

## Supporting Information

### Characterization of a

### Cross-Reactive Electronic Nose with Vapoluminescent Array Elements

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### Synthesis and Characterization of Compounds.

Isocyanides that were not commercially available were synthesized from the corresponding amine via an intermediate formamide derivative using the method of Ugi and Meyer.<sup>1</sup>  $\text{cis-Pt}(\text{CH}_3\text{CN})_2\text{Cl}_2$  was prepared from  $\text{K}_2[\text{PtCl}_4]$  as previously reported.<sup>2</sup>  $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2[\text{Pt}(\text{CN})_4]$  was prepared from  $[(n\text{-C}_4\text{H}_9)_4\text{N}]\text{Br}$  (Aldrich) and  $\text{K}_2[\text{Pt}(\text{CN})_4]$  (Strem) as previously reported.<sup>3</sup> Cyclododecylformamide, cyclododecylisocyanide and  $[\text{Pt}(\text{CN-cyclododecyl})_4][\text{Pt}(\text{CN})_4]$  (**1**) have been reported previously.<sup>4</sup> Infrared absorption spectra were obtained using the attenuated total reflectance (ATR) method on a Nicolet Magna-FTIR System 550 spectrometer equipped with a ZnSe trough HATR cell from PIKE Technologies. Sample films were coated on the ZnSe crystal from an ether suspension. Visible absorption spectra were also acquired using the ATR method. Sample films were coated onto a cubic zirconium ATR crystal from an ether suspension. An in-house constructed ATR crystal holder with fiber optic mounts was connected to an Ocean Optics CCD spectrophotometer from which visible absorption spectra were recorded. Elemental analysis was performed by QTI Analytical Laboratories.

$[\text{Pt}(\text{CN-cyclododecyl})_4][\text{Pt}(\text{CN})_4]$  (**1**). This compound was synthesized by a method previously reported.<sup>5</sup>

*[(phen)Pt(CN-cyclohexyl)<sub>2</sub>][Pt(CN)<sub>4</sub>] (2)*. A suspension containing 0.430 g (0.964 mmol) Pt(phen)Cl<sub>2</sub> (Aldrich) and 0.421 g (3.86 mmol) cyclohexylisocyanide, C<sub>6</sub>H<sub>11</sub>-NC, (Strem) in acetonitrile (50 mL) was stirred under argon for 15 minutes. To this solution, 0.756 g (0.964 mmol) solid [(*n*-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N]<sub>2</sub>[Pt(CN)<sub>4</sub>] was added. As the suspension was stirred over three days, the suspended solids gradually changed from yellow to red. The red precipitate was isolated by filtration and rinsed with acetonitrile (30 mL) and acetone (30 mL). The red-purple solid was dried in vacuo for 24 hours. Yield: 0.774 g, 0.867 mmol, 90%; IR (ZnSe ATR film, cm<sup>-1</sup>): ν(R-NC) 2280, 2261, ν(CN) 2124; vis-NIR (cubic zirconium ATR film, nm) λ<sub>max</sub> = 573; Anal. Calcd. for C<sub>30</sub>H<sub>30</sub>N<sub>8</sub>Pt<sub>2</sub>: C, 40.36; H, 3.39; N, 12.55. Found: C, 40.31; H, 3.60; N, 12.37.

*n-tetradecylformamide*. A solution of *n*-tetradecylamine (Aldrich), C<sub>14</sub>H<sub>29</sub>-NH<sub>2</sub>, (5.0 g, 23.4 mmol) and 90% formic acid (13.5 mL) in 75 mL of toluene was gently refluxed in a nitrogen purged flask with a Dean-Stark water separator for 12 hours. Partial evaporation of the solvent on the rotary evaporator produced a crop of white crystals (C<sub>14</sub>H<sub>29</sub>-NHCHO) that were collected via filtration. Yield 95%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.15 (d, <sup>3</sup>J<sub>HH</sub> = 1.3 Hz, 0.8H, *Z* isomer (H)CONHR), 8.03 (d, <sup>3</sup>J<sub>HH</sub> = 12.0 Hz, 0.2H, *E* isomer (H)CONHR), 5.74 (br d, 1H, *Z* and *E* isomers HCON(H)R), 3.28 (m, 1.6H, *Z* isomer HCONHC(H)<sub>2</sub>R), 3.21 (m, 0.4H, *E* isomer HCONHC(H)<sub>2</sub>R), 1.52 (m, 2H), 1.25 (m, 22H), 0.87 (t, <sup>3</sup>J<sub>HH</sub> = 6.6 Hz, 3H); IR (ZnSe ATR film, cm<sup>-1</sup>) ν(C=O) 1645 s.

*n-tetradecylisocyanide*. A solution of crude C<sub>14</sub>H<sub>29</sub>-NHCHO (3.3 g, 14 mmol) and triethylamine (9.6 mL, 69 mmol) in 80 mL dichloromethane was added to a flask under nitrogen. The triethylamine was purified by passing it through an activated neutral alumina column prior to starting the synthesis. The solution was purged with nitrogen for 30 minutes then a solution of POCl<sub>3</sub> (1.4 mL, 15 mmol in 10 mL dichloromethane) was added slowly to the reaction mixture

over a 15 minute period. The solution was allowed to stir for an additional hour. An aqueous solution of sodium acetate (25 g in 80 mL H<sub>2</sub>O) was then added to the reaction mixture and stirred for 10 minutes. The solution was then washed with 25 mL of water. The organic layer was separated and the aqueous layer was rinsed with 3 x 15 mL of dichloromethane. The combined organic layers were extracted with saturated aqueous sodium chloride (4 x 30 mL) and then dried with magnesium sulfate. The liquid was decanted off the drying agent and the solvent removed by rotary evaporation. The resulting product (C<sub>14</sub>H<sub>29</sub>-NC) was an oily brown liquid that was crystallized from ethanol. Yield: 52%; <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>Cl) δ 3.33 (tt, 2H), 1.62 (br m, 2H), 1.38 (br m, 2H), 1.25-1.15 (br m, 20H), 0.83 (t, 3H); IR (ZnSe ATR film, cm<sup>-1</sup>): ν(R-NC) 2148.

[Pt(CN-*n*-tetradecyl)<sub>4</sub>][Pt(CN)<sub>4</sub>] (3). Pt(CH<sub>3</sub>CN)<sub>2</sub>Cl<sub>2</sub> (0.15 g, 0.43 mmol), [(*n*-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N]<sub>2</sub>[Pt(CN)<sub>4</sub>] (0.34 g, 0.43 mmol), and C<sub>14</sub>H<sub>29</sub>-NC (0.38 g, 1.7 mmol) were placed in a flask under argon. Next, 50 mL of freshly distilled acetonitrile was added via syringe and the resulting solution was stirred under an argon atmosphere for about an hour. A bright yellow precipitate began to form almost immediately. The solid was collected by filtration and rinsed with 10 mL of distilled acetonitrile. A second crop of crystalline product was obtained by cooling the filtrate in the freezer followed by another filtration and wash. Yield 78%; IR (ZnSe ATR film, cm<sup>-1</sup>): ν(R-NC) 2285, ν(CN) 2124; Vis-NIR (cubic zirconium ATR film, nm) λ<sub>max</sub> = 469; Anal. Calcd. for C<sub>64</sub>H<sub>116</sub>N<sub>8</sub>Pt<sub>2</sub>: C, 55.39; H, 8.43; N, 8.07. Found: C, 55.69; H, 8.82; N, 7.49.

[(*phen*)Pt(CN-cyclododecyl)Cl]<sub>2</sub>[(*phen*)Pt(CN-cyclododecyl)<sub>2</sub>]<sub>2</sub>[Pt(CN)<sub>4</sub>]<sub>3</sub> (4). A solution of 0.864 g (1.50 mmol) [Pt(*phen*)(DMSO)Cl][BF<sub>4</sub>]<sup>6</sup> and 0.580 g (3.00 mmol) C<sub>12</sub>H<sub>23</sub>-NC in CH<sub>2</sub>Cl<sub>2</sub> (75 mL) was stirred under argon for 30 minutes. To this solution, 1.176 g (1.50

mmol)  $[(n\text{-C}_4\text{H}_9)_4\text{N}][\text{Pt}(\text{CN})_4]$  in  $\text{CH}_2\text{Cl}_2$  (25 mL) was added. A fine blue-purple precipitate formed immediately and the reaction mixture was stirred for 24 h. The solvent was removed by rotary evaporation. Acetone (50 mL) was added and a suspension formed, followed by vigorous stirring for 30 minutes. The suspension was then centrifuged and the acetone was decanted. The solid collected was then dried in vacuo for 24 hours. Yield: 1.267 g; IR (ZnSe ATR film,  $\text{cm}^{-1}$ ):  $\nu(\text{R-NC})$  2282, 2262 (sh), 2256,  $\nu(\text{CN})$  2120; vis-NIR (cubic zirconium ATR film, nm)  $\lambda_{\text{max}} = 607$ ; Anal. Calcd. for  $[(\text{phen})\text{Pt}(\text{CN-cyclododecyl})\text{Cl}]_2[(\text{phen})\text{Pt}(\text{CN-cyclododecyl})_2]_2[\text{Pt}(\text{CN})_4]_3$ : C, 45.66; H, 4.72; N, 10.03; Cl, 1.96. Found: C, 45.57; H, 4.77; N, 9.77; Cl, 1.81.

**Additional Evidence for the Formulation of Compound 4.** Compound 4 is best formulated as  $[(\text{phen})\text{Pt}(\text{CN-cyclododecyl})\text{Cl}]_2[(\text{phen})\text{Pt}(\text{CN-cyclododecyl})_2]_2[\text{Pt}(\text{CN})_4]_3$ . The platinum double salt compounds that contain the independent cations in 4 (namely  $[(\text{phen})\text{Pt}(\text{CN-cyclododecyl})\text{Cl}]_2[\text{Pt}(\text{CN})_4]$  (5) and  $[(\text{phen})\text{Pt}(\text{CN-cyclododecyl})_2][\text{Pt}(\text{CN})_4]$  (6)) have been synthesized, purified, and characterized independently.<sup>7</sup> As seen in Table S1 the ATR visible absorption spectra and solid-state luminescence spectra of compounds 4, 5, and 6 are all different. In addition, when the absorption spectra of compounds 5 and 6 are combined to simulate a simple 1:1 mixture, the absorption spectrum obtained is distinct from the ATR absorption spectrum of compound 4. The same is true when the solid-state luminescence spectra of compounds 5 and 6 are combined in a similar manner. These data support the formulation of compound 4 as a distinct material rather than a simple 1:1 mixture of compounds 5 and 6. Finally, elemental analysis of compounds 4, 5, and 6 support the formulations,  $[(\text{phen})\text{Pt}(\text{CN-cyclododecyl})\text{Cl}]_2[(\text{phen})\text{Pt}(\text{CN-cyclododecyl})_2]_2[\text{Pt}(\text{CN})_4]_3$ ,  $[(\text{phen})\text{Pt}(\text{CN-cyclododecyl})\text{Cl}]_2[(\text{phen})\text{Pt}(\text{CN-cyclododecyl})_2]_2[\text{Pt}(\text{CN})_4]_3$ ,  $[(\text{phen})\text{Pt}(\text{CN-cyclododecyl})_2][\text{Pt}(\text{CN})_4]$ ,  $[(\text{phen})\text{Pt}(\text{CN-cyclododecyl})\text{Cl}]_2[\text{Pt}(\text{CN})_4]$ , and  $[(\text{phen})\text{Pt}(\text{CN-cyclododecyl})_2][\text{Pt}(\text{CN})_4]$ .

cyclododecyl)Cl]<sub>2</sub>[Pt(CN)<sub>4</sub>], and [(phen)Pt(CN-cyclododecyl)<sub>2</sub>][Pt(CN)<sub>4</sub>], respectively.<sup>7</sup> Full characterization of **5** and **6** will be reported in the future.

**Table S1.** ATR absorption and luminescence data for compounds **4**, **5**, and **6**.

Compound	Absorption <sup>a</sup> $\lambda_{\text{max}}$ (nm)	Luminescence <sup>b</sup> $\lambda_{\text{max}}$ (nm)
<b>4</b>	607	760
<b>5</b>	c	645, 750 (sh)
<b>6</b>	633	856

a. ATR absorbance spectrum of film under N<sub>2</sub>. b. Solid-state luminescence spectrum under N<sub>2</sub>,  $\lambda_{\text{ex}}$  = 436 nm. c. No peak observed between 400 - 900nm.

**Partitioning Flow Apparatus Correction Factor.** An apparatus was constructed to dilute nitrogen streams saturated with solvent vapor as described in the Experimental section. The mass flow controllers that regulated the flow of nitrogen gas into the solvent bubbler and regulated the flow of the diluting nitrogen stream were controlled by a computer equipped with LabVIEW software. The LabVIEW software was designed to operate the mass flow controllers such that the total input flow was always 10 mL/min. For example, when the percentage 25% was entered into the LabVIEW software, 2.5 mL/min of nitrogen was passed into the solvent bubbler and the output of the bubbler was mixed with pure nitrogen flowing at 7.5 mL/min for a total nitrogen input flow rate of 10 mL/min. However, the total output flow rate is greater than the input flow rate due to the additional volume of evaporated solvent. The amount of solvent vapor added to the stream is a function of the vapor pressure of the solvent. Based on these parameters, an equation was derived to relate the computer flow setting ( $X_s$ ) to the actual flow achieved ( $X_a$ ),

$$X_a = \frac{\phi X_s}{(\phi - 1)X_s + 1} \quad (\text{S1})$$

where  $\phi$  is defined as the flow enhancement factor:

$$\phi = \frac{P_{\text{nitrogen}} + P_{\text{vapor}}}{P_{\text{nitrogen}}} \quad (\text{S2})$$

For equation S2  $P_{\text{nitrogen}}$  is the input pressure of pure nitrogen, which should be very close to atmospheric pressure assuming minimal back pressure, and  $P_{\text{vapor}}$  is the vapor pressure of the solvent. The validity of these equations was tested by flowing acetone into an FTIR gas cell and monitoring the area under the carbonyl stretch IR peak over a range of  $X_s$  values. The type of curvature predicted by equation S1 was observed in the peak area versus  $X_s$  plot. Using the denominator of equation S1, the total output flow rate can be calculated as a function of  $X_s$ . For acetone, this total flow rate ranges from 10 mL/min for an  $X_s$  value of zero to a flow rate of 12.6 mL/min for an  $X_s$  value of one. The corrections for the concentrations for Figure 7 in the text are given in the Table S2.

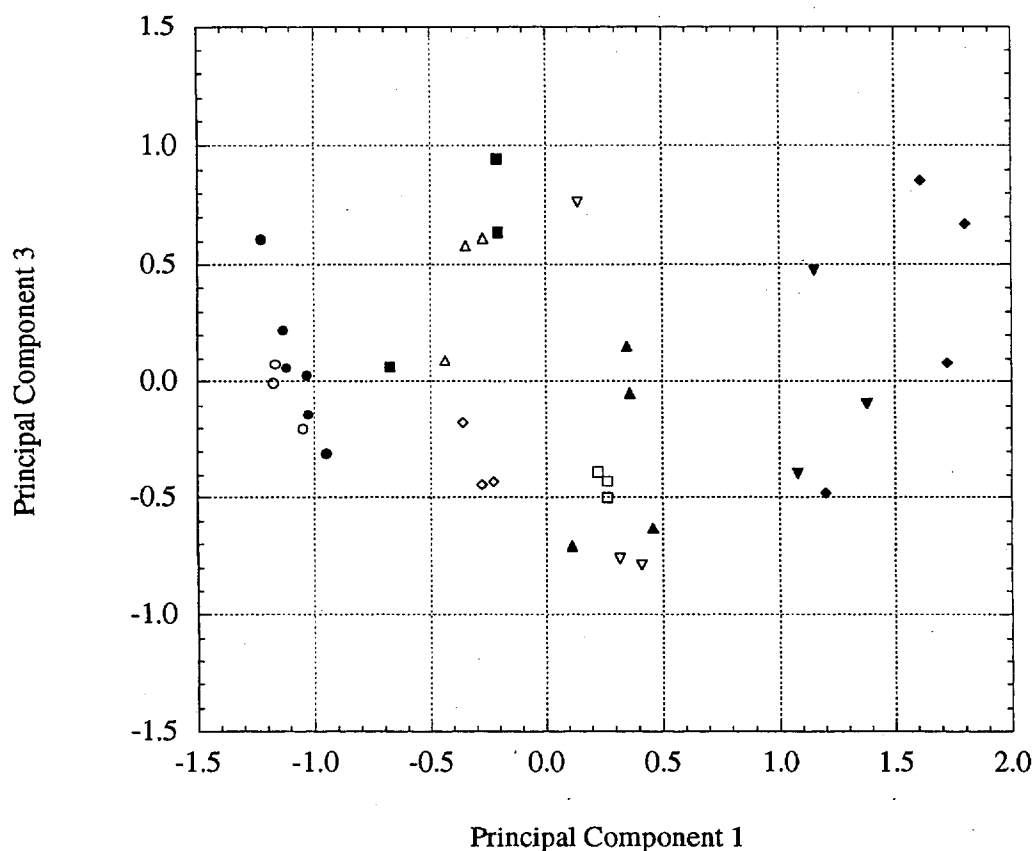
**Table S2.** Concentration Corrections for Figure 7.

Acetone Setting %	Acetone Actual %	Methanol Setting %	Methanol Actual %
1	1	1	1
5	6	5	6
10	12	10	11
20	24	20	22
50	56	50	54
75	79	75	78
100	100	100	100

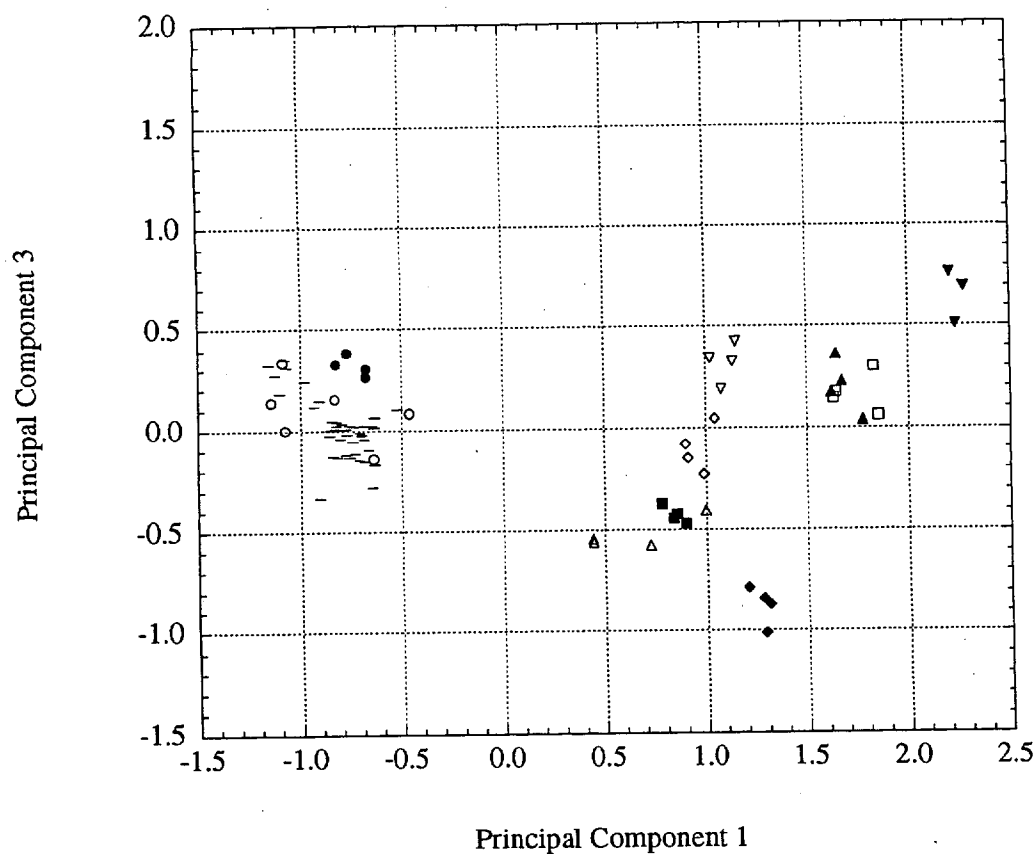
## References

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7. Unpublished results.

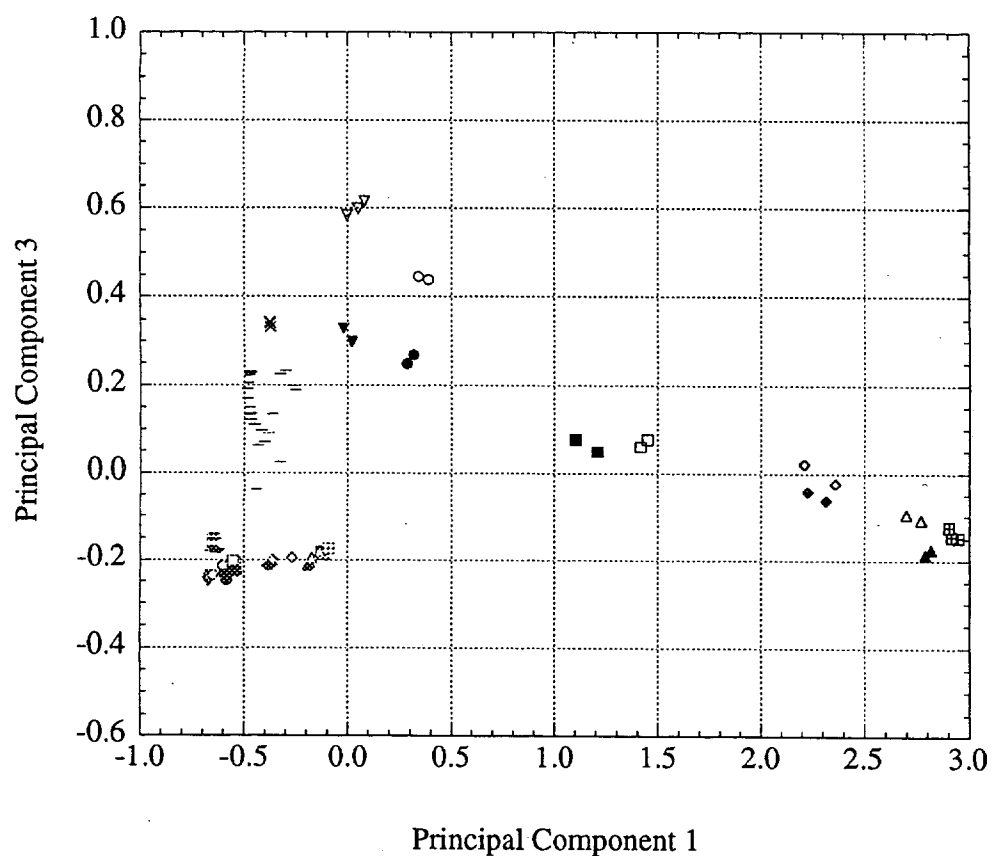


**Supporting Figure 2b.** PC3 vs PC1 score plot of luminescence spectra acquired with array I with intervening acetone exposures ( $T = 22^{\circ}\text{C}$ ). Individual percent variances PC1 48 %; PC3 18 %. Solvent vapors: acetone ( $\bullet$ ), 1-propanol ( $\square$ ), 2-propanol ( $\diamond$ ), benzene ( $\Delta$ ), cyclohexane ( $\circ$ ), chloroform ( $\blacksquare$ ), dichloromethane ( $\blacklozenge$ ), water ( $\blacktriangle$ ), methanol ( $\blacktriangledown$ ), ethanol ( $\triangledown$ ).



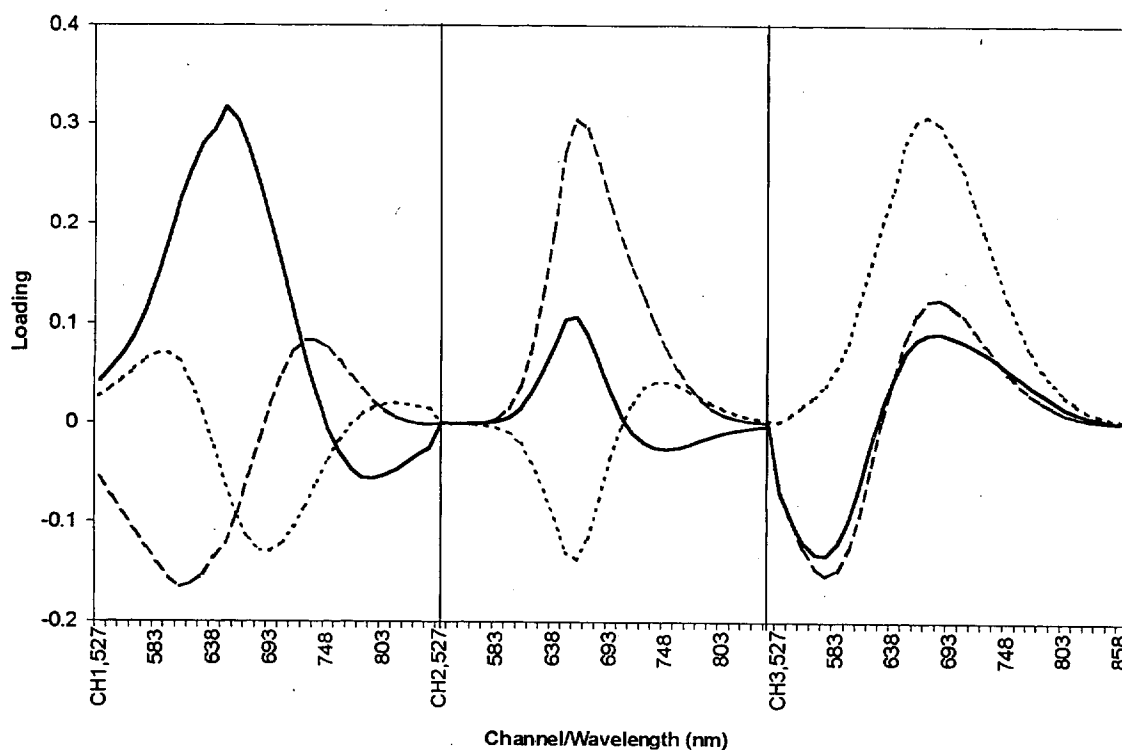
**Supporting Figure 3b.** PC3 vs PC1 score plot of luminescence spectra acquired with array **I** with intervening temperature programming under nitrogen. Only compounds **1** and **2** are directly heated, ramp up to 80°C, then cool to  $25 \pm 1^\circ\text{C}$  before acquiring spectra. Individual percent variances: PC1 70 %; PC3 6.7 %. Solvent vapors: acetone (●), 1-propanol (□), 2-propanol (◇), benzene (Δ), cyclohexane (○), chloroform (■), dichloromethane (◆), water (▲), methanol (▼), ethanol (▽), nitrogen (-).



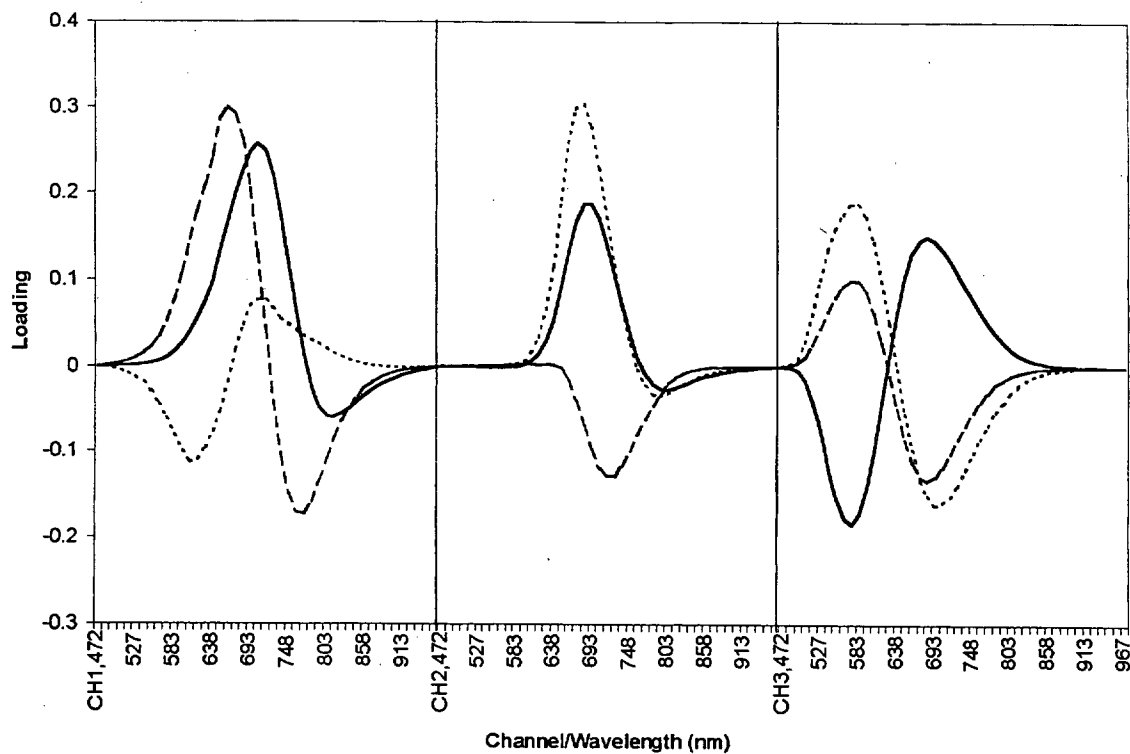


**Supporting Figure 7b.** PC3 vs PC1 score plot from PCA of luminescence spectra of array **I** with varying acetone (red) and methanol (blue) concentrations in nitrogen. Filled points were used to plot the ascending concentration data and open points were used for the descending concentration data. Only compounds **1** and **2** are directly heated, ramp up to 80°C, then cool to  $25 \pm 1^\circ\text{C}$  before acquiring spectra. Individual percent variances: PC1 84%; PC3 3.8%. Approximate concentrations (percent saturation): 0 % (-), 1 % (x), 5 % ( $\nabla$ ), 10 % (O), 20 % ( $\square$ ), 50 % ( $\diamond$ ), 75 % ( $\Delta$ ), 100 % ( $\boxplus$ ); see Supporting Information for exact concentrations.

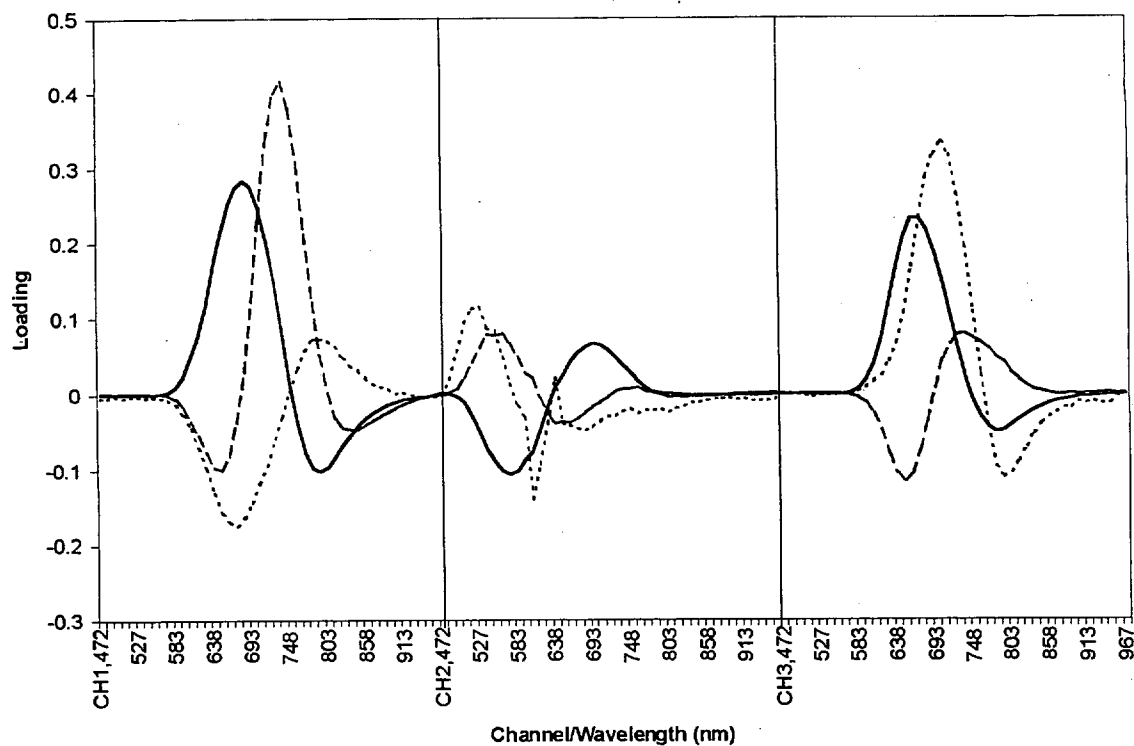
**Loadings Plots for Figures 2, 3, and 7.** The loadings plots given in Figures S1, S2, and S3 were obtained for the score plots noted in their corresponding figure captions.



**Figure S1.** Loading data for the score plot presented in Figure 2. PC1 (solid), PC2 (dashed), PC3 (dotted). CH1 is the luminescence from 1; CH2 is the luminescence from 2; CH3 is the luminescence from 3.



**Figure S2.** Loading data for the score plot presented in Figure 3. PC1 (solid), PC2 (dashed), PC3 (dotted). CH1 is the luminescence from 1; CH2 is the luminescence from 2; CH3 is the luminescence from 3.



**Figure S3.** Loading data for the score plot presented in Figure 7. PC1 (solid), PC2 (dashed), PC3 (dotted). CH1 is the luminescence from 1; CH2 is the luminescence from 2; CH3 is the luminescence from 3.

**Rf Table for Methanol and Acetone Concentration Data.** The score plots shown in Figure 7 were examined using an rf analysis as described in the Experimental section. The resulting rf values are presented in Table S2.

**Table S2.** Rf values for data in Figure 7.

	N <sub>2</sub> (actn)	actn 6 %	actn 12 %	actn 24 %	actn 56 %	actn 79 %	actn 100%	N <sub>2</sub> (MeOH)	MeOH 1 %	MeOH 6 %	MeOH 11 %	MeOH 22 %	MeOH 54 %	MeOH 78 %
actn 6 %	2.76													
actn 12 %	1.91	2.05												
actn 24 %	4.64	8.01	1.93											
actn 56 %	8.93	11.20	5.75	5.46										
actn 79 %	15.76	22.15	10.38	12.77	4.39									
actn 100 %	18.41	27.35	12.26	16.01	6.33	2.15								
N <sub>2</sub> (MeOH)	5.91	7.71	7.45	6.42	6.99	8.90	9.54							
MeOH 1 %	20.30	59.24	38.30	25.98	27.54	37.90	33.80	1.93						
MeOH 6 %	18.84	23.10	18.76	23.40	24.18	91.62	77.97	6.29	10.48					
MeOH 11 %	9.37	9.86	8.69	8.67	7.14	9.27	12.36	6.35	8.66	10.39				
MeOH 22 %	11.71	12.09	11.34	11.30	10.00	10.52	11.00	9.51	10.21	8.53	6.54			
MeOH 54 %	53.00	56.42	47.59	51.25	36.28	42.51	43.02	29.43	44.91	32.03	30.15	8.13		
MeOH 78 %	58.05	53.42	47.74	47.67	37.05	39.08	38.55	31.88	43.28	32.77	30.08	11.83	5.10	
MeOH 100 %	244.31	151.33	105.66	125.76	66.94	111.45	121.26	43.08	130.04	80.68	92.45	16.61	10.55	2.07

MeOH = methanol, actn = acetone