Quantitative Assessment of the Connection Between Steric Hindrance and Electronic Coupling in 2,5-bis(alkoxy)Benzene Based Mixed-Valence Dimers

*Angela M. Bischof†, Shaopeng Zhang‡, Tara Y. Meyer‡, Benjamin J. Lear†**

†Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania, 16802, United States

‡Department of Chemistry, University of Pittsburgh, 219 Parkman Avenue, Pittsburgh, Pennsylvania, 15260, United States

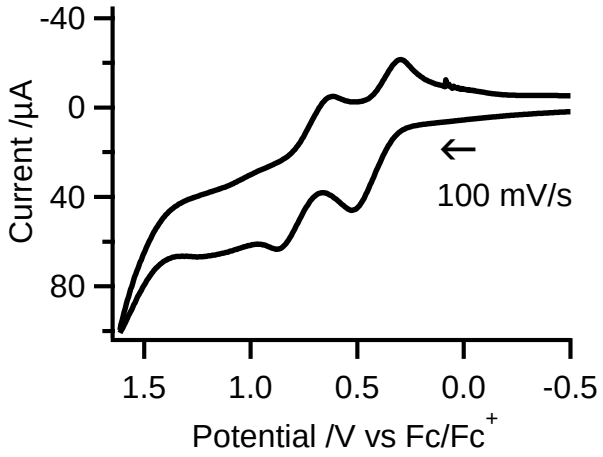

Figure S1. Cyclic Voltammogram of **2** in 0.1 M $TBAPF_6$ in CH_2Cl_2.

Table S1. Peak Position (and Intensity) for the Electronic Spectra of Dimeric Models of Conducting Polymers, **1**, **2**, and **3**, in Various Redox States[a]

2	$\mathbf{2}^{\bullet+}$	$\mathbf{2}^{2+}$	$\mathbf{1}^{\bullet+b}$	$\mathbf{3}^{\bullet+b}$
231 (1.6)	231 (2.9)	231 (2.2)	2150 (0.48)[c]	1570 (0.39)[c]
290 (1.2)	292 (1.2)	292 (1.3)		
360 (2.0)	460 (0.57)	458 (0.33)		
	502 (1.2)	486 (0.37)		
	585 (0.52)	761 (0.25)		
	1619 (1.5)[c]	929 (0.097)		
		994 (0.092)		

[a] Wavelength of maximum absorption given in nm and extinction coefficient (parenthesis) given in 10^4 $M^{-1}cm^{-1}$. [b] Values reported by Kochi, *et al.*;[1] values were only given for the NIR absorptions. [c] IVCT band.

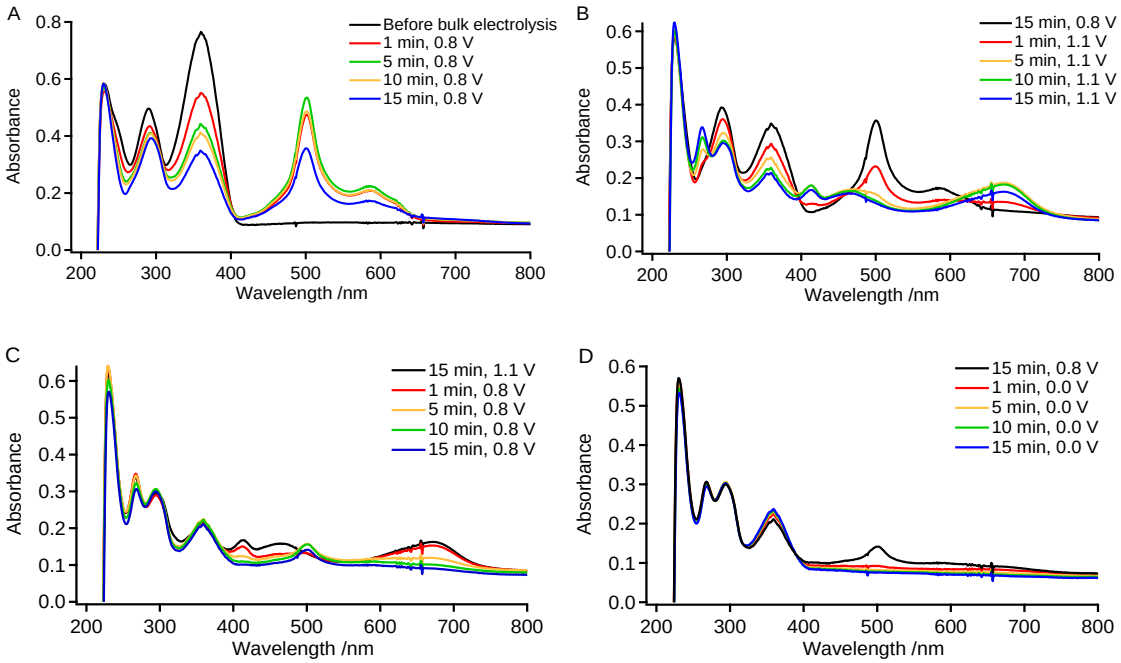

Figure S2. UV-Vis-SEC showing: A) oxidation from **2** to $\mathbf{2}^{\bullet+}$; B) oxidation from $\mathbf{2}^{\bullet+}$ to $\mathbf{2}^{2+}$;

C) reduction from $\mathbf{2}^{2+}$ to $\mathbf{2}^{\bullet+}$. D) reduction from $\mathbf{2}^{\bullet+}$ to **2**.

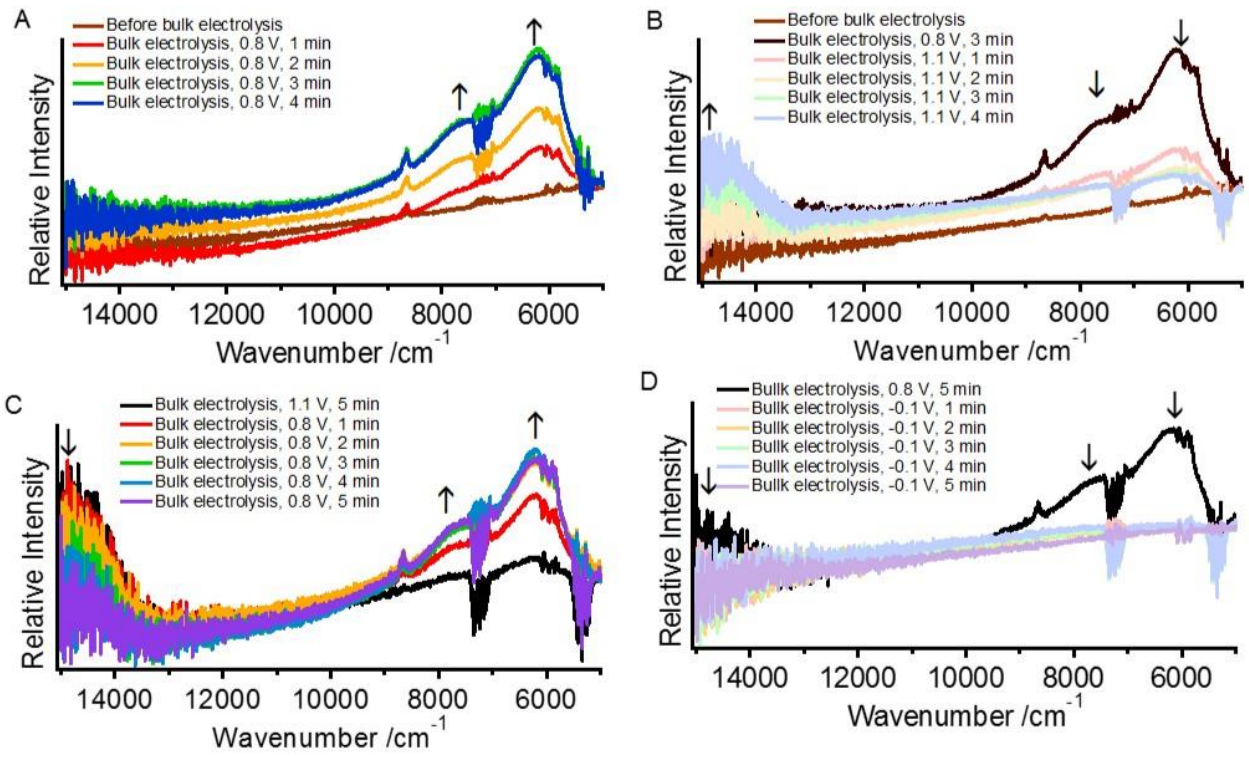

Figure S3. NIR-SEC showing: A) oxidation from **2** to $\mathbf{2}^{\bullet+}$; B) oxidation from $\mathbf{2}^{\bullet+}$ to $\mathbf{2}^{2+}$; C) reduction from $\mathbf{2}^{2+}$ to $\mathbf{2}^{\bullet+}$; D) reduction from $\mathbf{2}^{\bullet+}$ to **2**.

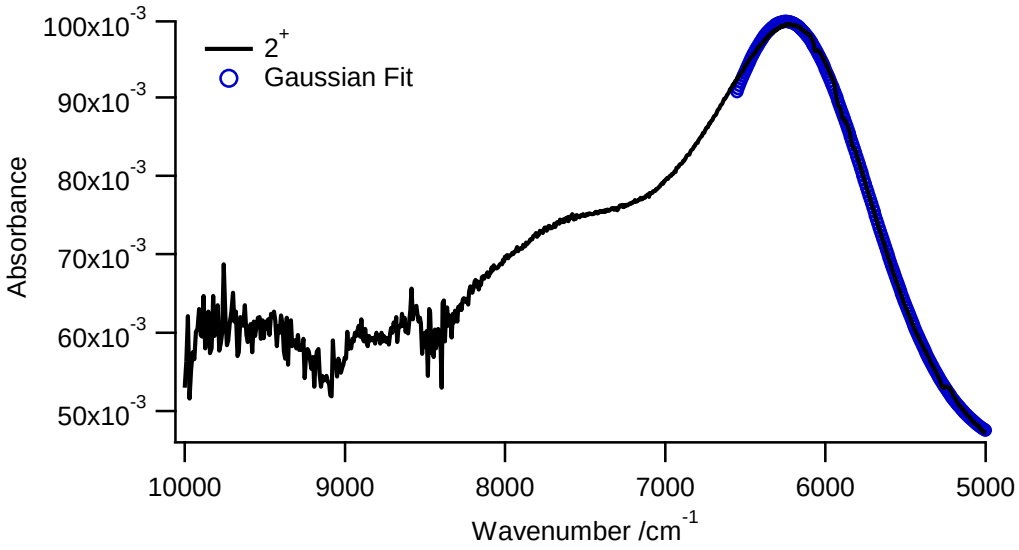

Figure S4. Gaussian fitting of low energy side of IVCT band for $\mathbf{2}^{\bullet+}$.

The low energy side of the IVCT band was fitted to a Gaussian peak shape, and the FWHM of the Gaussian fit was used as $\Delta\nu$. This approach was used so that the vibronic progression was not included in the determination of the width of the IVCT band.

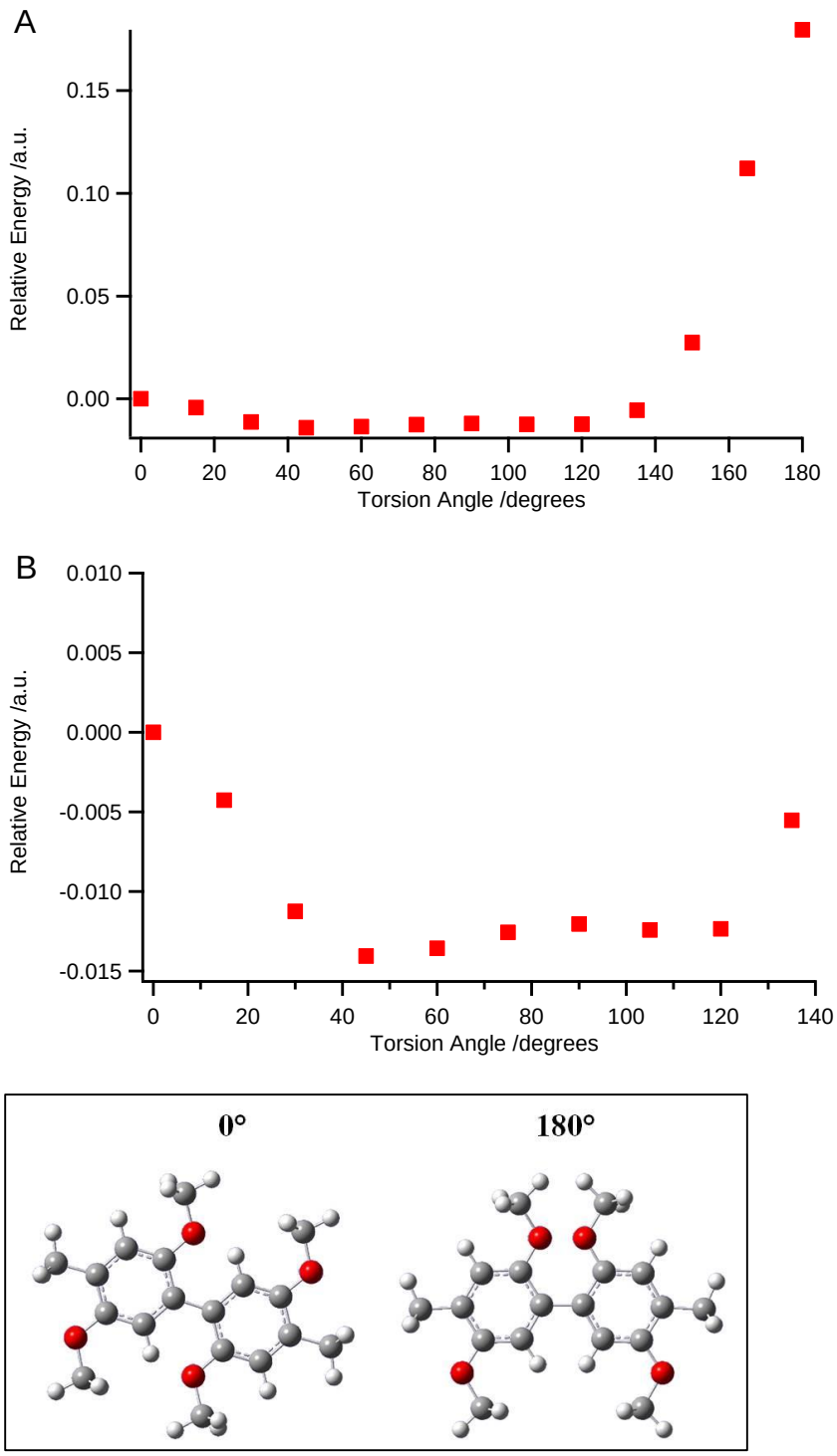

Figure S5. Relative energy as a function of torsion angle for A – **1**, B – **1** with points after 135° removed because the drastic energy increase is a result of the two methoxy groups coming in close proximity with one another, not necessarily the rotational energy barrier about the central bond.

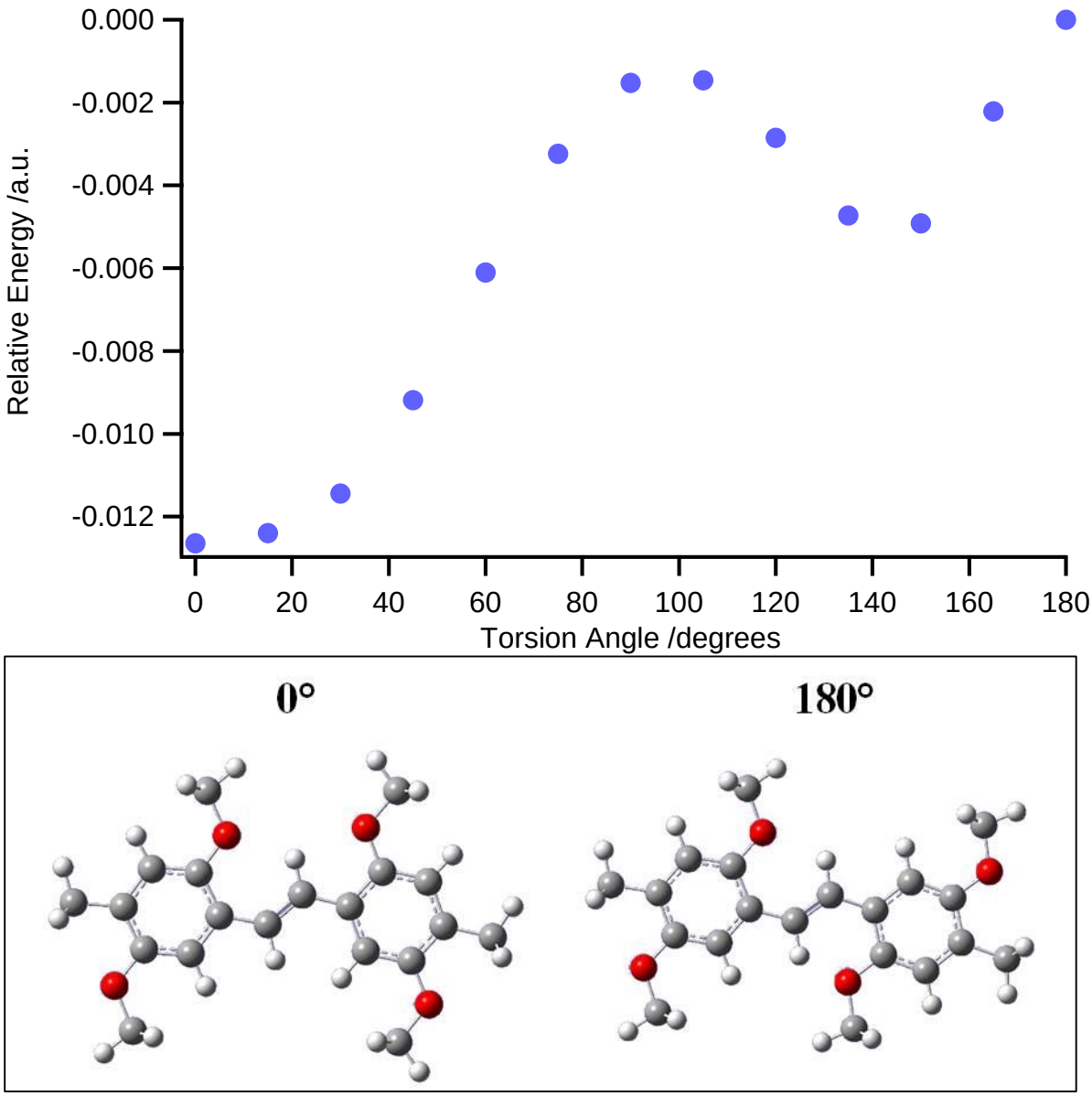

Figure S6. Relative energy as a function of torsion angle for **2**, The 0° and 180° configurations are shown.

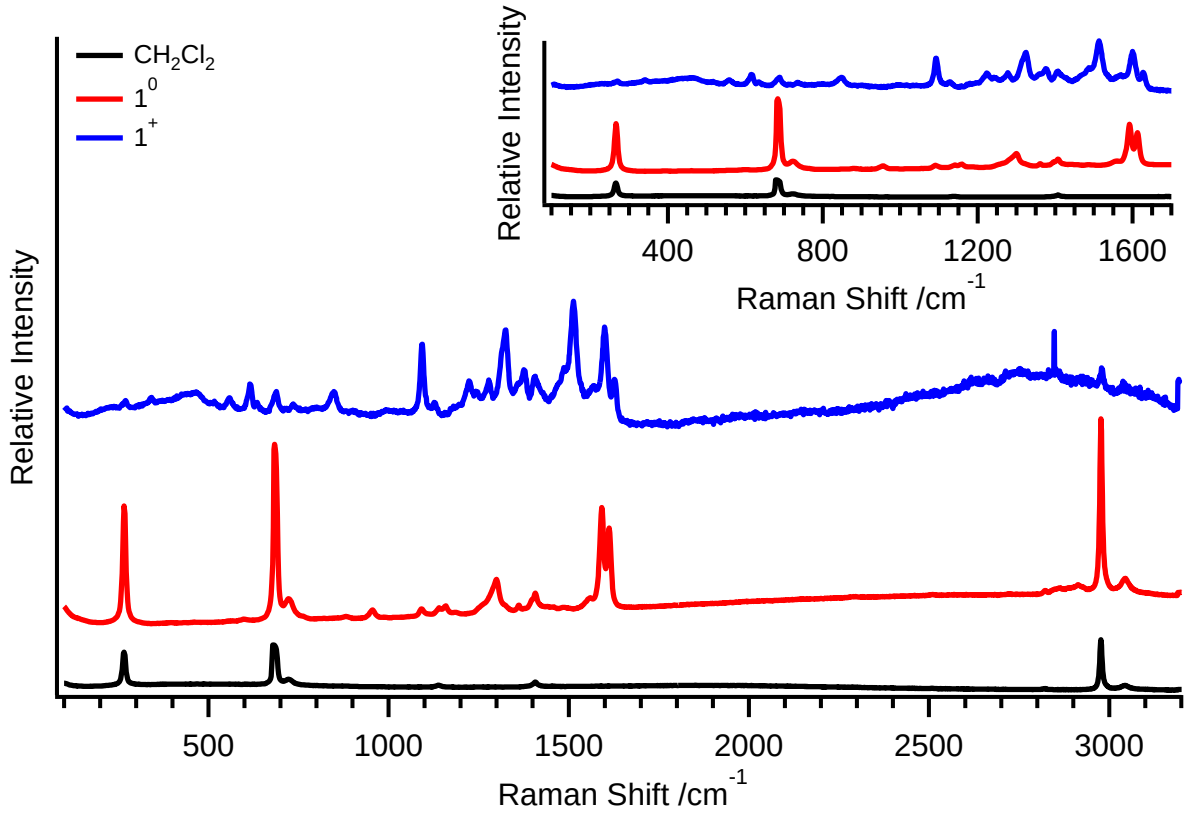

Figure S7. Raman spectra of CH_2Cl_2 (black), **2** (red) in CH_2Cl_2, and $\mathbf{2}^{\bullet+}$ (blue) in CH_2Cl_2. Inset shows the range from 100-1700cm^{-1}.

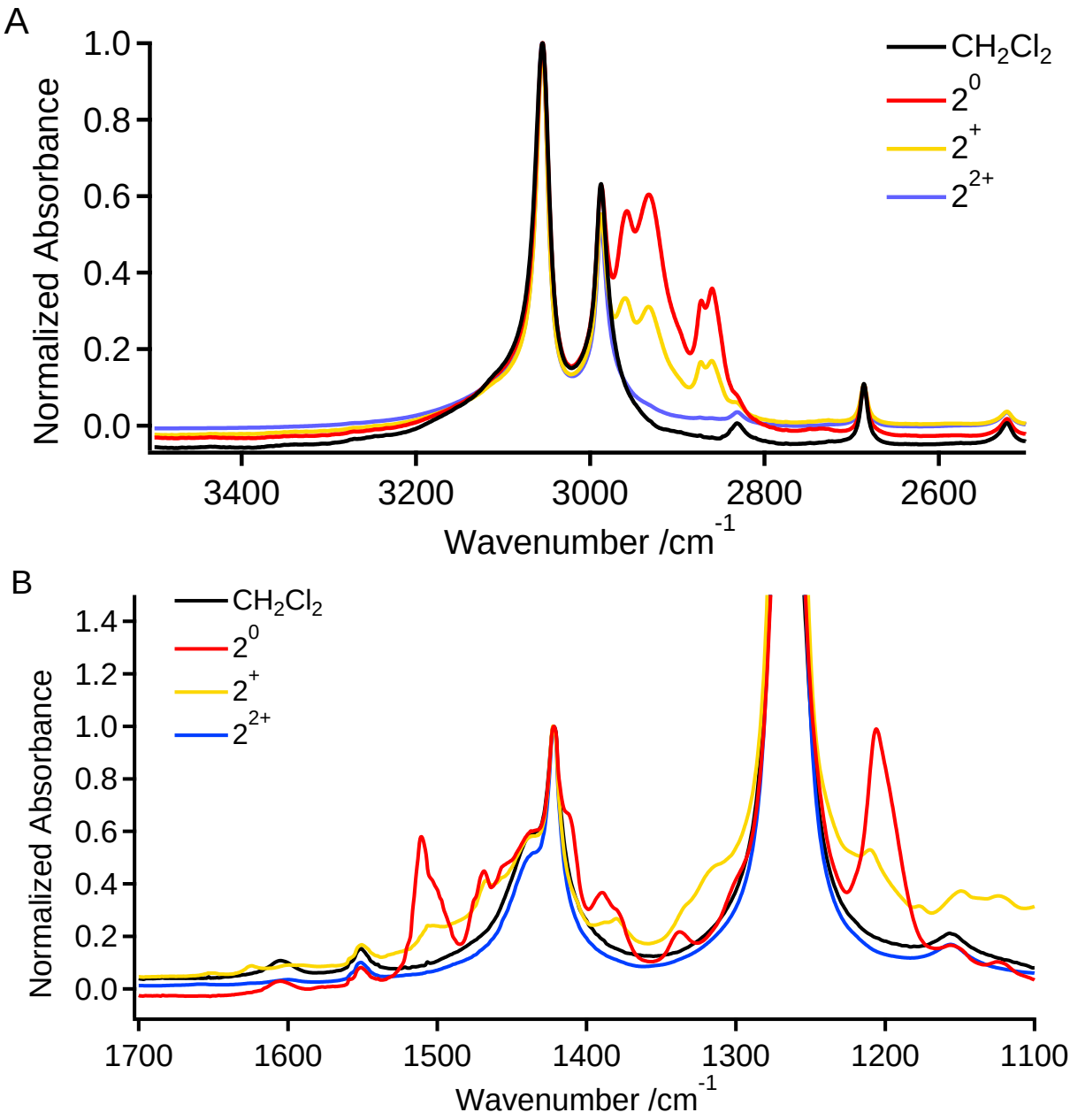

Figure S8. IR of **2**, **2**$^{\bullet+}$, and **2**$^{2+}$showing: A) ν(C-H) modes; B) showing aromatic stretching region.

REFERENCES

1. Lindeman, S. V., Rosokha, S. V., Sun, D. and Kochi, J. K. X-Ray Structure Analysis and the Intervalent Electron Transfer in Organic Mixed-Valence Crystals with Bridged Aromatic Cation Radicals. J. Am. Chem. Soc. 2002, 124, 843-855.

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