Supplementary Information

Luminescent Properties of a 3,5-diphenylpyrazole Bridged Pt(II) Dimer

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1. X-Ray Crystallography

1.1 Single Crystal X-ray Diffraction

Table S1. Crystal data and structure refinement for **3** at 100 K.

Identification code	shelx	
Empirical formula	C49 H37 Cl4 F6 N6 P Pt2	
Formula weight	1386.79	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 13.3294(2) Å	α = 116.327(2)°.
	b = 14.2532(2) Å	β = 110.712(2)°.
	c = 15.2190(3) Å	γ = 95.0050(10)°.
Volume	2318.99(8) Å^3	
Z	2	
Density (calculated)	1.986 Mg/m^3	
Absorption coefficient	14.152 mm^{-1}	
F(000)	1332	
Crystal size	0.2251 x 0.1513 x 0.0939 mm^3	
Theta range for data collection	3.579 to 75.847°.	
Index ranges	-16<=h<=15, -17<=k<=17, -19<=l<=18	
Reflections collected	26257	
Independent reflections	9361 [R(int) = 0.0210]	
Completeness to theta = 67.684°	99.6 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.652 and 0.395	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9361 / 90 / 641	
Goodness-of-fit on F^2	1.127	
Final R indices [I>2sigma(I)]	R1 = 0.0200, wR2 = 0.0507	
R indices (all data)	R1 = 0.0204, wR2 = 0.0510	
Extinction coefficient	n/a	

Largest diff. peak and hole	0.766 and -0.710 e.Å^{-3}

Table S2. Crystal data and structure refinement for **3** at 150 K.

Identification code	shelx	
Empirical formula	C49 H37 Cl4 F6 N6 P Pt2	
Formula weight	1386.79	
Temperature	150(2) K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 13.3658(3) Å	α = 116.225(2)°.
	b = 14.2507(3) Å	β = 110.754(2)°.
	c = 15.2735(4) Å	γ = 94.835(2)°.
Volume	2337.60(11) Å^3	
Z	2	
Density (calculated)	1.970 Mg/m^3	
Absorption coefficient	14.040 mm^{-1}	
F(000)	1332	
Crystal size	0.2251 x 0.1513 x 0.0939 mm^3	
Theta range for data collection	3.576 to 66.599°.	
Index ranges	-15<=h<=15, -16<=k<=16, -18<=l<=18	
Reflections collected	24450	
Independent reflections	8231 [R(int) = 0.0160]	
Completeness to theta = 66.599°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.52877	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8231 / 78 / 641	
Goodness-of-fit on F^2	1.092	
Final R indices [I>2sigma(I)]	R1 = 0.0199, wR2 = 0.0481	
R indices (all data)	R1 = 0.0205, wR2 = 0.0485	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.622 and -1.115 e.Å^{-3}	

Table S3. Crystal data and structure refinement for **3** at 200 K.

Identification code	shelx	
Empirical formula	C32.67 H24.67 Cl2.67 F4 N4 P0.67 Pt1.33	
Formula weight	924.53	
Temperature	200(2) K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 13.3738(3) Å	α = 116.222(2)°.
	b = 14.2394(2) Å	β = 110.687(2)°.
	c = 15.3804(4) Å	γ = 94.6010(10)°.
Volume	2358.67(10) Å^3	
Z	3	
Density (calculated)	1.953 Mg/m^3	
Absorption coefficient	13.914 mm^{-1}	
F(000)	1332	
Crystal size	0.2251 x 0.1513 x 0.0939 mm^3	
Theta range for data collection	3.557 to 66.598°.	
Index ranges	-15<=h<=15, -16<=k<=16, -18<=l<=18	
Reflections collected	24961	
Independent reflections	8298 [R(int) = 0.0175]	
Completeness to theta = 66.598°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.54189	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8298 / 165 / 641	
Goodness-of-fit on F^2	1.070	
Final R indices [I>2sigma(I)]	R1 = 0.0239, wR2 = 0.0597	
R indices (all data)	R1 = 0.0247, wR2 = 0.0603	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.635 and -1.269 e.Å^{-3}	

Table S4. Crystal data and structure refinement for **3** at 250 K.

Identification code	shelx	
Empirical formula	C32 H23.33 Cl1.33 F4 N4 P0.67 Pt1.33	
Formula weight	867.91	
Temperature	250(2) K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 13.4179(2) Å	α = 116.174(2)°.
	b = 14.2402(2) Å	β = 110.742(2)°.
	c = 15.4690(3) Å	γ = 94.4190(10)°.
Volume	2382.96(8) $Å^3$	
Z	3	
Density (calculated)	1.814 Mg/m^3	
Absorption coefficient	12.717 mm^{-1}	
F(000)	1248	
Crystal size	0.2251 x 0.1513 x 0.0939 mm^3	
Theta range for data collection	3.533 to 74.894°.	
Index ranges	-16<=h<=16, -17<=k<=17, -19<=l<=19	
Reflections collected	27281	
Independent reflections	9502 [R(int) = 0.0185]	
Completeness to theta = 67.684°	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.53340	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9502 / 171 / 587	
Goodness-of-fit on F^2	1.035	
Final R indices [I>2sigma(I)]	R1 = 0.0212, wR2 = 0.0536	
R indices (all data)	R1 = 0.0227, wR2 = 0.0548	
Extinction coefficient	0.000561(19)	
Largest diff. peak and hole	0.846 and -0.769 $e.Å^{-3}$	

1.2 Polycrystalline X-Ray Diffraction

Polycrystalline X-ray diffraction (PXRD) data for **2** was collected on an Agilent Technologies SuperNova Dual Source diffractometer using a μ-focus Cu Kα radiation source (λ = 1.5418 Å) equipped with collimating mirror monochromators at 100 K. Sample was mounted to a nylon thread loop using Paratone oil. Data collection was performed using CrysAlisPro.[1] Data was processed using EVA.[2] Theoretical PXRD spectrum was generated using the HKL data from the single crystal at 100 K and PLATON98[3]. All PXRD graphs were constructed using OrginPro 8.[4]

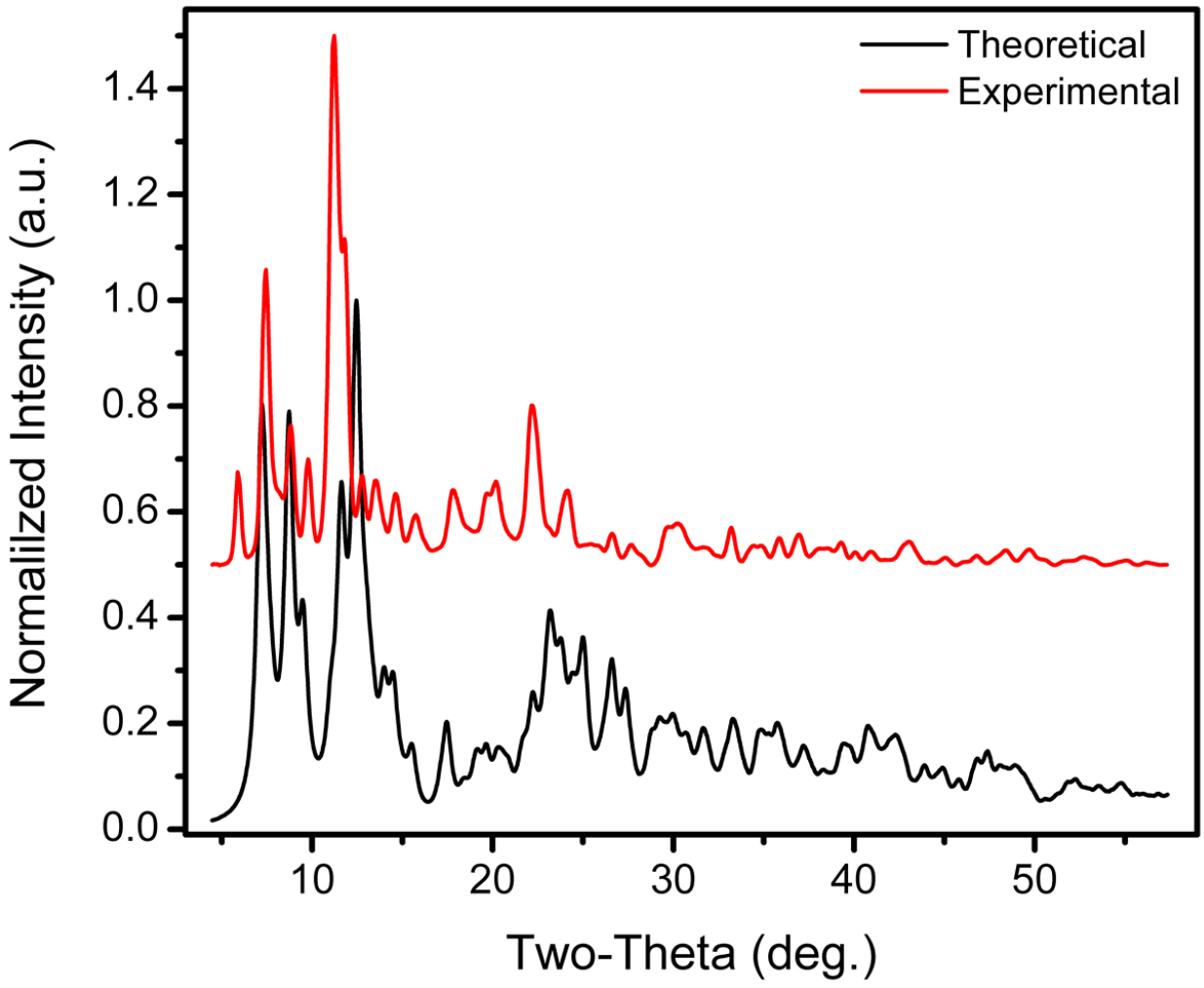

Figure S1. Experimental and theoretical polycrystalline X-ray diffraction patterns of **2**.

2. Electrochemistry

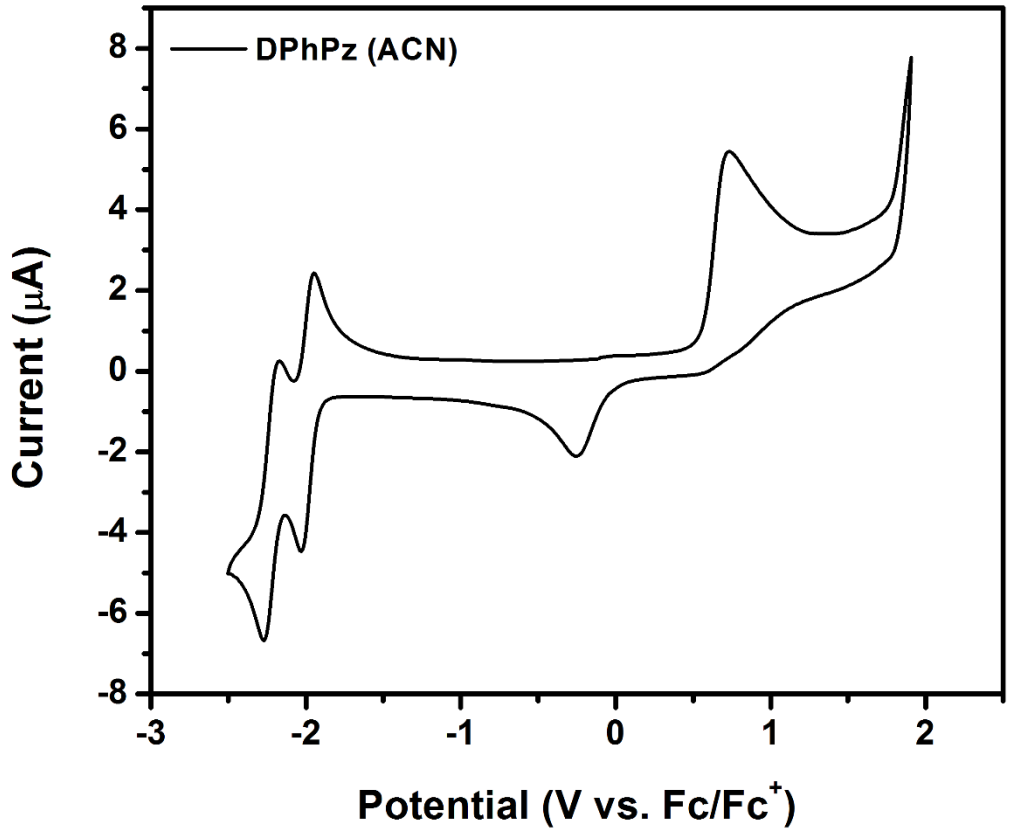

Figure S2. Cyclic voltammogram of complex **2** in acetonitrile from 2.0 V to -2.4 V.

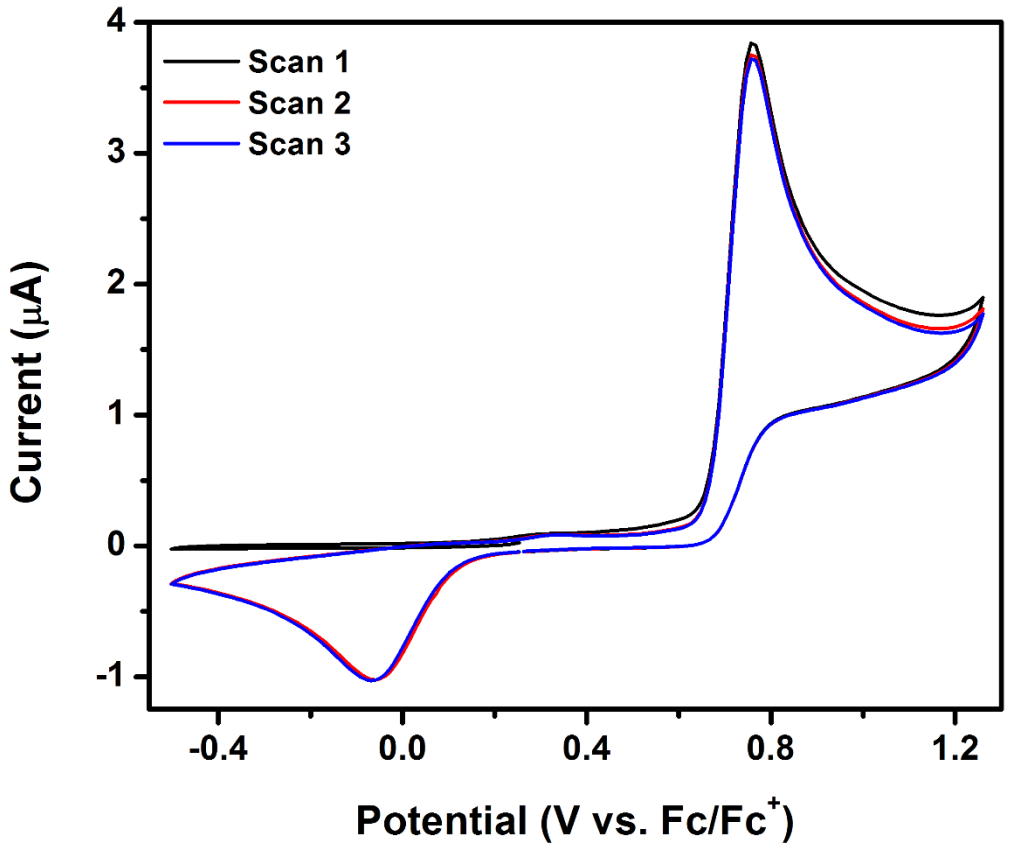

Figure S3. Cyclic voltammogram of **2** in DCM. Start potential was 0.50 V, which was allowed to equilibrate for 10 seconds before starting scans. Scans were first performed by scanning to reductive potentials (-0.25 V) before scanning to oxidative potentials (1.50 V). Results revealed that the reductive event just below 0.00 V did not appear until the oxidative event at 0.80 V had occurred.

3. Optical Spectroscopy

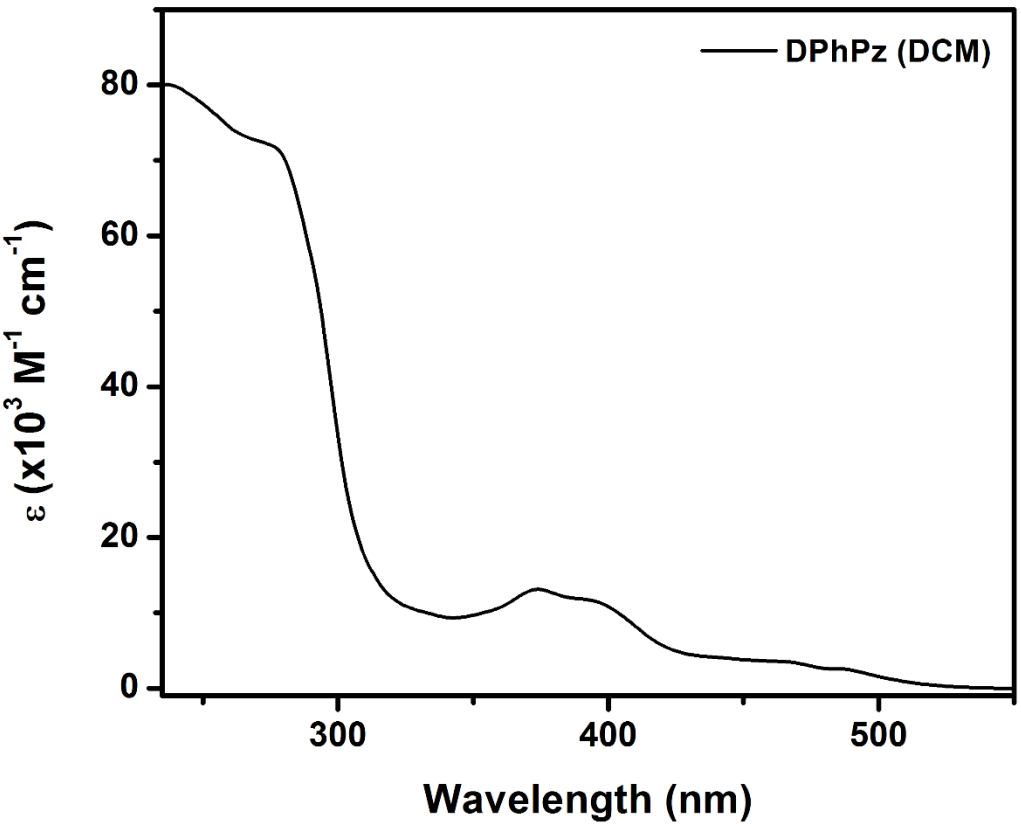

Figure S4. UV-visible spectrum of **3** in dichloromethane at room temperature.

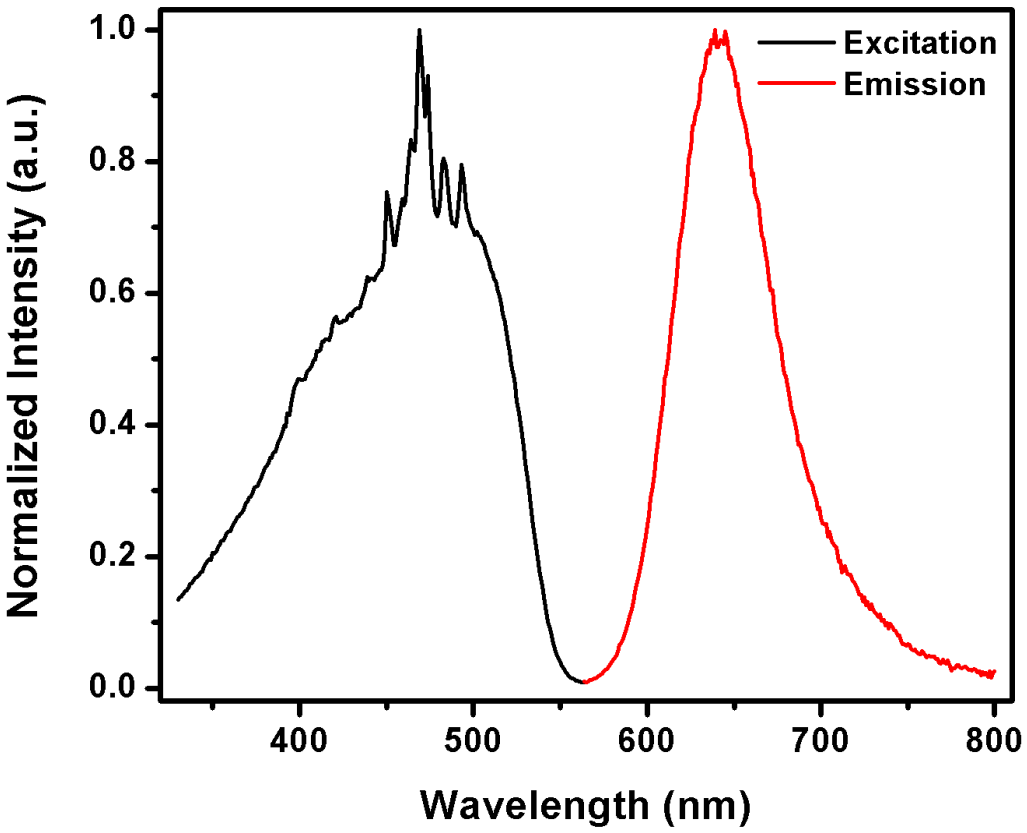

Figure S5. Solid-state excitation and emission profile of **3** at 77 K.

4. Infrared Spectroscopy

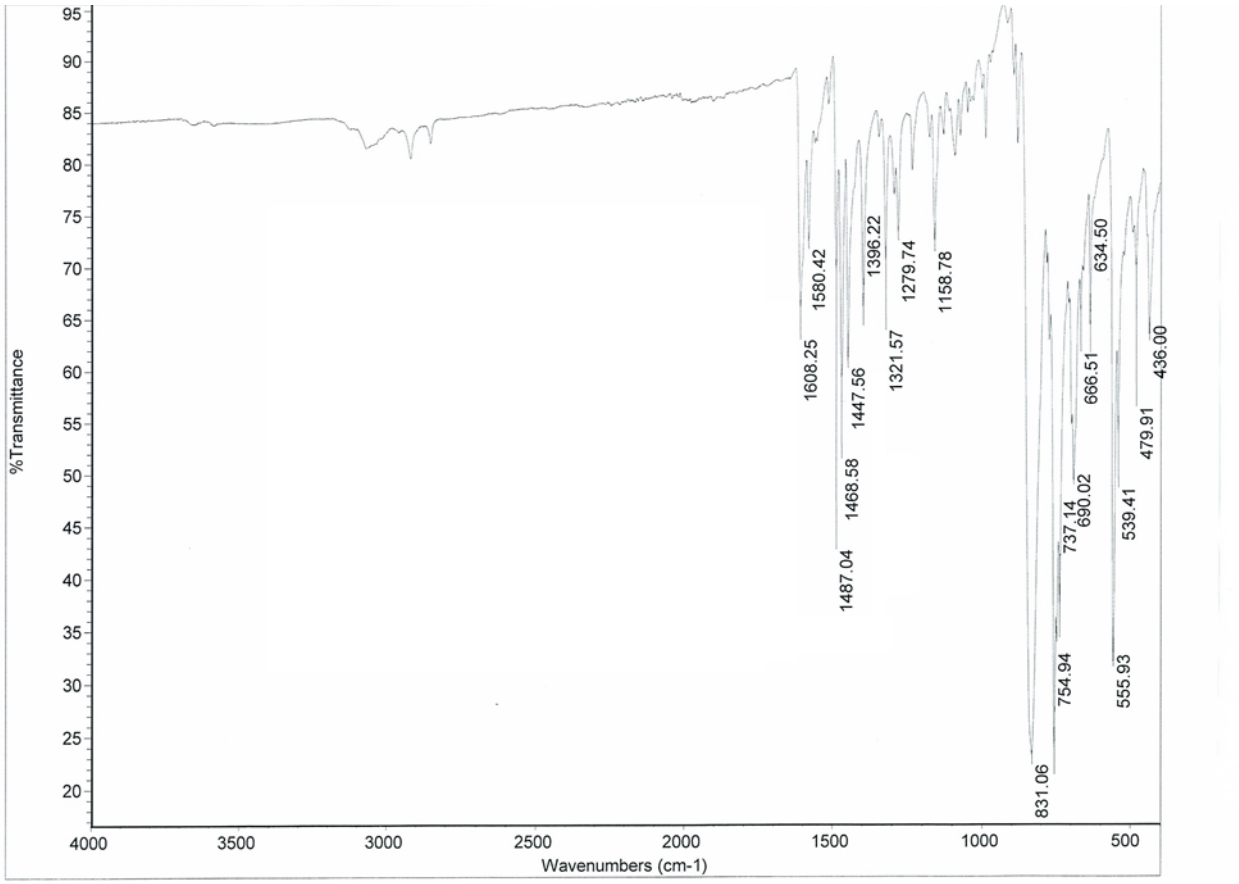

Figure S6. Infrared spectrum of **3**.

5. References

(1) Katagiri, S.; Sakamoto, R.; Maeda, H.; Nishimori, Y.; Kurita, T.; Nishihara, H. *Chemistry* **2013**, *19*, 5088–5096.

(2) EVA, version 15.0.0.0.; Bruker-AXS Inc.: Madison, WI 53711-5373, USA, 2009.

(3) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115−119.

(4) OrginPro, version 8; OriginLab Corporation: Northampton, MA 01060, USA, 2016.