

# Palladium Induced Macrocyclic Preorganization for Stabilization of a Tetrathiafulvalene Mixed-Valence Dimer

Christopher Bejger,<sup>†</sup> Christina M. Davis,<sup>†</sup> Jung Su Park,<sup>†</sup>  
Vincent Lynch,<sup>†</sup> Jason B. Love,<sup>§</sup> and Jonathan L. Sessler<sup>\*†,‡</sup>

<sup>†</sup>*Department of Chemistry and Biochemistry, The University of Texas at Austin, 1 University Station A5300, Austin, Texas, 78712*

<sup>‡</sup>*Department of Chemistry, Yonsei University, Seoul 120-749, South Korea*

<sup>§</sup>*EaStCHEM School of Chemistry, University of Edinburgh, The King's Buildings, West Mains Road, Edinburgh EH9 3JJ, U. K.*

*sessler@mail.utexas.edu*

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### 1. Generalities

Starting materials were purchased from Sigma-Aldrich (St. Louis, MO) and TCI America (Portland, OR). <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured at 25 °C using a 400 MHz Varian Unity Innova instrument. UV-vis spectra were recorded on a BECKMAN DU 640B spectrophotometer. High resolution ESI mass spectra were obtained on a Varian Ion Spec (9.4 T FTMS) ESI Source mass spectrometer. Electrochemistry was done on a CV-50W Voltammetric Analyzer. EPR spectra were recorded on a Bruker EMX Plus spectrometer.

## 2. Synthetic Experimental

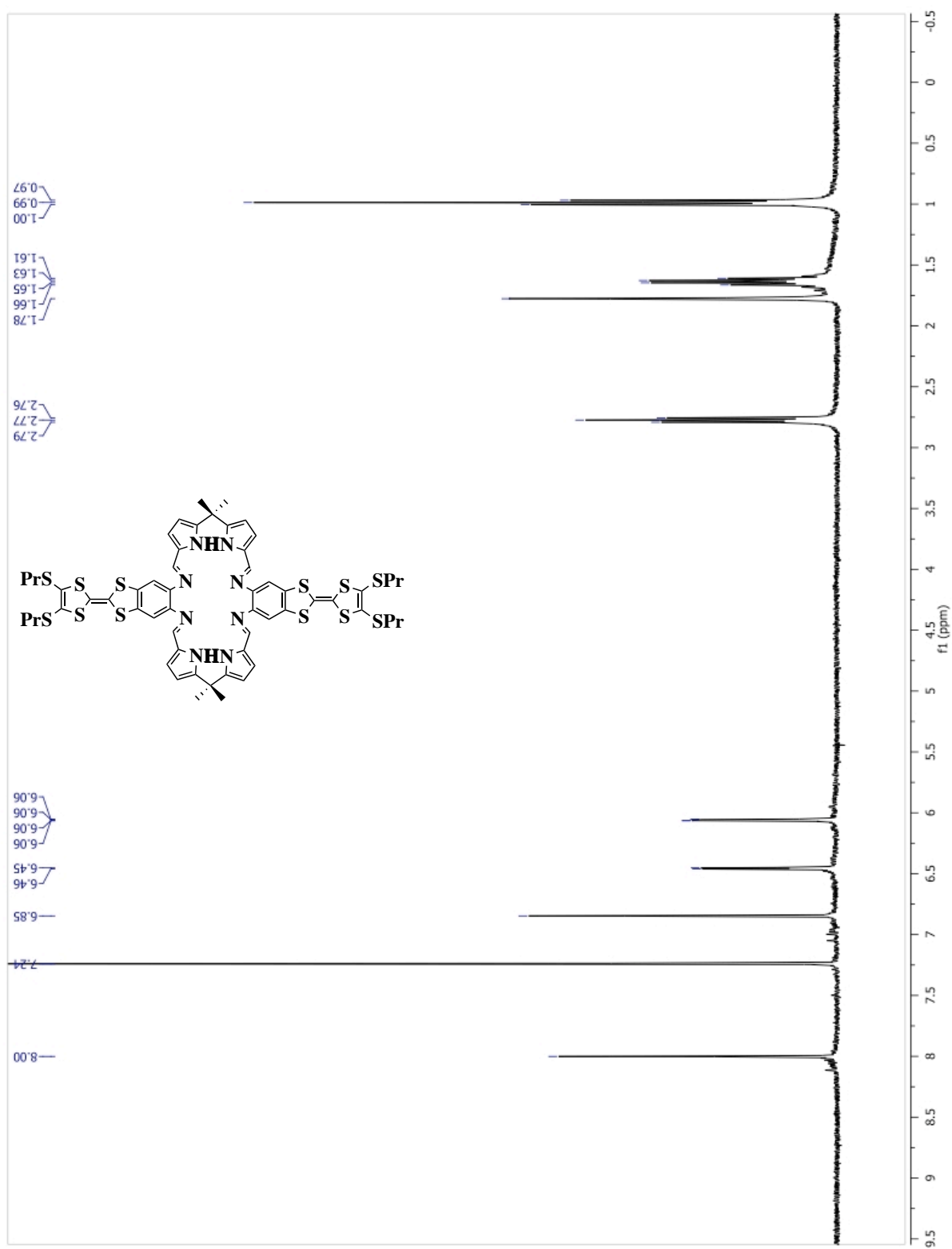
### Preparation of 2

A mixture of **5** (100 mg, 0.231 mmol) and **4** (53 mg, 0.231 mmol) in methanol was warmed until most of the solids had dissolved. *Para*-toluene sulfonic acid monohydrate (88 mg, 0.463 mmol) was added slowly in portions to the solution over one hour. The reaction mixture was allowed to stir for 1 hour. Triethylamine (0.25 mL) was slowly added to the solution causing precipitation of a yellow/orange solid, which was filtered, washed with methanol, and dried *in vacuo* to afford the title compound **2** (225 mg, 78%) as a light orange solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 8.0 (s, N-H, 4H), 6.85 (s, Ar-H, 4H), 6.46 (d, *J* = 3.69 Hz, C-H pyrrole, 4H), 6.06 (d, *J* = 3.70 Hz, C-H pyrrole, 4H), 2.77 (t, *J* = 7.33 Hz, -S-CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, 4H), 1.78 (s, *meso*-CH<sub>3</sub>, 6H), 1.63 (m, -S-CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, 4H), 0.99 (t, *J* = 7.36 Hz, -S-CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, 4H) ppm. HRMS (ESI) *m/z* calcd for (C<sub>58</sub>H<sub>61</sub>N<sub>8</sub>S<sub>12</sub>)<sup>+</sup> 1253.16661, found 1253.16622.

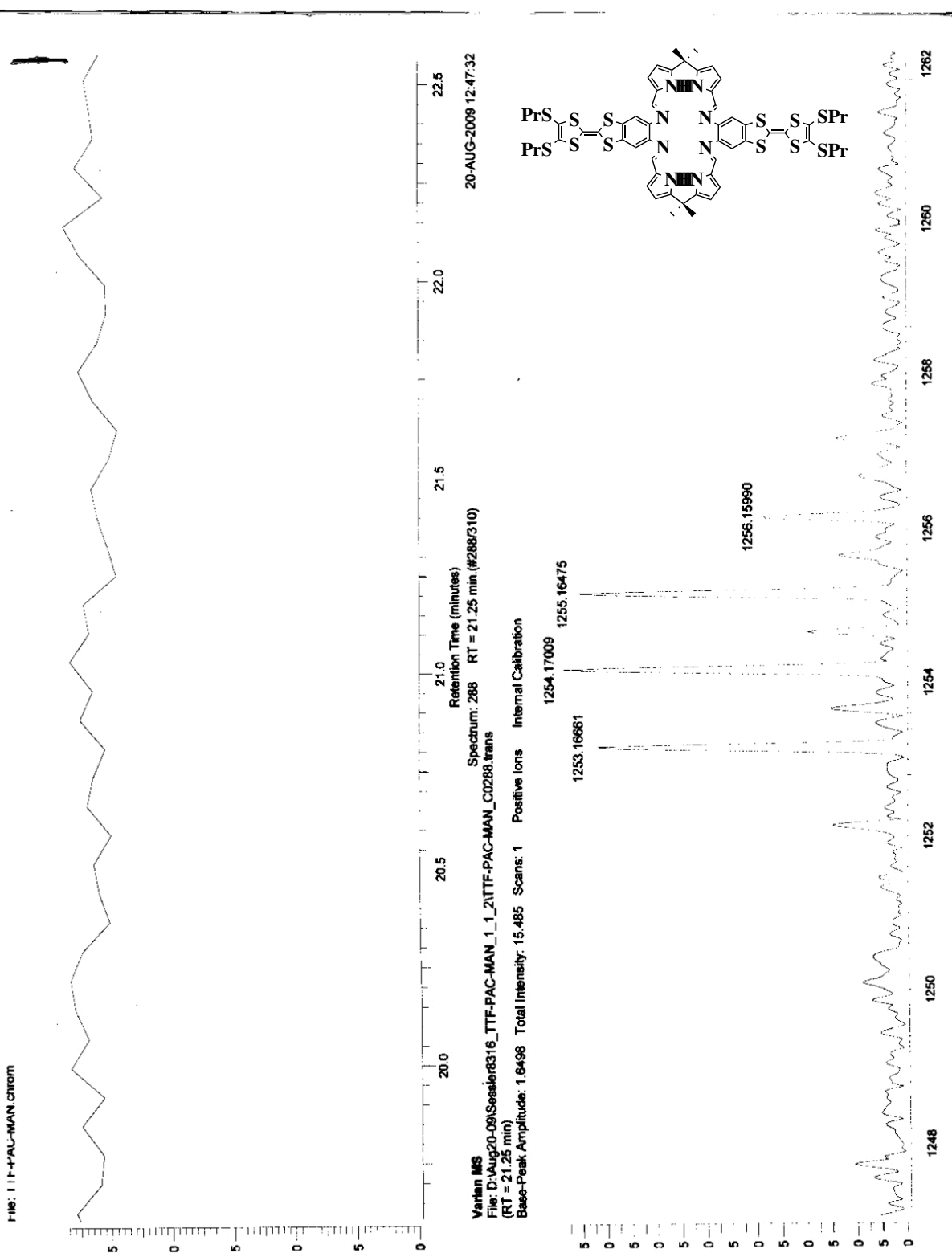
### Preparation of 3

Palladium acetate (33mg, 0.160 mmol) was added to a solution of free ligand **2** (100 mg, 0.08 mmol) dissolved in CH<sub>2</sub>Cl<sub>2</sub> (15 mL). After 30 minutes, triethylamine (0.2 mL) was added to the reaction mixture and the solution was allowed to stir at room temperature overnight. Pentane (50 mL) was added to the reaction and a brown solid precipitated, which was filtered and purified via column chromatography (silica gel, eluent: CH<sub>2</sub>Cl<sub>2</sub>/hexanes 2:1) to yield the title compound as a yellow solid (35 mg, 30%). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 7.26 (s, N-H, 4H), 6.80 (d, *J* = 3.8 Hz, C-H pyrrole, 4H), 6.66 (s, Ar-H, 4H), 6.23 (d, *J* = 3.72, C-H pyrrole, 4H), 2.79 (m, -S-CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, 8H), 1.66 (m, -S-CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, 8H), 1.62 (s, *meso*-CH<sub>3</sub>, 6H), 1.54 (s, *meso*-CH<sub>3</sub>, 6H), 1.00 (t, *J* = 7.27, -S-CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, 12H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ = 159.1, 153.1, 141.3, 136.4, 135.1, 127.4, 119.7, 117.1, 112.6, 108.8, 108.3, 43.5, 38.1, 32.4, 30.6, 29.7, 23.2, 13.3 ppm, HRMS (MALDI) *m/z* (C<sub>58</sub>H<sub>57</sub>N<sub>8</sub>Pd<sub>2</sub>S<sub>12</sub>) found 1463.92879.

<sup>1</sup>H-NMR of 2



## Mass Spec. for 2



**Elemental Composition Search Report:**

**Target Mass:**

Target m/z = 1253.16661 ± .002

Charge = +1

**Possible Elements:**

Element: Exact Mass: Min: Max:

C 12.000000 0 101

H 1.007825 0 110

N 14.003074 8 10

S 31.972071 12 14

**Additional Search Restrictions:**

None

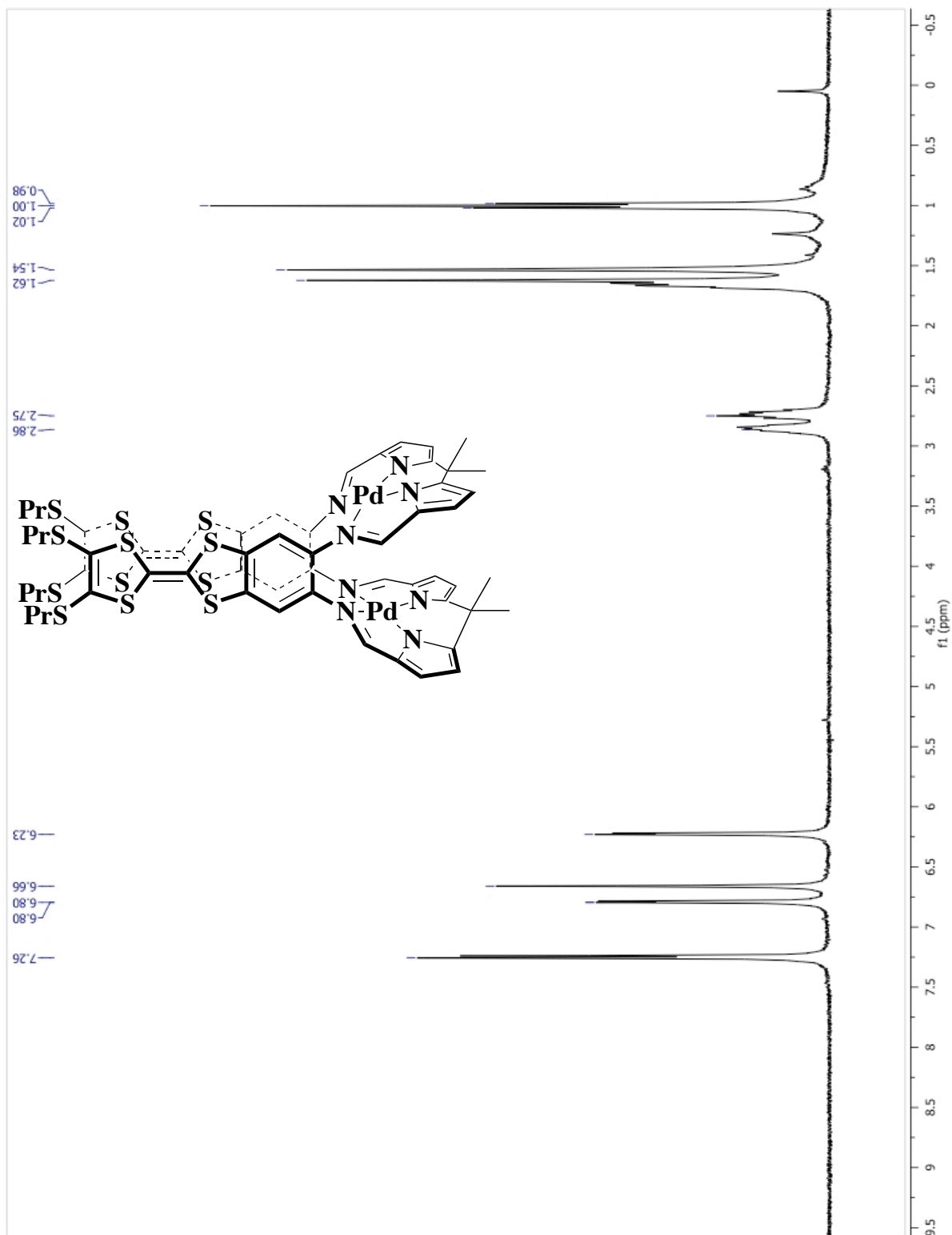
**Search Results:**

Number of Hits = 1

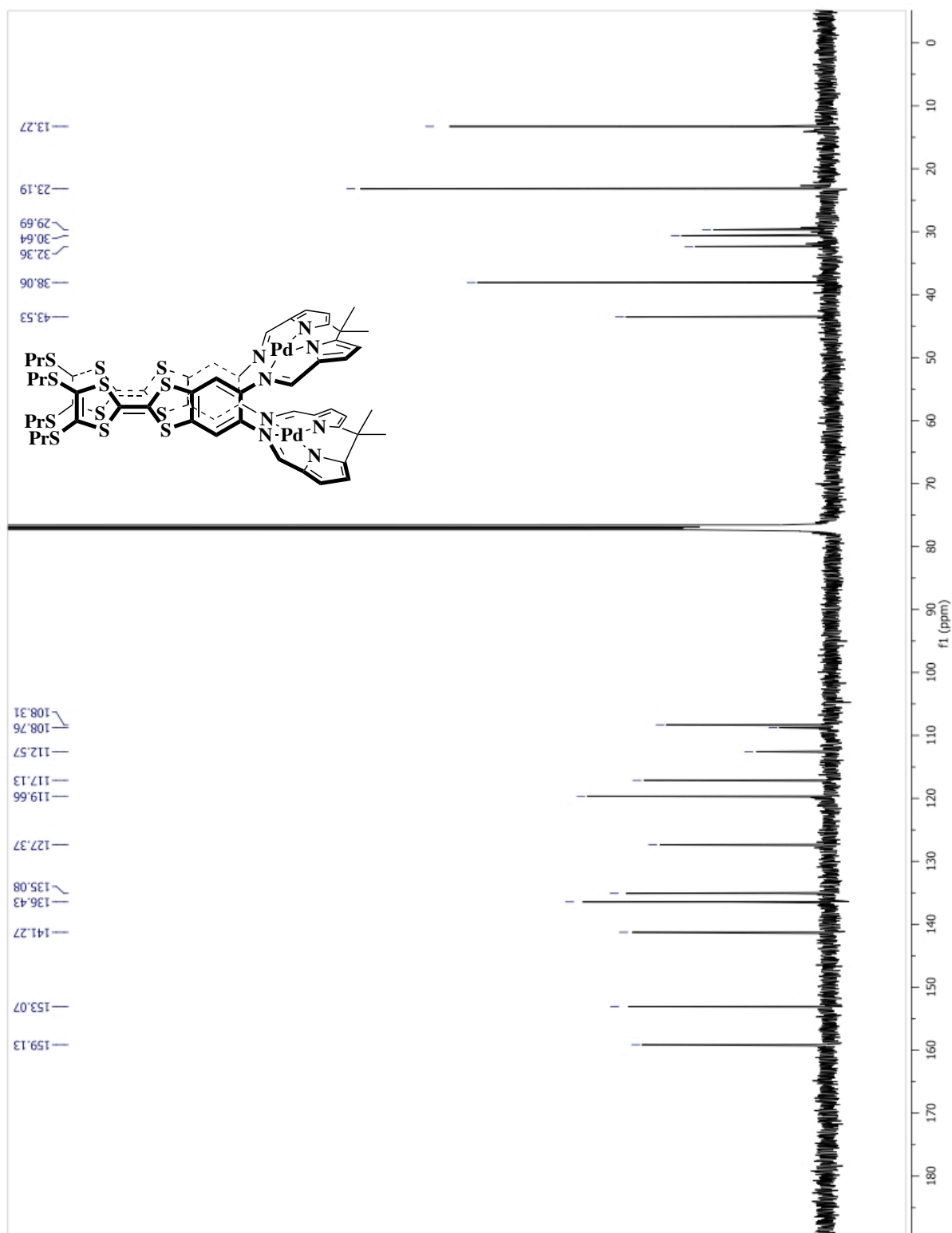
m/z Delta m/z DBE Formula

1253.16622 0.00039 32.5 C<sub>58</sub>H<sub>61</sub>N<sub>6</sub>S<sub>12</sub><sup>+</sup>

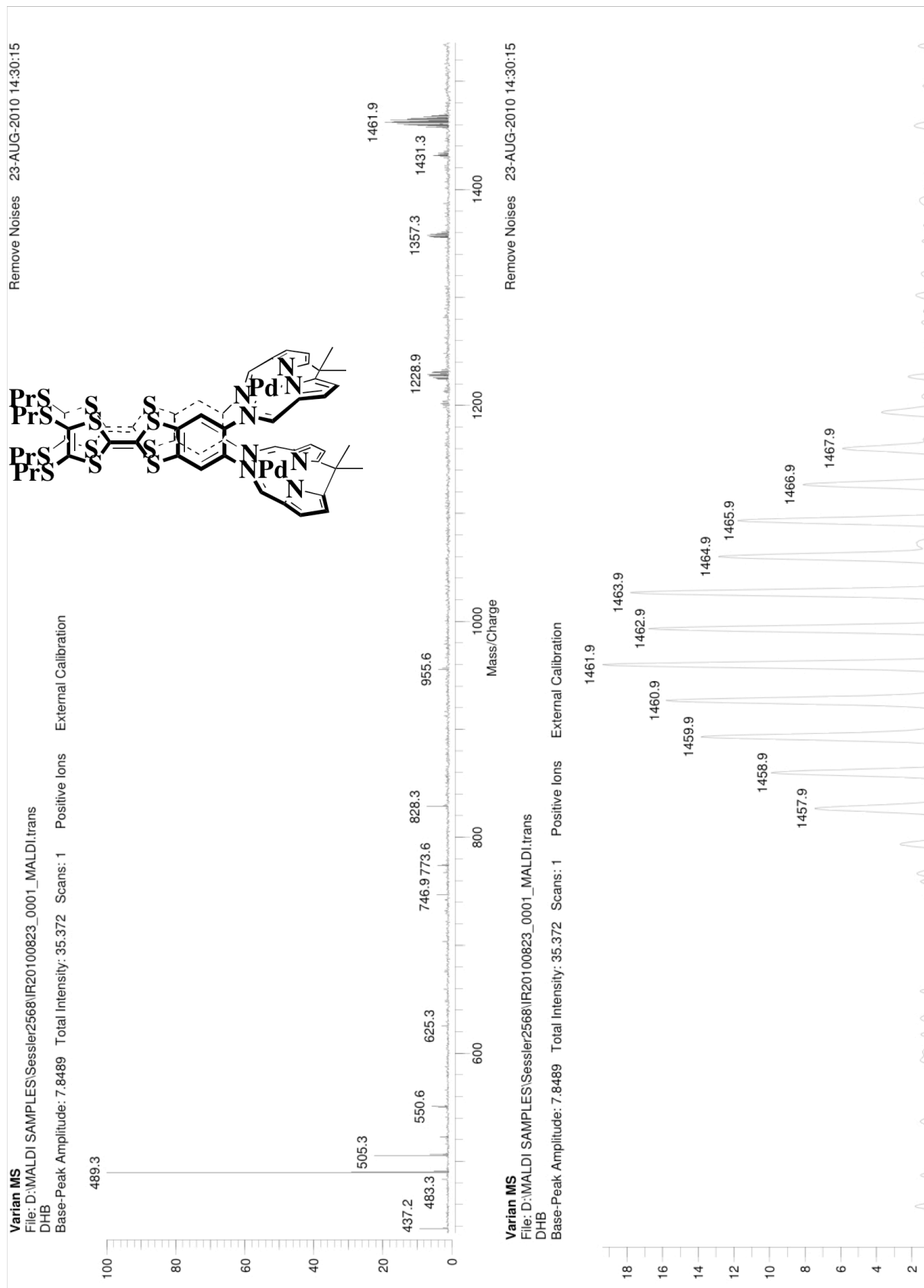
<sup>1</sup>H-NMR of 3



<sup>13</sup>C-NMR of 3

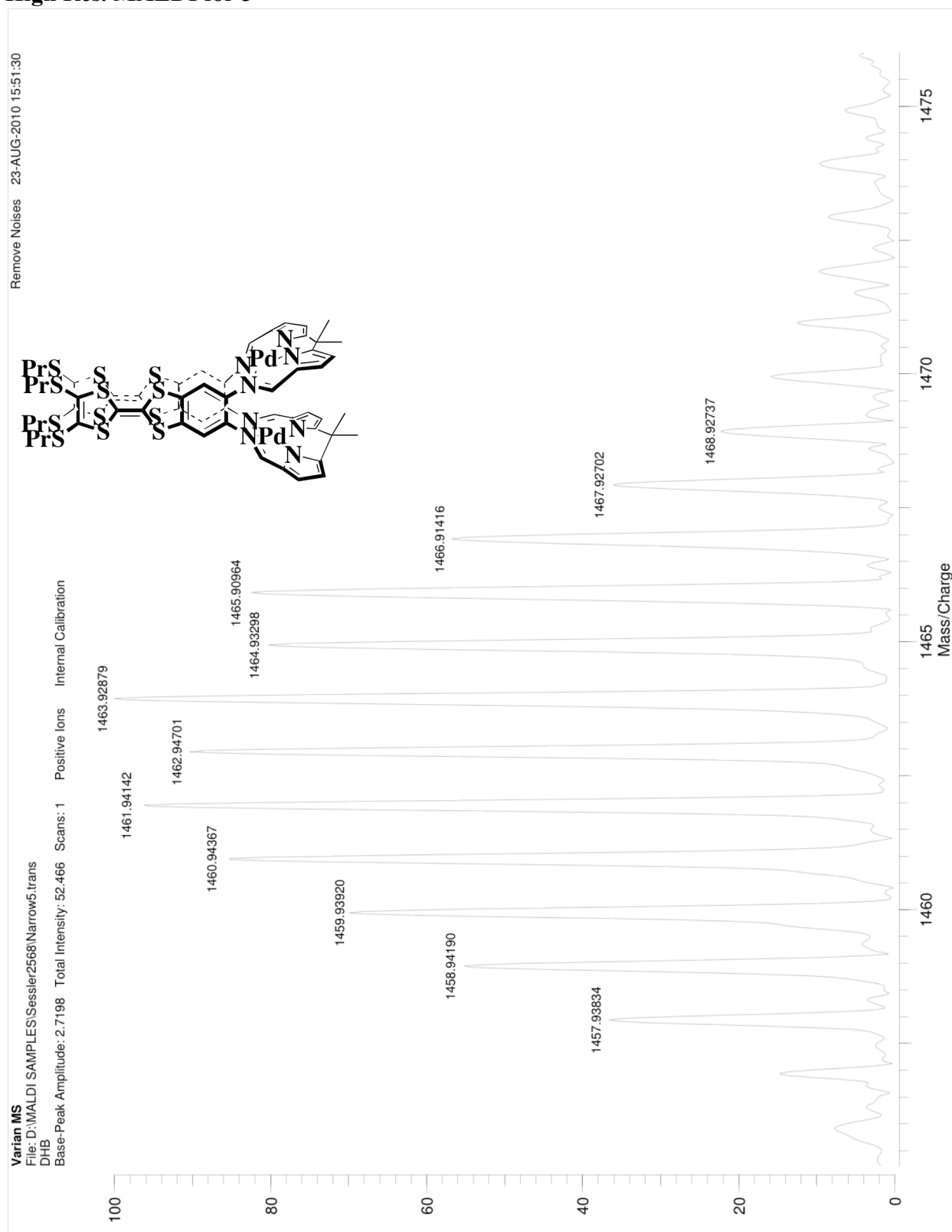


# Low Res. MALDI for 3





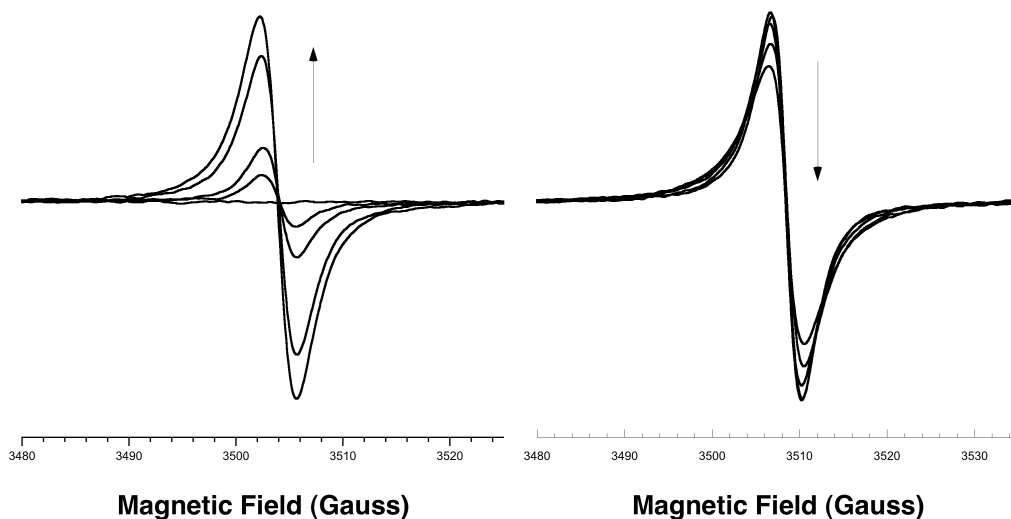
# High Res. MALDI for 3



### 3. EPR Data

EPR spectra of **2** (0.2 mM in CH<sub>2</sub>Cl<sub>2</sub>, 295 K) recorded upon stepwise oxidation with “Magic Blue”.

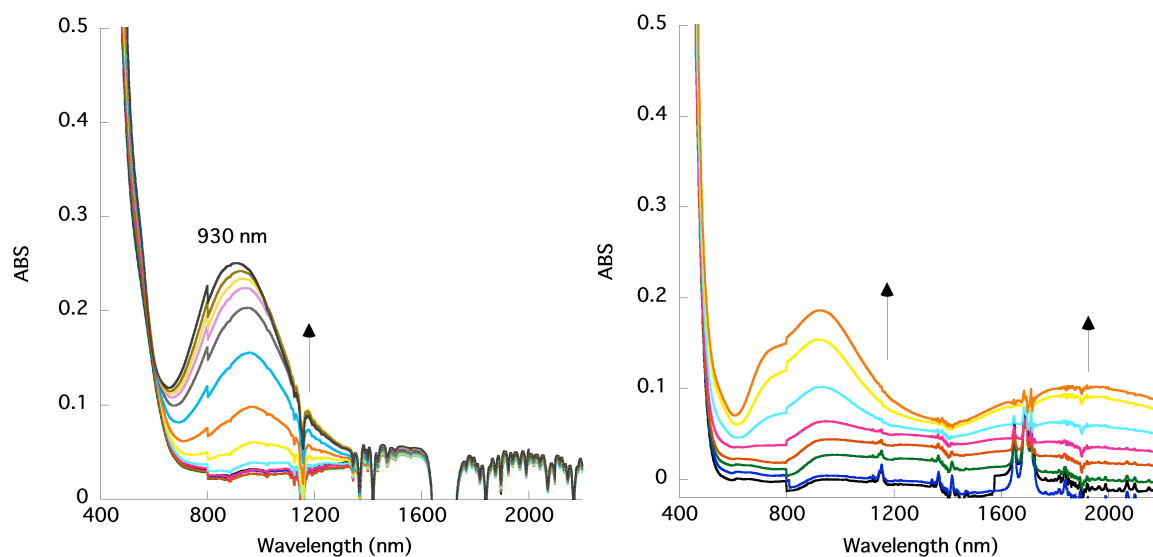
#### Free ligand **2**



Recorded from 0 - 2.0 equiv (left) and 2.0 – 3.0 equiv (right) of chemical oxidant.

### 4. Spectroelectrochemistry

UV-vis-NIR spectra of **2** (left) and **3** (right) measured in CH<sub>2</sub>Cl<sub>2</sub> (0.25 mM) in a spectroelectrochemical quartz UV cell upon bulk electrolysis of the cell contents at various potentials using TBA•PF<sub>6</sub> (0.2 M) as the supporting electrolyte, glassy carbon and Pt as the working and counter electrodes, respectively. Potentials were measured against a Ag/Ag<sup>+</sup> reference electrode at 100 mV/s.



## 6. Crystal Data

Single crystals were grown as yellow laths by slow evaporation of **3** dissolved in an equal volume of a solution of dichloromethane and hexanes. X-ray crystallographic data was collected at  $-50\text{ }^{\circ}\text{C}$  on a Rigaku SCX-Mini diffractometer using a monochromatized  $\text{MoK}\alpha$  source ( $\lambda = 0.71070\text{ \AA}$ ) equipped with a Mercury CCD area detector. The frame data was integrated and corrected for absorption effects using the Rigaku/MSO CrystalClear program package.<sup>1</sup> The structures were solved by direct methods and refined by full-matrix least-squares on  $F^2$  with anisotropic displacement parameters for the non-H atoms using SHELXL-97.<sup>2</sup> The function,  $w(|F_o|^2 - |F_c|^2)^2$ , was minimized, where  $w = 1/[(\sigma(F_o))^2 + (X \cdot P)^2 + (Y \cdot P)]$  and  $P = (|F_o|^2 + 2|F_c|^2)/3$  and the parameters, X and Y, are suggested during the refinement process. The hydrogen atoms were calculated in ideal positions with isotropic displacement parameters set to  $1.2 \times \text{Ueq}$  of the attached atom ( $1.5 \times \text{Ueq}$  for methyl hydrogen atoms). Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).<sup>3</sup> All the calculations were carried out with the SHELXTL program.<sup>4</sup> The details of the crystallographic data for **1** are summarized in Table S1. Further details of the structure can be obtained from the Cambridge Crystallographic Data Centre by quoting CCDC 828008.

Table 1. Crystal data and structure refinement for **3**.

Empirical formula	$\text{C}_{60}\text{H}_{60}\text{Cl}_4\text{N}_8\text{Pd}_2\text{S}_{12}$	
Formula weight	1632.48	
Temperature	153(2) K	
Wavelength	0.71069 $\text{\AA}$	
Crystal system	Monoclinic	
Space group	P21/n	
Unit cell dimensions	$a = 18.0698(6)\text{ \AA}$	$\alpha = 90.000(5)^{\circ}$ .
	$b = 18.8957(7)\text{ \AA}$	$\beta = 96.632(2)^{\circ}$ .
	$c = 19.9815(7)\text{ \AA}$	$\gamma = 90.000(5)^{\circ}$ .

Volume	6776.9(4) Å <sup>3</sup>
Z	4
Density (calculated)	1.600 Mg/m <sup>3</sup>
Absorption coefficient	1.104 mm <sup>-1</sup>
F(000)	3312
Crystal size	0.30 x 0.28 x 0.25 mm
Theta range for data collection	2.16 to 27.48°.
Index ranges	-23<=h<=23, -24<=k<=24, -25<=l<=25
Reflections collected	30338
Independent reflections	15512 [R(int) = 0.0287]
Completeness to theta = 27.48°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.06 and 0.934
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	15512 / 0 / 759
Goodness-of-fit on F <sup>2</sup>	1.058
Final R indices [I>2sigma(I)]	R1 = 0.0406, wR2 = 0.1078
R indices (all data)	R1 = 0.0585, wR2 = 0.1162
Largest diff. peak and hole	1.232 and -0.708 e.Å <sup>-3</sup>

## 6. References for Supporting Information

1. CrystalClear 1.40, Rigaku Americas Corporation, The Woodlands, TX, 2008.
2. Sheldrick, G. M. SHELXL97, *Program for the Refinement of Crystal Structure*; University of Gottingen, Germany, 1994,.
3. Wilson, A. J. C. *International Tables for X-ray Crystallography Vol. C*; Kluwer Academic Press: Boston, 1992, Tables 4.2.6.8 and 6.1.1.4
4. Sheldrick, G. M. SHELXTL/PC (Version 5.03). Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA, 199