{CH}_3\text{CN}/1,2-\text{C}_2\text{H}_4\text{Cl}_2$  (1:4) with 0.1 M  $\text{NEt}_4\text{PF}_6$ .  $c = 0.25$  mM. Working electrode: ITO;  $S = 1 \text{ cm}^2$ ; scan rate:  $0.1 \text{ V s}^{-1}$ .



**Figure S3.** Cyclic voltammograms recorded during the electropolymerization of trans- $H_2Py_2Ph_2P$  in the presence of  $ZnOEP(Cl)_2$  in  $CH_3CN/1,2-C_2H_4Cl_2$  (1:4) with 0.1 M  $NEt_4PF_6$ . working electrode: ITO;  $S = 1 \text{ cm}^2$ ; scan rate:  $0.1 \text{ V s}^{-1}$ .



**Scheme S2.** Tentative representation of copolymers: (A) poly-H<sub>2</sub>Py<sub>3</sub>PhP-ZnOEP and (B) poly-H<sub>2</sub>Py<sub>4</sub>P-ZnOEP.



**Figure S4.** Atomic force micrographs and normalized UV-visible absorption spectra of ITO electrodes (black lines) modified with (A) poly-trans-H<sub>2</sub>Py<sub>2</sub>Ph<sub>2</sub>P-ZnOEP, (B) poly-trans-H<sub>2</sub>Py<sub>2</sub>Ph<sub>2</sub>P-ZnOEP(Cl)<sub>2</sub>, (C) poly-H<sub>2</sub>Py<sub>3</sub>PhP-ZnOEP and (D) poly-H<sub>2</sub>Py<sub>4</sub>P-ZnOEP (red lines: absorption spectra of the monomers ZnOEP or ZnOEP(Cl)<sub>2</sub> according to the copolymer (in 1,2-C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>) and blue lines: absorption spectra of the pendant pyridyl porphyrin monomers used for each copolymer (in 1,2-C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>)).