

## Donor-Acceptor Type Random Copolymers For Full Visible Light Absorption

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### Electronic Supplementary Information

#### Experimental

##### General

All reagents were obtained from commercial sources and were used without further purification unless otherwise mentioned. <sup>1</sup>H NMR spectra referenced to tetramethylsilane were recorded in CDCl<sub>3</sub> on Bruker Spectrospin Avance DPX-400 Spectrometer. Electrochemical studies were performed in a three electrode cell consisting of an Indium Tin Oxide doped glass slide (ITO) as the working electrode, platinum wire as the counter electrode, and Ag wire as the pseudo reference electrode under ambient conditions using a Voltalab 50 potentiostat. The reference electrode and all the results were subsequently calibrated to Fc/Fc<sup>+</sup> and the band energies were calculated relative to the vacuum level considering that the value of NHE is -4.75 eV vs. vacuum.<sup>1</sup> Spectroelectrochemical studies for copolymers were carried out by using Varian Cary 5000 UV-Vis spectrophotometer. Average molecular weights of copolymers were determined in tetrahydrofuran (THF) via gel permeation chromatography (GPC) on a Polymer Laboratories PL-GPC 220 by using PS standard calibration method.

##### Synthesis of Polymers

The synthetic route to each of alternating copolymers P1, P2 and P3 consists of three components by keeping two of them constant. All of the components for the synthesis of copolymers were synthesized by following previously published procedures. 5,8-Dibromo-2,3-bis(4-*tert*-butylphenyl)quinoxaline,<sup>2</sup> 5,8-dibromo-2,3-di(thiophen-2-yl)quinoxaline<sup>3</sup> and 4,7-dibromobenzo[c][1,2,5]selenadiazole<sup>4</sup> units were separately combined with the 4,7-dibromo-2-dodecyl-2H-benzo[d][1,2,3]triazole<sup>5</sup> unit and the 2,5-bis(tributylstannyl)thiophene<sup>6</sup> moiety via Stille coupling. The detailed synthetic route to these new DA type alternating copolymers CoP1, CoP2 and CoP3 is given in Scheme ESI-1.

### Synthesis of CoP1

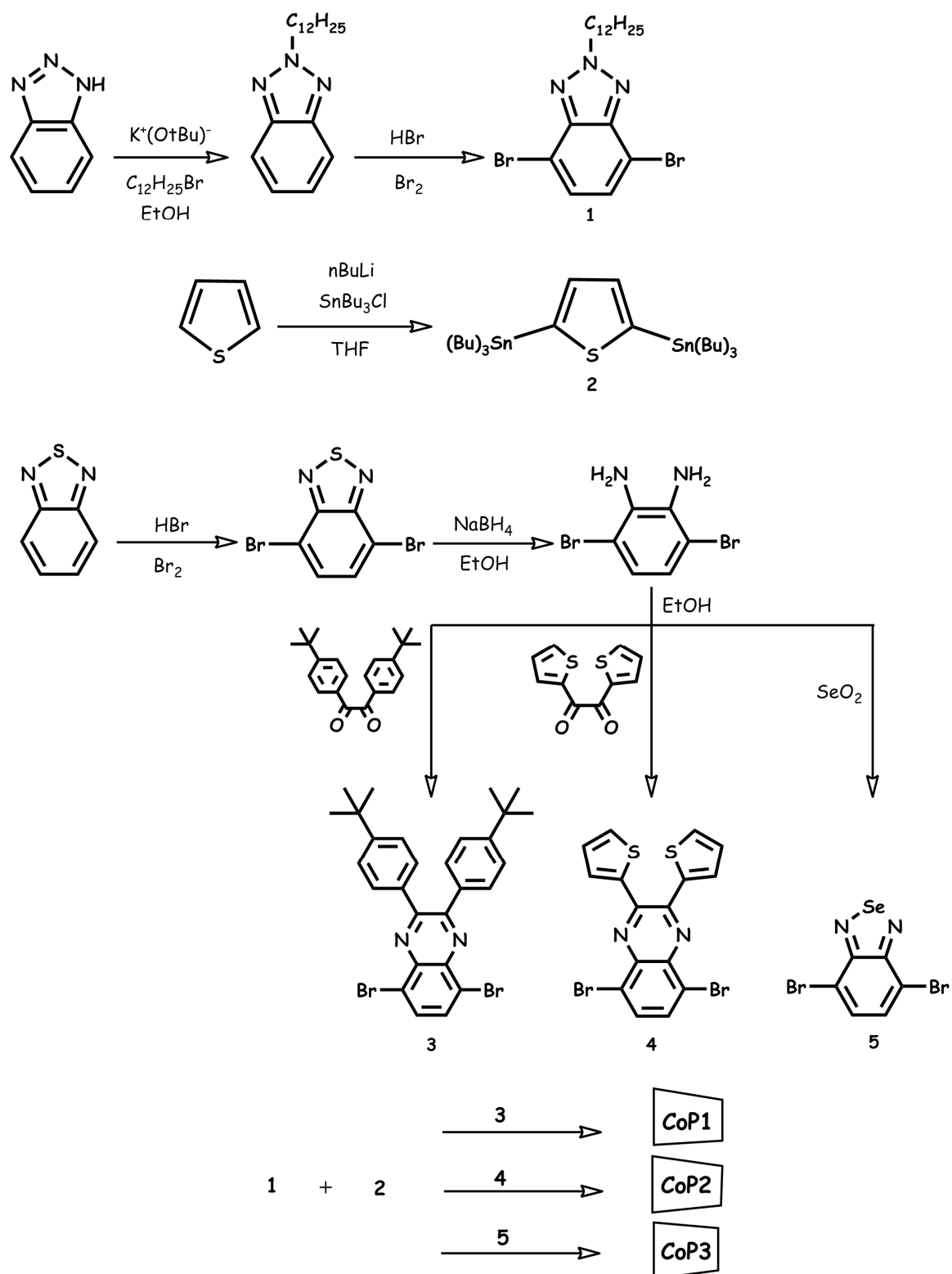
The equivalent number of moles of 5,8-dibromo-2,3-bis(4-*tert*-butylphenyl)quinoxaline (0.186 g, 0.338 mmol) and 4,7-dibromo-2-dodecyl-2H-benzo[d][1,2,3]triazole (0.150 g, 0.338 mmol) and 2,5-bis(tributylstannyl)thiophene (0.450 g, 0.678 mmol) were mixed in dried THF (70 ml) in the presence of Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (70 mg, 0.100 mmol) as the catalyst and refluxed overnight under argon atmosphere. Thereafter, the solvent was removed under vacuum; product was washed with methanol and acetone several times to remove the short chain oligomers and remnant catalyst. CoP1 was obtained as purple solid. GPC (THF):  $M_w = 29\,258\text{ g mol}^{-1}$ ,  $M_n = 18\,703\text{ g mol}^{-1}$ ,  $M_z = 42\,748\text{ g mol}^{-1}$ , *polydispersity index* = 1.56. <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>, δ): 7.9 (benzotriazole), 7.7 (quinoxaline), 7.3 (thiophene), 7.0 (benzene), 4.7 (N-CH<sub>2</sub>), 2.2 (C-CH<sub>2</sub>), 1.9-0.5 (pendant alkyl chains).

### Synthesis of CoP2

In order to synthesize CoP2, same procedure was followed as for CoP1 with 5,8-dibromo-2,3-di(thiophen-2-yl)quinoxaline (0.152 g, 0.338 mmol), 4,7-dibromo-2-dodecyl-2H-benzo[d][1,2,3]triazole (0.150 g, 0.338 mmol) and 2,5-bis(tributylstannyl)thiophene (0.450 g, 0.678 mmol). CoP2 was obtained as black solid. GPC (THF):  $M_w = 66\,871\text{ g mol}^{-1}$ ,  $M_n = 15\,640\text{ g mol}^{-1}$ ,  $M_z = 235\,751\text{ g mol}^{-1}$ , *polydispersity index* = 4.28. <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>, δ): 7.6 (benzotriazole), 7.5 (quinoxaline), 7.3 (thiophene), 7.0 (thiophene), 6.9 (thiophene), 6.5 (thiophene), 4.6 (N-CH<sub>2</sub>), 2.1 (C-CH<sub>2</sub>), 1.8-0.8 (pendant alkyl chains).

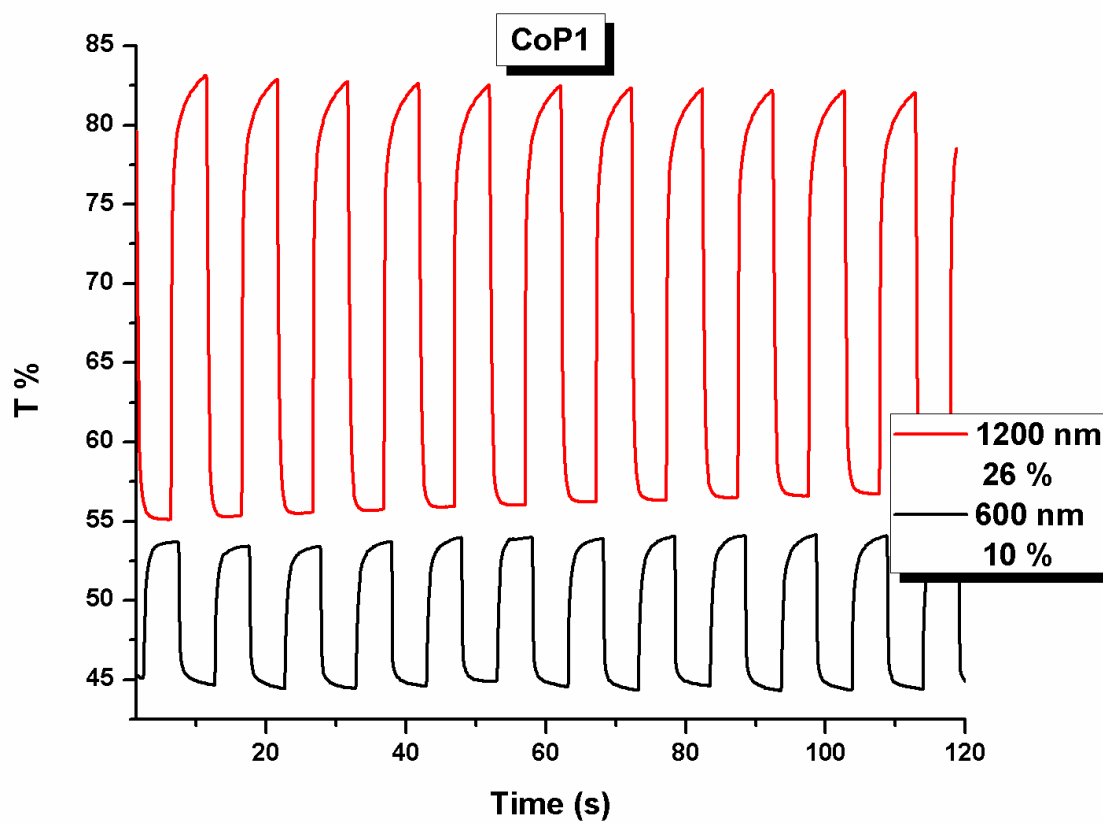
### Synthesis of CoP3

The same procedure was followed as for CoP1, with 4,7-dibromobenzo[c][1,2,5]selenadiazole (0.115 g, 0.338 mmol), 4,7-dibromo-2-dodecyl-2H-benzo[d][1,2,3]triazole (0.150 g, 0.338 mmol) and 2,5-bis(tributylstannyl)thiophene (0.450 g, 0.678 mmol). CoP3 was obtained as purplish brown solid. GPC (THF):  $M_w = 38\,317\text{ g mol}^{-1}$ ,  $M_n = 7\,896\text{ g mol}^{-1}$ ,  $M_z = 133\,133\text{ g mol}^{-1}$ , *polydispersity index* = 4.85. <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>, δ): 7.8 (benzotriazole), 7.4 (benzoselenadiazole), 7.0 (thiophene), 4.7 (N-CH<sub>2</sub>), 2.0 (C-CH<sub>2</sub>), 1.5-0.7 (pendant alkyl chains).

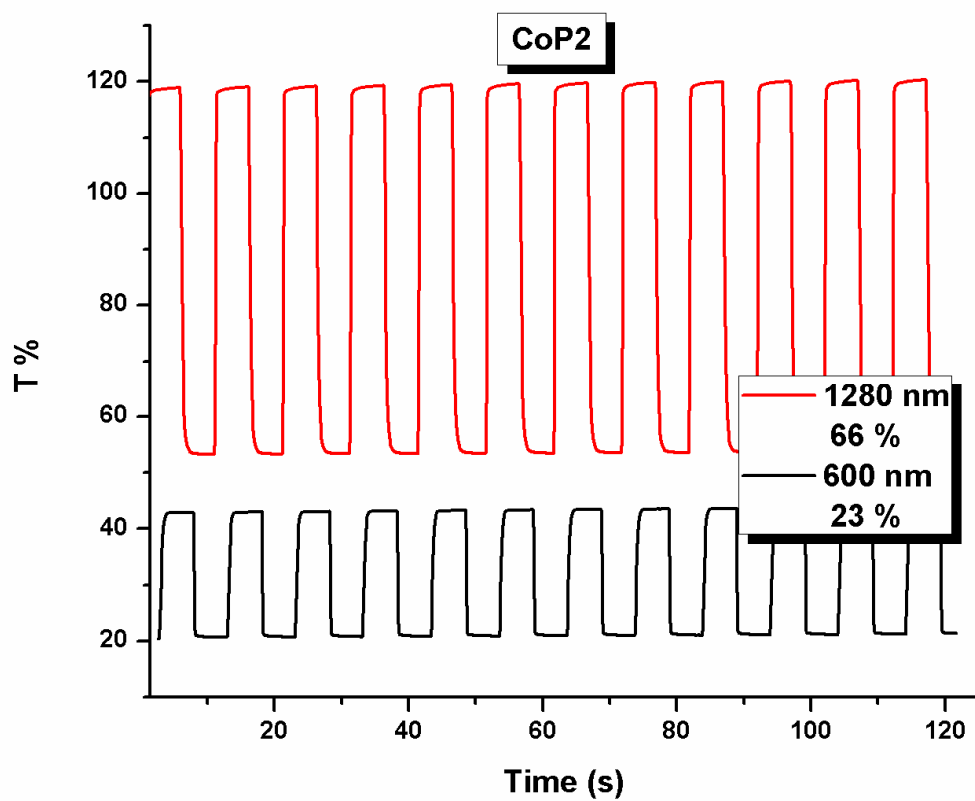


**Scheme ESI-1:** Synthetic route for copolymers and their precursors.

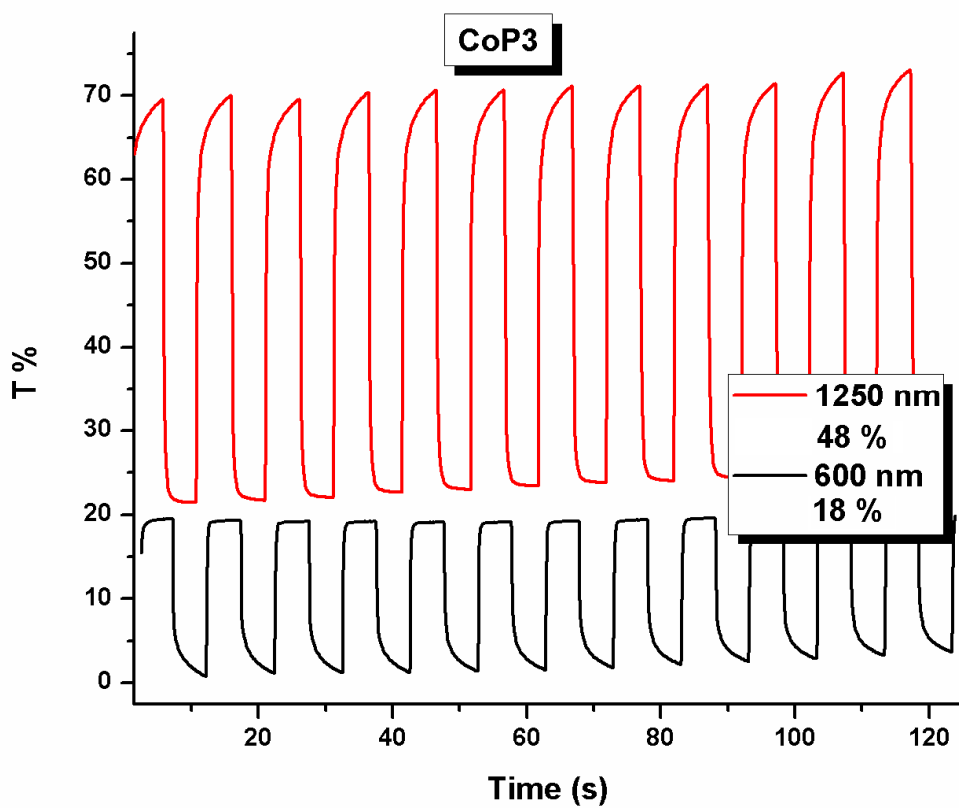
## Figures



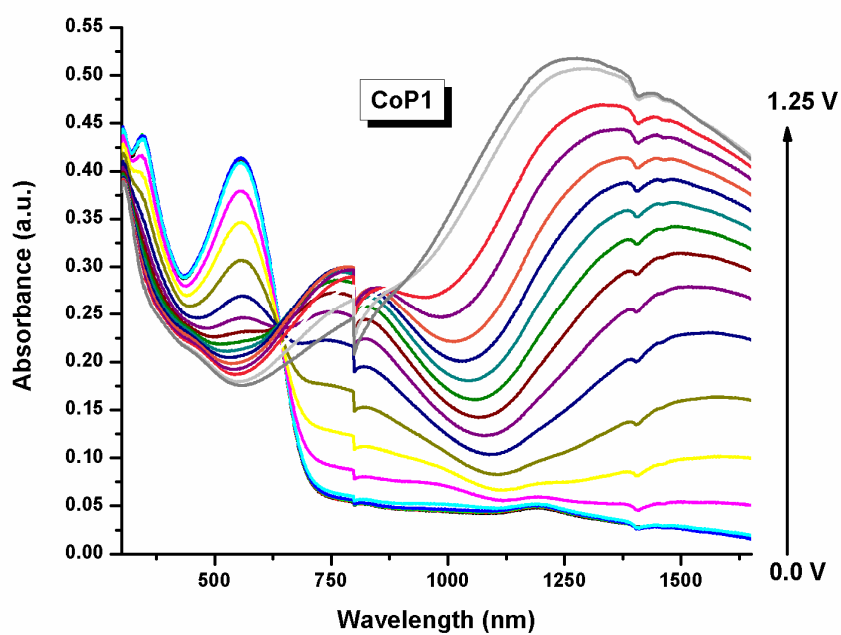
**Figure ESI-1:** Optical contrast changes of CoP1 film at 600 and 1200 nm when switched between its neutral and fully oxidized states. (0.0 V and 1.2 V)



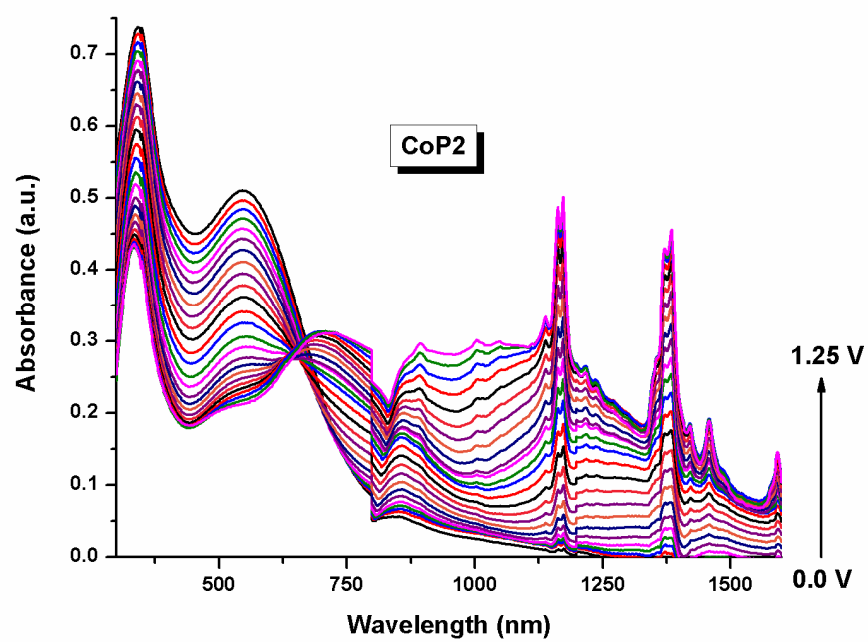
**Figure ESI-2:** Optical contrast changes of CoP2 film at 600 and 1280 nm when switched between its neutral and fully oxidized states. ( 0.0 V and 1.2 V).



**Figure ESI-3:** Optical contrast changes of CoP1 film at 600 and 1250 nm when switched between its neutral and fully oxidized states. (0.0 V and 1.2 V)

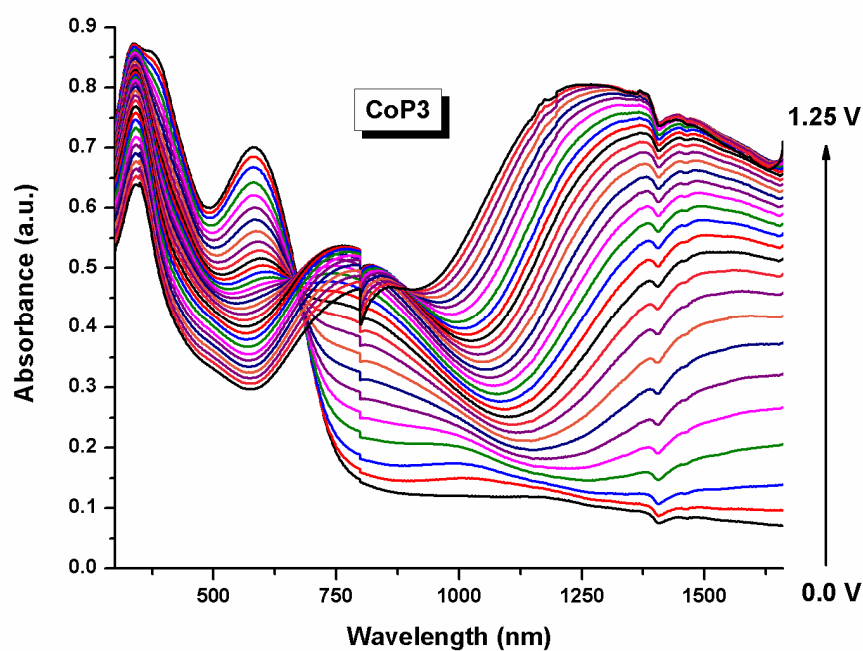


**Figure ESI-4:** Spectroelectrochemistry of CoP1 film in 0.1 M TBAPF<sub>6</sub>/ACN solution between 0.0 V and 1.25 V within 0.1 V potential intervals.



**Figure ESI-5:** Spectroelectrochemistry of CoP2 film in 0.1 M TBAPF<sub>6</sub>/ACN solution between 0.0 V and 1.25 V within 0.05 V potential intervals.





**Figure ESI-6:** Spectroelectrochemistry of CoP3 film in 0.1 M TBAPF<sub>6</sub>/ACN solution between 0.0 V and 1.25 V within 0.05 V potential intervals.

#### References:

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