

## Supporting Information

### Observation of Super-Nernstian Proton-Coupled Electron Transfer and Elucidation of Nature of Charge Carriers in a Multiredox Conjugated Polymer

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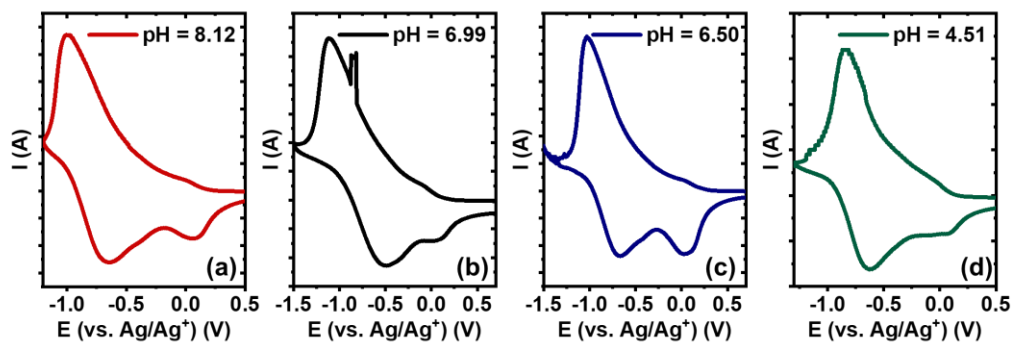
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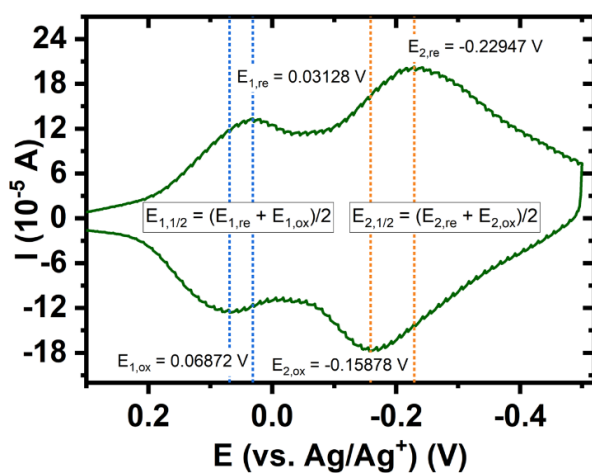
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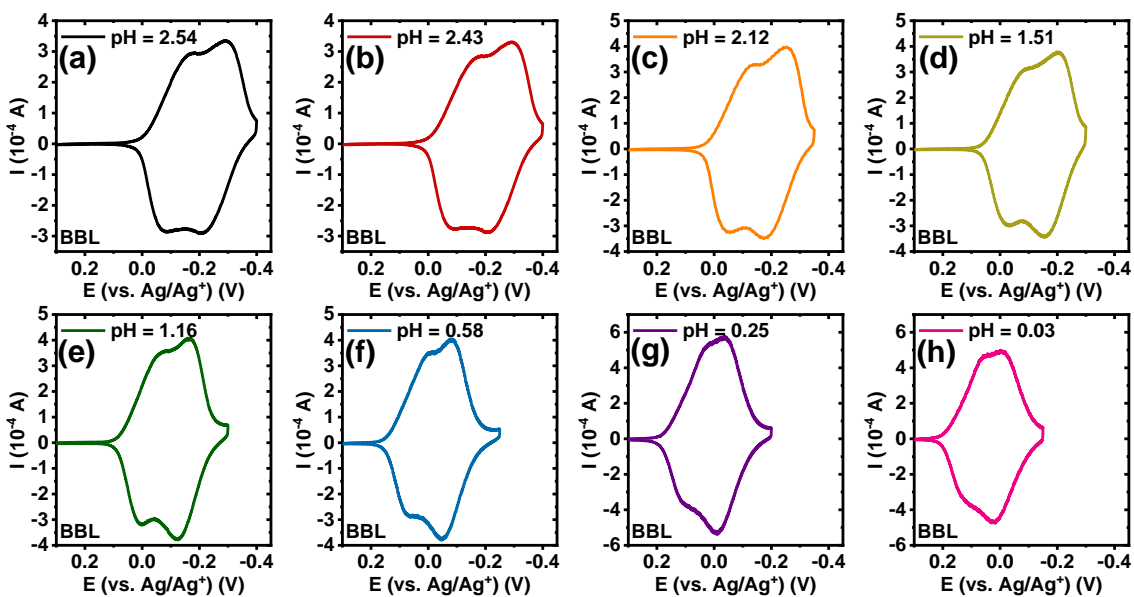
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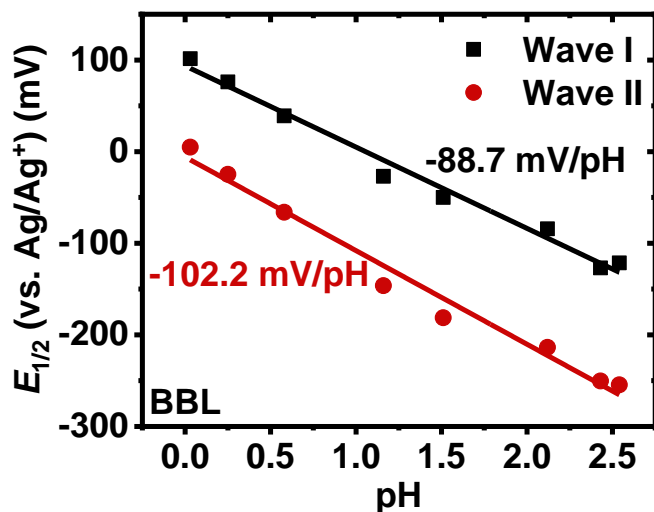
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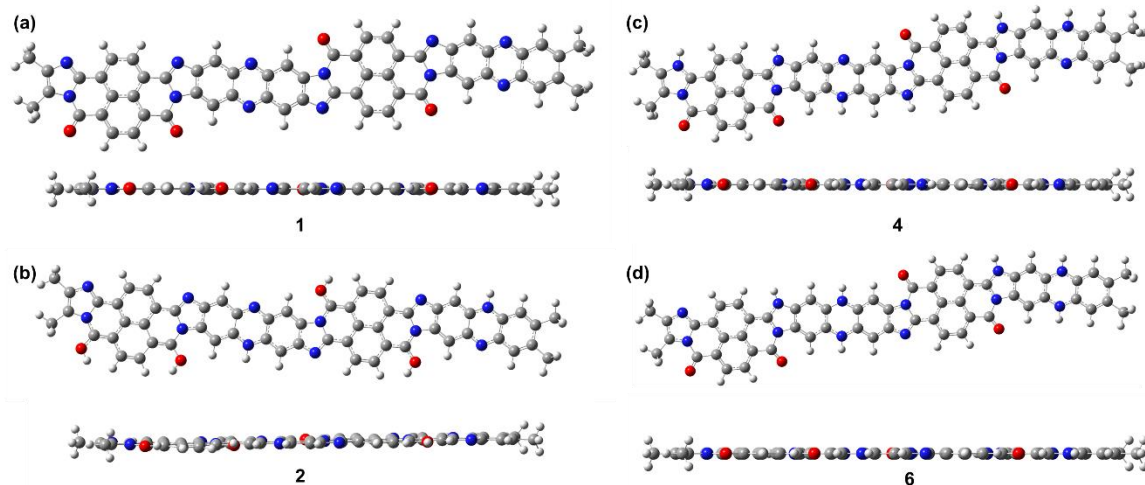
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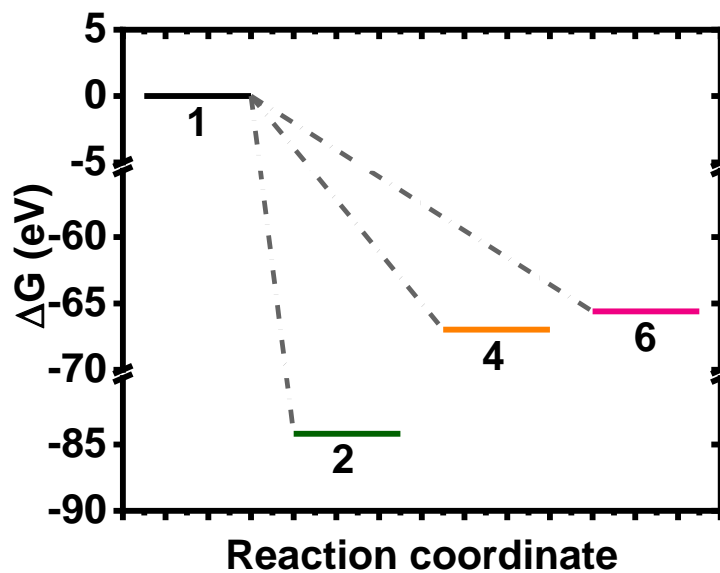
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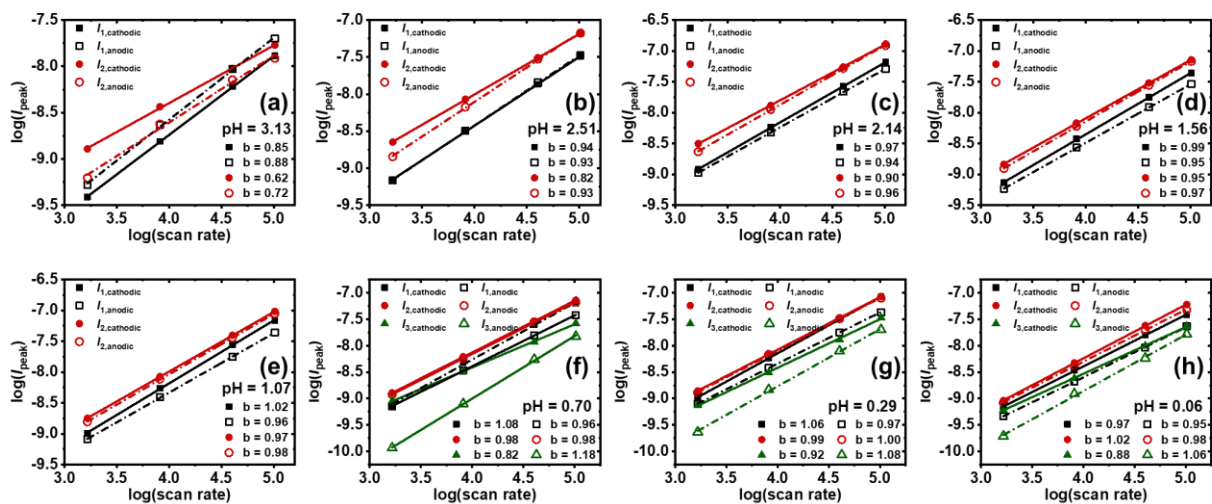
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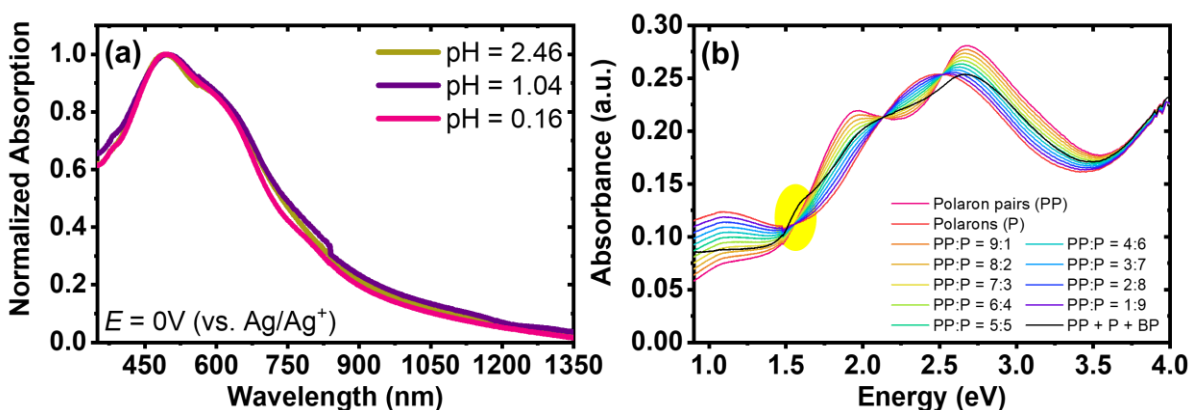
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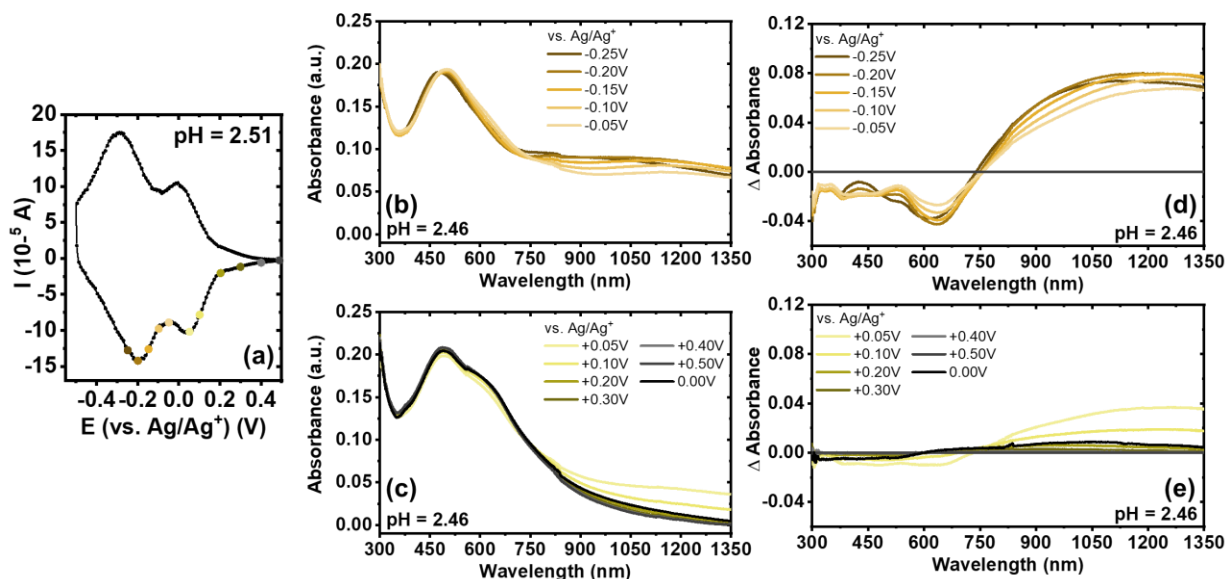
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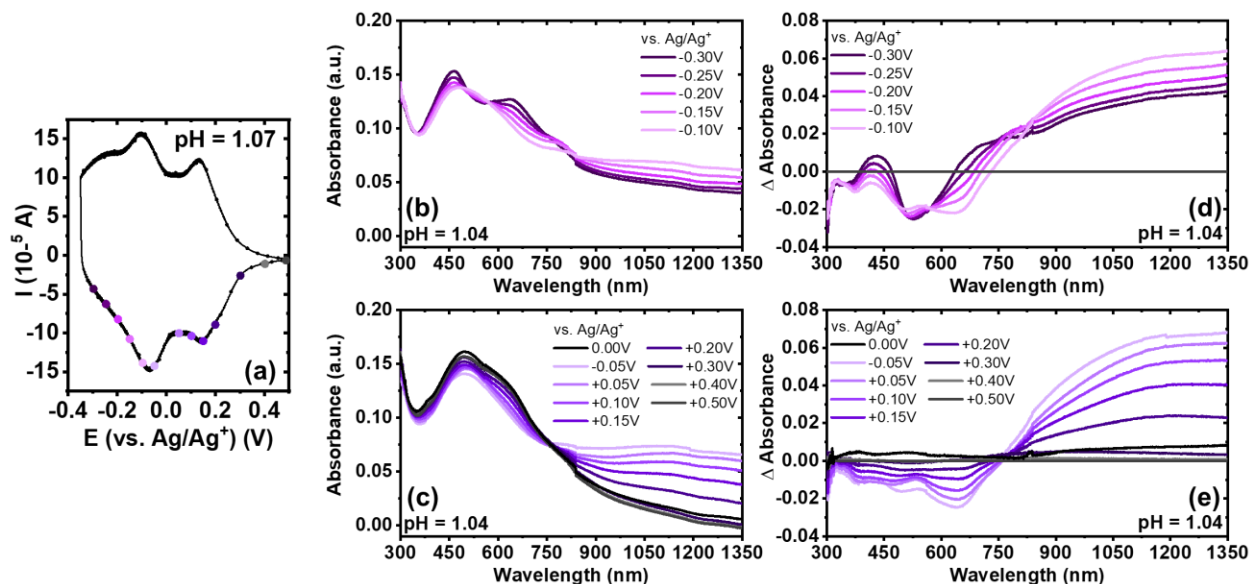
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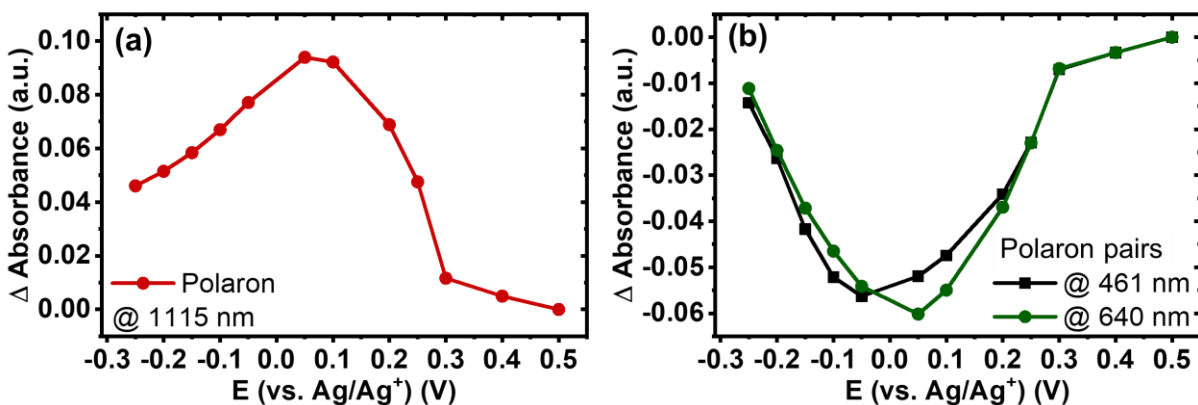
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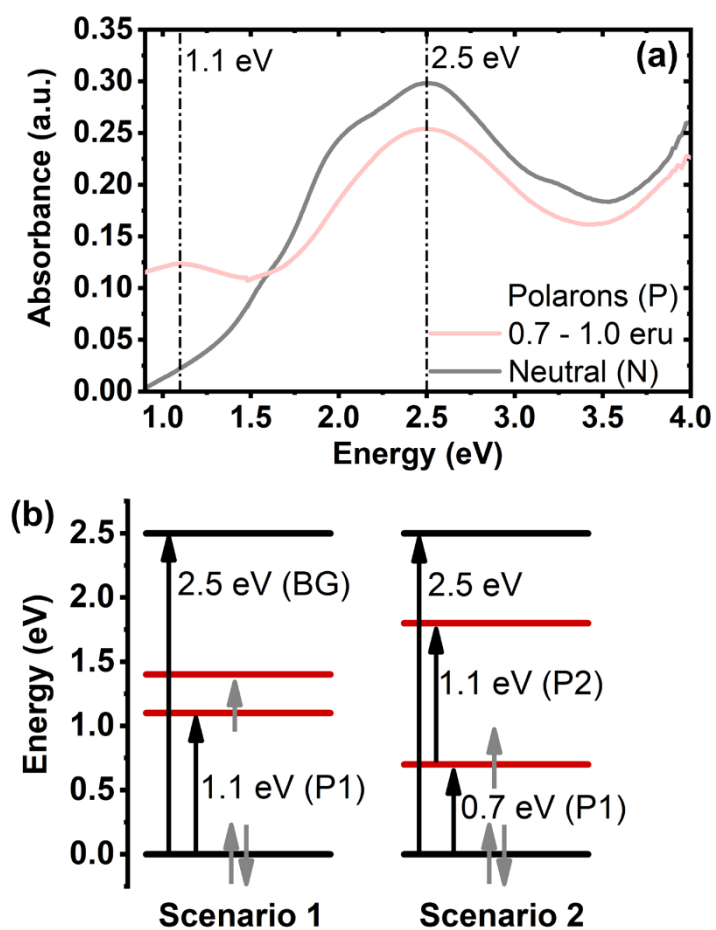
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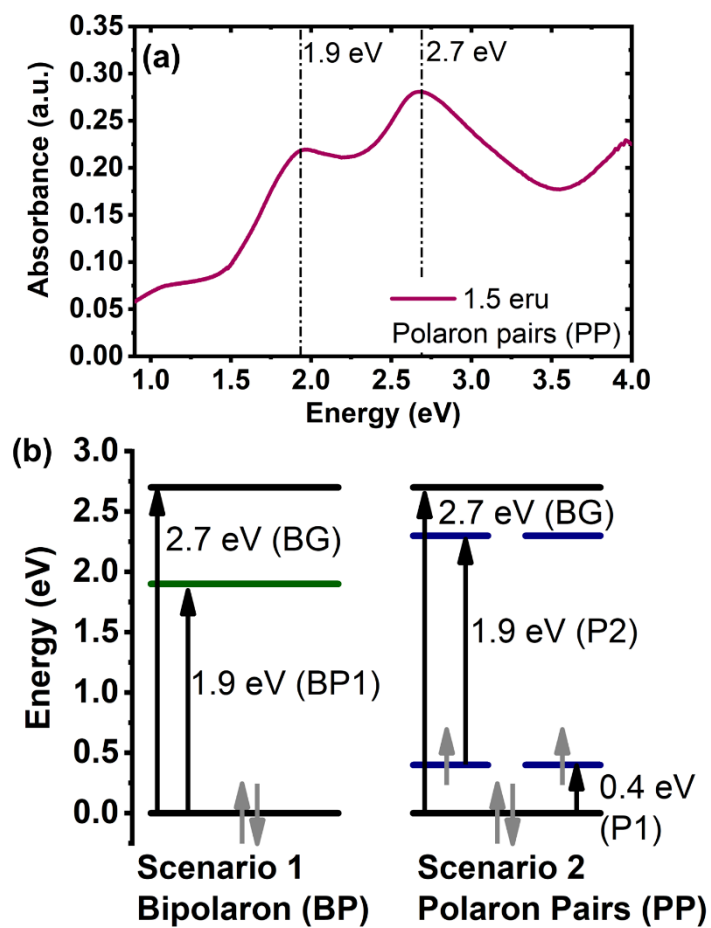


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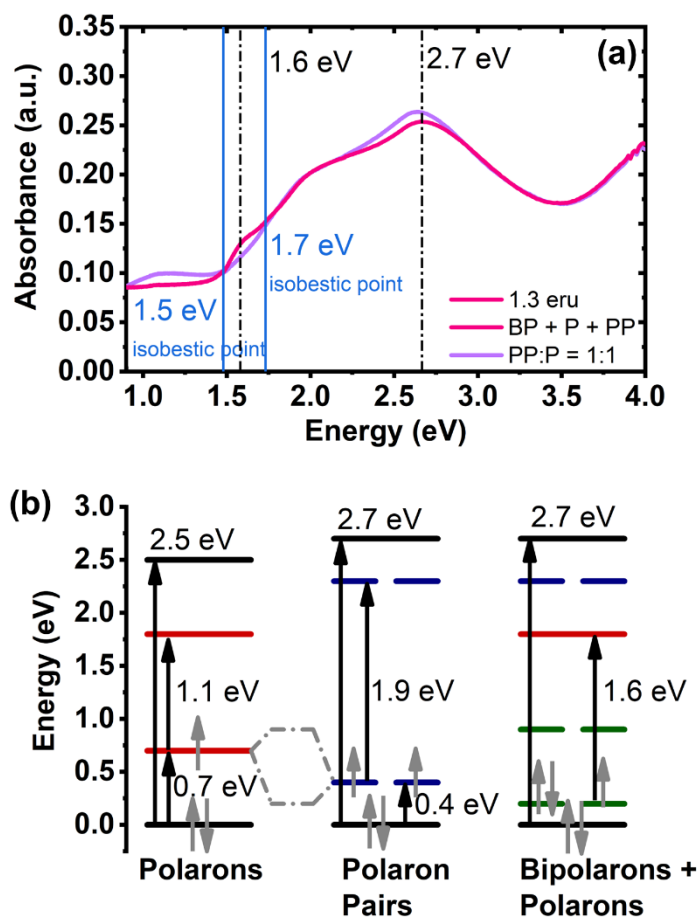


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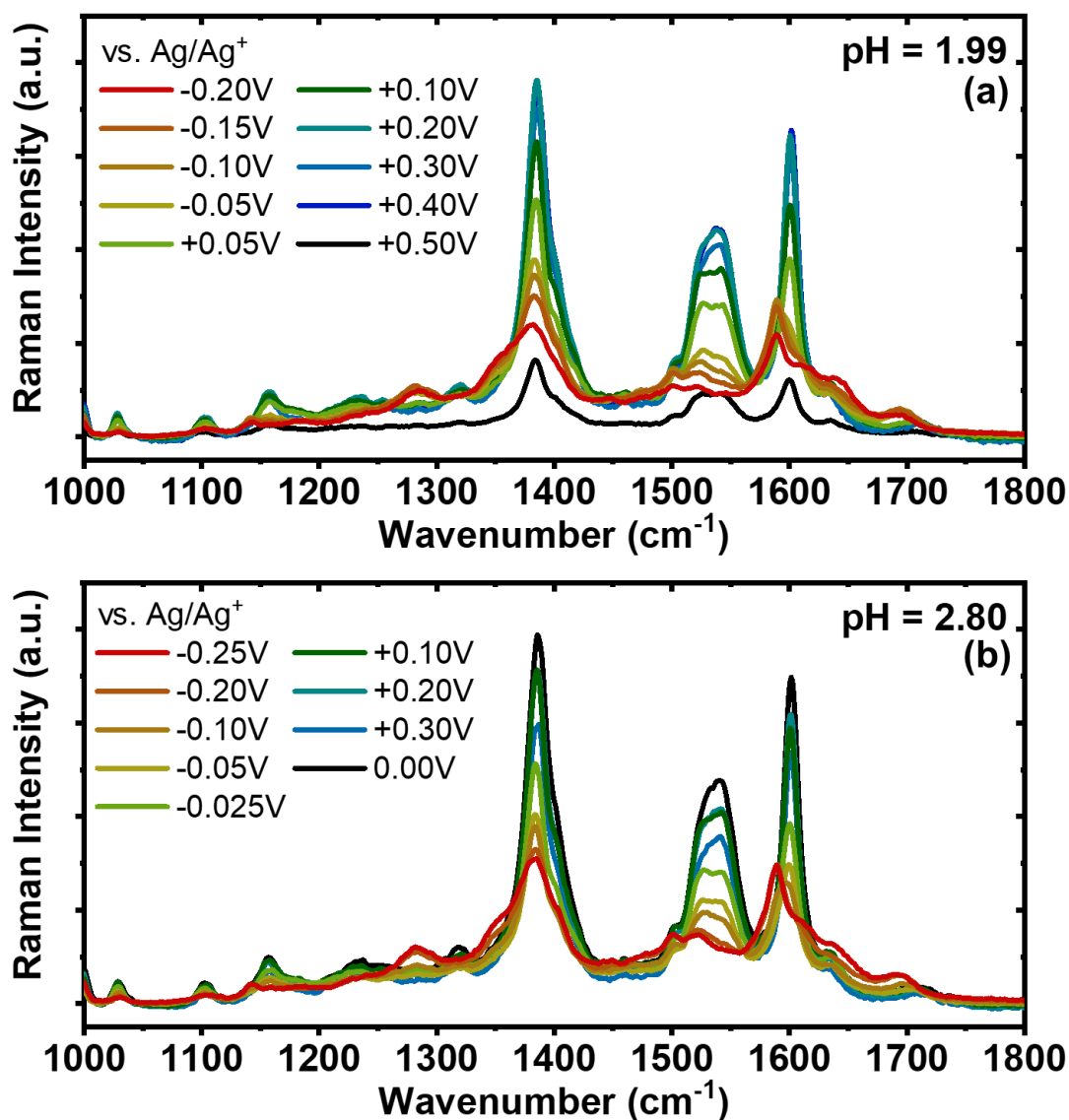




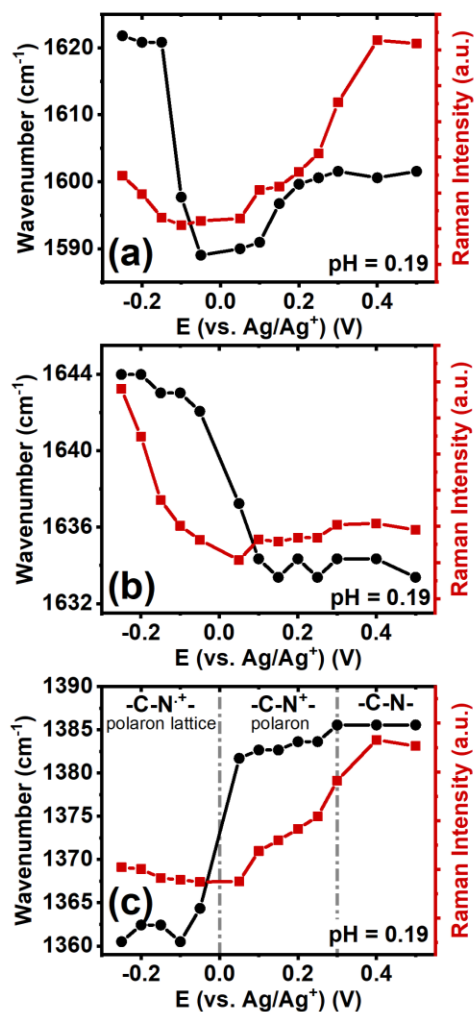
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**Figure S15.** *In-operando* Raman spectra of BBL-P films collected in 0.1M  $\text{KCl}_{(\text{aq})}$  electrolyte of varying pH value: (a) pH = 1.99, and (b) pH = 2.80. Raman measurements were collected using 532 nm excitation with BBL-P films coated on gold covered glass substrates as the working electrode, Pt mesh as the counter electrode,  $\text{Ag}/\text{AgCl}$  pellet as reference electrode positioned away from the illuminated area.




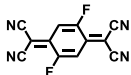
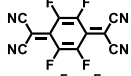
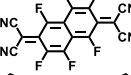
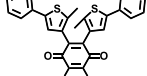






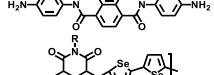
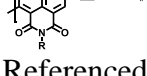
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**Table S1.** Quantification of Proton-Coupled Electron Transfer Processes of BBL Thin Films.

Wave	Slope <sup>(a)</sup> (mV/pH)	$n_{\text{H}^+}/n_{\text{e}^-}$ <sup>(b)</sup>
I	$-89.2 \pm 5.2$	$1.5 \pm 0.1$
II	$-99.8 \pm 3.9$	$1.7 \pm 0.1$

<sup>(a)</sup>slope, average slope calculated from Pourbaix diagram (+/- one standard deviation); <sup>(b)</sup> $n_{\text{H}^+}/n_{\text{e}^-}$ , number of protons per electrons transferred in each reduction event of BBL-P (+/- one standard deviation). Average values and standard deviations were calculated from 5 different samples.

**Table S2.** Summary of reduction potential of some redox active molecules.

Molecular Structure	$E_1$ (V) ( $M \rightarrow M^{\cdot-}$ )	$E_2$ (V) ( $M^{\cdot-} \rightarrow M^{2-}$ )	$\Delta E$ (V)	References
	-1.4	-2.12	0.72	2, 3
	0.01 <sup>(a)</sup>	-0.59 <sup>(a)</sup>	0.60	4
	0.11 <sup>(a)</sup>	-0.39 <sup>(a)</sup>	0.50	4
	0.21 <sup>(a)</sup>	-0.29 <sup>(a)</sup>	0.50	4
	-0.58 <sup>(b)</sup>	-1.23 <sup>(b)</sup>	0.65	5
	-0.66 <sup>(b)</sup>	-1.37 <sup>(b)</sup>	0.71	5
	-0.24 <sup>(b)</sup>	-0.97 <sup>(b)</sup>	0.73	5
	-0.35 <sup>(b)</sup>	-1.1 <sup>(b)</sup>	0.75	5
	-0.69 <sup>(b)</sup>	-1.34 <sup>(b)</sup>	0.65	5
	-0.54 <sup>(b)</sup>	-1.27 <sup>(b)</sup>	0.73	5
	-0.77 <sup>(b)</sup>	-1.39 <sup>(b)</sup>	0.62	5
	-0.96 <sup>(c)</sup>	-1.43 <sup>(c)</sup>	0.47	6
	-0.85 <sup>(a)</sup>	-1.29 <sup>(a)</sup>	0.44	7

<sup>(a)</sup> Referenced vs. Ag/Ag<sup>+</sup>.  
<sup>(b)</sup> Referenced vs. SCE.  
<sup>(c)</sup> Referenced vs. Ag/AgClO<sub>4</sub>

**Table S3.** Density Functional Theory (DFT) Computed Atomic Charge Distribution of BBL-P Dimers in its Neutral State (Structure 1), Reduced at Carbonyl Oxygen State (Structure 1a), and Protonated Reduced State (Structure 2).

Atomic Position	Structure 1	Structure 1a	Structure 2b
N46 (C=N, naphthalene)	-0.529	-0.549	-0.536
O48 (C=O, carbonyl)	-0.475	-0.558	-0.541
N45 (C=N, naphthalene)	-0.561	-0.588	-0.574
O47 (C=O, carbonyl)	-0.480	-0.557	-0.574
N81 (C=N, phenazine)	-0.562	-0.566	-0.520
N82 (C=N, phenazine)	-0.561	-0.574	-0.718
N24 (C=N, naphthalene)	-0.557	-0.598	-0.591
O23 (C=O, carbonyl)	-0.480	-0.544	-0.538
O18 (C=O, carbonyl)	-0.480	-0.547	-0.539
N17 (C=N, naphthalene)	-0.557	-0.600	-0.590
N69 (C=N, phenazine)	-0.561	-0.563	-0.715
N70 (C=N, phenazine)	-0.558	-0.564	-0.513

**Table S4.** Density Functional Theory (DFT) Computed Atomic Charge Distribution of BBL-P Dimers in its Neutral State (Structure 1), Protonated at Naphthalene Imine (Structure 3), Reduced Protonated at Naphthalene Imine (Structure 4a), and Reduced Double Protonated at Naphthalene Imine and Phenazine Imine (Structure 4b).

Atomic Position	Structure 1	Structure 3	Structure 4a	Structure 4b
N46 (C=N, naphthalene)	-0.529	-0.503	-0.670	-0.644
O48 (C=O, carbonyl)	-0.475	-0.435	-0.455	-0.385
N45 (C=N, naphthalene)	-0.561	-0.738	-0.744	-0.721
O47 (C=O, carbonyl)	-0.480	-0.443	-0.464	-0.410
N81 (C=N, phenazine)	-0.562	-0.557	-0.569	-0.567
N82 (C=N, phenazine)	-0.561	-0.546	-0.567	-0.745
N24 (C=N, naphthalene)	-0.557	-0.537	-0.737	-0.726
O23 (C=O, carbonyl)	-0.480	-0.457	-0.466	-0.464
O18 (C=O, carbonyl)	-0.480	-0.429	-0.454	-0.478
N17 (C=N, naphthalene)	-0.557	-0.722	-0.735	-0.751
N69 (C=N, phenazine)	-0.561	-0.557	-0.560	-0.709
N70 (C=N, phenazine)	-0.558	-0.548	-0.549	-0.501

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