Structure−Optical Property Relationships in Organometallic Sydnones

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As part of an effort to develop a spectroscopic structure−property relationship in platinum acetylide oligomers, we have prepared a series of mesoionic bidentate $Pt(PBu_3)_2L_2$ compounds containing sydnone groups. The ligand is the series *o*-*Syd*-$(C_6H_4-C\equiv C)_n$-H, where $n = 1-3$, designated as *Syd*-PEn-H. The terminal oligomer unit consists of a sydnone group ortho to the acetylene carbon. We synthesized the platinum complex (*Syd*-PEn-Pt), the unmodified ligands (PEn-H), and the unmodified platinum complexes (PEn-Pt). The compounds were characterized by various methods, including X-ray diffraction, ^{13}C NMR, ground-state absorption, fluorescence, phosphorescence, and laser flash photolysis. From solving the structure of *Syd*-PE1-Pt, we find the angle between the sydnone group and the phenyl group is 45°. By comparison of the ^{13}C NMR spectra of the sydnone-containing ligands, the sydnone complexes with the corresponding unmodified ligands and complexes not containing the sydnone group, the sydnone group is shown to polarize the nearest acetylenes and have a charge-transfer interaction with the platinum center. Ground-state absorption spectra of the complexes in various solvents give evidence that the *Syd*-PE1-Pt complex has an excited state less polar than the ground state, while the PE1-Pt complex has an excited state more polar than the ground state. In all the higher complexes the excited state is more polar than the ground state. The phosphorescence spectrum of the *Syd*-PE1-Pt complex has an intense vibronic progression distinctly different from the PE1-Pt complex. The sydnone effect is small in *Syd*-PE2-Pt and negligible in *Syd*-PE3-Pt. From absorption and emission spectra, we measured the singlet-state energy E_S, the triplet-state energy E_T, and the singlet−triplet splitting ΔE_{ST}. By comparison with energies obtained from the unmodified complexes, attachment of the sydnone lowers E_S by ∼0.1 eV and raises E_T by ∼0.1 eV. As a result, the sydnone group lowers ΔE_{ST} by ∼0.2 eV. The trends suggest one of the triplet-state singly occupied molecular orbitals (SOMOs) is localized on the sydnone group, while the other SOMO resides on the rest of the ligand.

Introduction

The photophysics and photochemistry of transition-metal acetylide complexes have recently received considerable attention. This class of compounds is an emerging nanomaterial with applications in electroluminescence and photonics. These compounds contain d^8 transition metals with four ligands bound in a planar structure. The ligands include phosphines, arsines, cyano groups, acetylenes, and imines. A wide variety of structures have been made, including oligomers,[1] polymers,[2] dendrimers,[3] rods,[4,5] self-assembled systems,[6] and glass-forming liquids.[7] The spin−orbit coupling resulting from the presence of the heavy platinum atom promotes formation of the triplet state. Platinum acetylide complexes are good systems to learn about spin-forbidden phenomena such as ground-state absorption to the triplet state ($S_0 \rightarrow T_1$), intersystem crossing ($S_1 \rightarrow T_1$), triplet state absorption spectrum ($T_1 \rightarrow T_n$), and phosphorescence ($T_1 \rightarrow S_0$). In our group, we have been investigating the relation between chemical structure and spectroscopic properties in platinum acetylide complexes such as *trans*-$Pt(PBu_3)_2((C\equiv CC_6H_4)_nC\equiv CC_6H_5)_2$, where $n = 0-2$.[8−10]

Sydnones are mesoionic compounds, defined to be planar five-membered heterocyclic betaines with dipole moments around 6 D and the electrons delocalized over two regions separated by single bonds.[11] The electronic structure of sydnones has been investigated by semiempirical and ab initio methods. Although their geometry can be predicted by ab initio methods, the calculated charge distributions do not agree with experimental results.[12] Published studies of the photophysics of sydnones include a flash photolysis study,[13] an investigation of photochromism,[14] and nonlinear optical properties.[15,16] Our previous work has focused on a series of hydrophobic platinum acetylide complexes. In this paper, we describe the optical properties of a series of polar sydnone-containing platinum acetylides.

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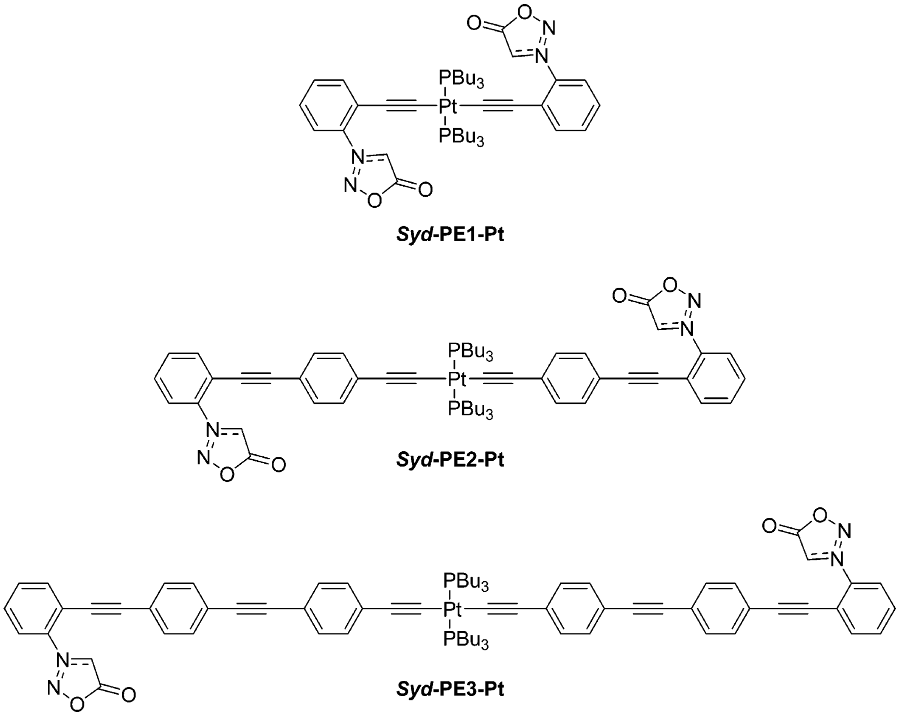

Figure 1. Chemical formulas of sydnone complexes. We also investigated the sydnone ligands *Syd*-PE1-H, *Syd*-PE2-H, and *Syd*-PE3-H, the unmodified ligands PE1-H, PE2-H, and PE3-H and the unmodified platinum complexes PE1-Pt, PE2-Pt, and PE3-Pt.

Experimental Section

Sydnone-containing ligand synthesis will be described in a separate publication.[17] The unmodified platinum complexes were synthesized as previously described.[10] The sydnone-containing platinum complexes were synthesized as described in the Supporting Information. Their chemical formulas are listed in Figure 1. NMR spectra were collected on a Varian Innova 300-MHz spectrometer. Ground-state UV/vis absorption spectra were measured on a Cary 500 spectrophotometer. Emission spectra were measured using a Perkin-Elmer model LS 50B fluorometer. Nanosecond transient absorption measurements were carried out using the third harmonic (355-nm) of a Q-switched Nd:YAG laser (Quantel Brilliant, pulse width ca. 5 ns). Pulse fluences of up to 8 mJ cm^{-2} at the excitation wavelength were typically used. A detailed description of the laser flash photolysis apparatus has been published earlier.[9,10] Variable temperature emission and excitation spectra were collected as published.[1]

We were able to grow X-ray quality crystals of *Syd*-PE1-Pt by slow evaporation of a DCM/MeOH solution. For X-ray examination and data collection, a suitable crystal measuring approximately 0.40 × 0.30 × 0.20 mm was mounted in a Cryoloop with silicon grease and transferred immediately to the goniostat bathed in a cold stream. Intensity data were collected at 150 K on a SMART6000 charge-coupled device (CCD) diffractometer using graphite-monochromated Mo Kα radiation, $\lambda = 0.71073$ Å. The detector was set at a distance of 5.15 cm from the crystal. A series of 3-s data frames measured at 0.3° increments of ω were collected to calculate a unit cell. Data collection frames were measured for a duration of 3-s at 0.3° intervals of ω, which combined measured nearly a sphere of intensity out to ~60° in 2θ. The data frames were processed using the program SAINT. The data were corrected for decay, Lorentz, and polarization effects as well as absorption and beam corrections based on the multiscan technique used in SADABS. $C_{44}H_{64}N_4O_4P_2Pt$, MW = 970.02, $Z = 1$, triclinic P-1, $a = 10.9367(3)$, $b = 11.2973(3)$, $c = 11.4492(3)$ Å, $\alpha = 110.7380(10)$, $\beta = 109.7960(10)$, $\gamma = 104.5780(10)$, $V = 1128.32(5)$ Å^3, $\rho_{\text{calc}} = 1.428$ g cm^{-3}, 15739 reflections measured, 5593 unique reflections, 5591 reflections used for refinement ($I \geq 2\sigma(I)$), $\theta_{\max} = 28.29°$, $\mu = 3.224\ \text{mm}^{-1}$, anisotropic, hydrogen atoms isotropic, $R = 0.0243$ all reflections, $R = 0.0243 > 2\sigma(I)$, w$R = 0.0580$ all reflections, w$R = 0.0580 > 2\sigma(I)$, residual electron density minimum −1.480, residual electron density maximum 2.028 Å^{-3}.

Results and Discussion

The crystallographic structure of *Syd*-PE1-Pt is shown in Figure 2, along with selected bond lengths and bond angles in Table 1. We compared our results with compiled sydnone crystallographic data.[16] The sydnone group bond lengths and bond angles were similar to published values.[12] The picture that emerges from crystallographic data and theoretical calculations is that $C_{10}-O_2$ is a double bond, N_1-N_2 and N_1-C_9 have double bond character, while C_9-C_{10}, N_2-O_1, and $C_{10}-O_1$ are single bonds. Sydnone groups are seen as having two conjugated regions separated by single bonds rather than having aromatic character.[11] The dihedral angle between the sydnone group and the phenyl ring is 45°. In comparison, a survey of the structure of a series of 3- and 4-phenyl sydnones reveals the twist angle between the phenyl group and the sydnone ring varies from 2 to 79°.[18] We also find the $Pt-C_1-C_2$ and $C_1-C_2-C_3$ bond angles both significantly deviate from 180°. A review on the crystal structure of conjugated polyynes describes similar features, associated with bow and S-shaped C_n conformations.[4]

What is the effect of the sydnone group on the electronic structure of these chromophores? To obtain information about the charge distribution, we collected proton-decoupled and proton-coupled ^{13}C NMR spectra of the ligands and platinum complexes, both with and without sydnone groups. The ^{13}C NMR spectra are shown in Figures S1−S24 of the Supporting Information. By comparison of the proton-decoupled and proton-coupled ^{13}C NMR spectra, we were able to assign the acetylenic carbon resonances. The assignments and logic behind them are listed in Tables S1−S4 of Supporting Information and sum-

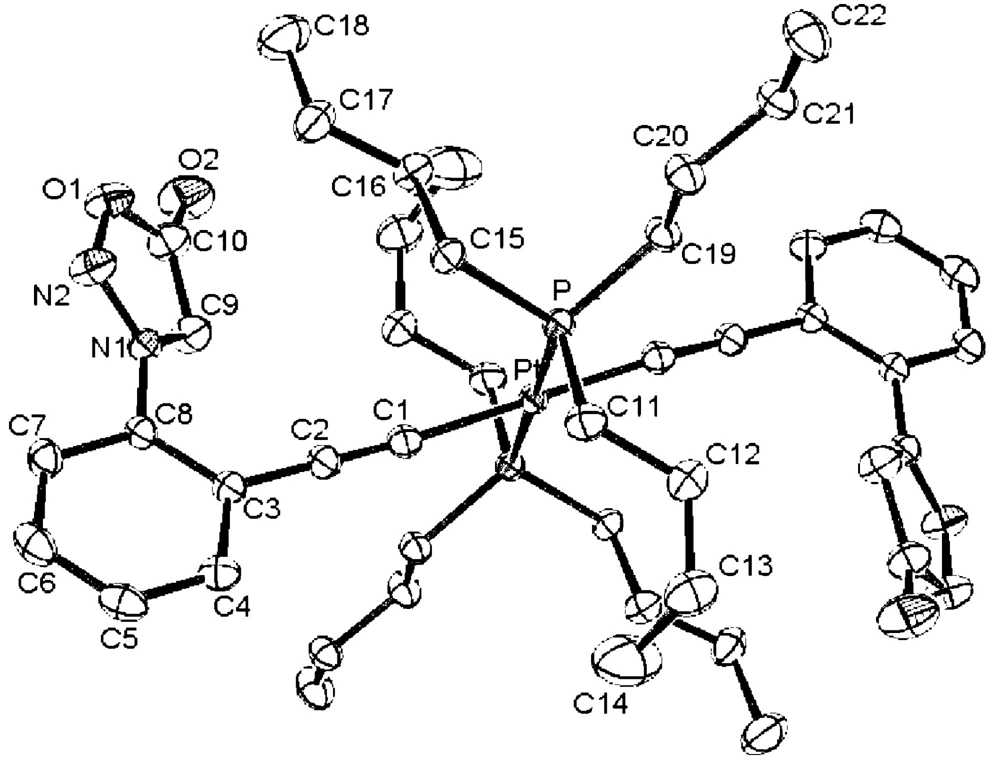

Figure 2. ORTEP drawing of *Syd*-PE1-Pt X-ray structure.

TABLE 1: Selected Bond Distances (angstroms) and Angles (degrees) for *Syd*-PE1-Pt

Pt_1-C_1	1.992(2)	N_1-N_2	1.316(3)	C_1-C_2	1.211(3)
Pt_1-P	2.3051(5)	N_1-C_9	1.335(3)	C_3-C_2	1.434(3)
$P-C_{11}$	1.816(2)	N_1-C_8	1.437(3)	O_2-C_{10}	1.216(3)
$P-C_{15}$	1.821(2)	O_1-N_2	1.376(3)	$C_{10}-C_9$	1.412(3)
$P-C_{19}$	1.832(2)	O_1-C_{10}	1.406(4)		
C_1-Pt_1-P	94.10(6)	$N_2-O_1-C_{10}$	111.20(18)	$C_3-C_8-N_1$	121.10(18)
$C_{11}-P-C_{15}$	103.57(11)	$C_{16}-C_{15}-P$	114.32(16)	$N_1-N_2-O_1$	103.88(19)
$C_{11}-P-C_{19}$	106.67(11)	$C_2-C_1-Pt_1$	175.0(2)	$C_1-C_2-C_3$	176.1(2)
$C_{15}-P-C_{19}$	105.68(10)	$C_7-C_8-N_1$	116.4(2)	$O_2-C_{10}-O_1$	120.4(2)
$C_{11}-P-Pt_1$	110.03(9)	$N_2-N_1-C_9$	115.0(2)	$O_2-C_{10}-C_9$	136.0(3)
$C_{15}-P-Pt_1$	115.00(7)	$N_2-N_1-C_8$	116.66(19)	$O_1-C_{10}-C_9$	103.5(2)
$C_{19}-P-Pt_1$	114.98(8)	$C_9-N_1-C_8$	128.4(2)	$N_1-C_9-C_{10}$	106.4(2)

TABLE 2: ^{13}C NMR Assignments of Acetylene Carbons in ppm

	acetylene carbon					
compound	1[a]	2	3	4	5	6
PE1-H	77.5	83.9				
PE2-H	79.2	83.5	90.4[b]	90.4[b]		
PE3-H	79.3	83.5	90.8[b]	90.8[b]	90.8[b]	90.8[b]
PE1-Pt	108.3	109.1				
PE2-Pt	112.0	109.6	90.2[b]	90.2[b]		
PE3-Pt	112.4	109.6	90.8[b]	90.8[b]	90.8[b]	90.8[b]
Syd-PE1-H	86.1	76.9				
Syd-PE2-H	80.1	83.2	97.1	84.3		
Syd-PE3-H	79.4	83.4	91.3[b]	91.3[b]	97.4	84.3
Syd-PE1-Pt	121.5	102.7				
Syd-PE2-Pt	114.0	109.7	98.9	83.1		
Syd-PE3-Pt	112.7	109.7	91.4[b]	91.4[b]	97.6[c]	84.1

[a] Acetylene carbons numbered from the platinum C out as shown in Figure 3. [b] Average chemical shift calculated from values where no assignment could be made. [c] Chemical shift assigned based on behavior of *Syd*-PE3-H.

marized in Table 2. For certain acetylenic carbons (for example, carbons 3−5 of PE3-Pt) where no unique assignment was possible, we averaged their chemical shifts.

The contributions of the various groups to the acetylene carbon chemical shift were calculated according to the expression

$$\delta = A + Bx_{\mathrm{Pt}} + Cx_{\mathrm{Syd}} + Dx_{\mathrm{Pt}}x_{\mathrm{Syd}}$$

where A is the chemical shift for an acetylenic carbon in PEn-H and x_{Pt} and x_{syd} are either 0 or 1 if the ligand is bound to Pt or has a sydnone group attached. B and C measure the contribution of platinum and the sydnone group. The cross term D measures any interaction between platinum and the sydnone group. The values of $A-D$ are shown in Figure 3. The values of A compare very favorably to acetylenic chemical shifts reported for rodlike conjugated polyynes[19,20] where chemical shifts for the terminal acetylene are near 83 ppm (***C***≡CH) and 79 ppm (C≡***C***H) and values for interior acetylenic carbons range from 90.8 to 91.2 ppm. Our NMR data show end effects are significant only in the terminal acetylene group (carbons 1 and 2) while no end effects appear in the other carbons. Upon the formation of a C−Pt bond, the B coefficient has a large downfield shift (∼+30 ppm) in the resonances of carbons 1 and 2 but no effect in carbons 3−6. Similar chemical shifts are reported in a recent publication describing numerous platinum(II) complexes.[21] This

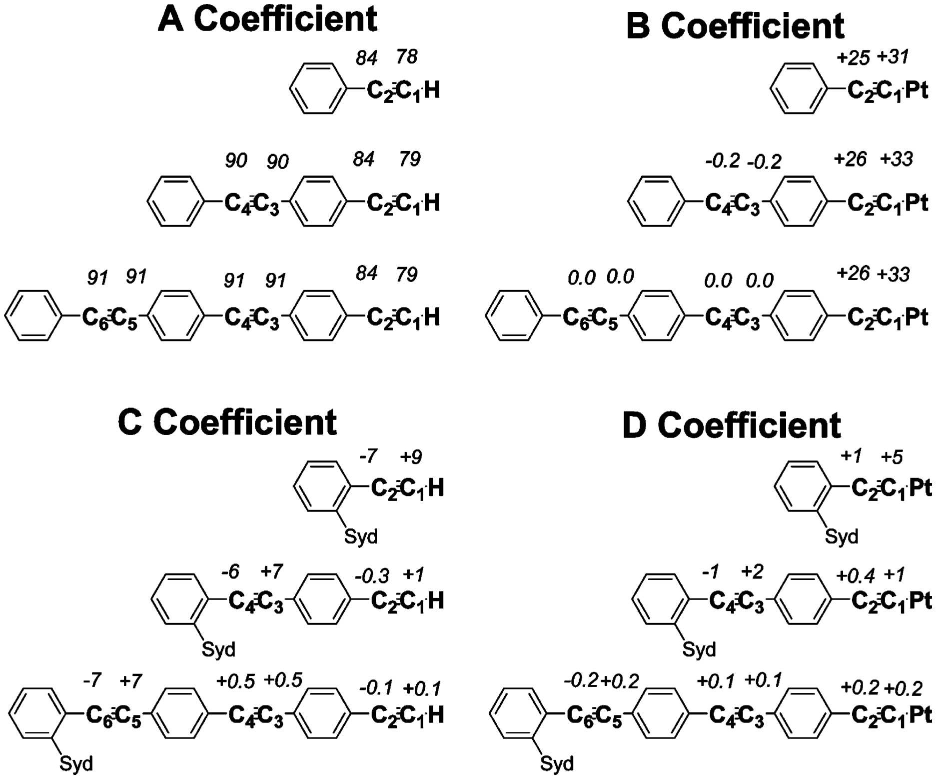

Figure 3. Values of *A*−*D* coefficients in ppm for the acetylenic carbons calculated from ^{13}C NMR spectra. A negative value refers to an upfield shift, while a positive value refers to a downfield shift.

article also gives an X-ray structure of PE2-Pt. The length of PE2-Pt's $C_1{\equiv}C_2$ triple bond (1.214 Å) attached to the platinum atom is significantly longer than the $C_3{\equiv}C_4$ triple bond (1.199 Å). The bond lengthening is attributed to electron donation via back bonding of the platinum to the ligand. The decreased $C_1{\equiv}C_2$ bond order accounts for the downfield shifts of the *B* coefficients. In the X-ray structure of *Syd*-PE1-Pt, the $C_1{\equiv}C_2$ bond length is 1.214 Å, also suggesting electron donation from Pt to the ligand occurs here.

The C coefficient measures the influence of the sydnone group on acetylenic carbon resonances. In all three *Syd*-PEn-H systems, the sydnone group causes an upfield shift (∼−7 ppm) in acetylene carbons α to the sydnone group and a downfield shift (+7 ppm) in the *β* carbons. The other acetylenic carbons have shifts less than 1 ppm. In all three systems, the magnitude of the sydnone effect remains constant with increasing ligand size. Sydnones have dipole moments on the order of 6.5−7.0 D, comparable to *p*-nitroaniline.[12] These results suggest the electrostatic field of the sydnone group has an effect on the electron density of the nearest acetylenic carbons. The upfield shift results from an increase in electron density, while the downfield shift results from a decrease in electron density on the acetylenic carbons. The close proximity of the sydnone C−H group to the acetylene suggests the chemical shift effects are caused by an inductive effect. In support of this idea, distances obtained from the X-ray structure of *Syd*-PE1-Pt show the distance from the sydnone carbon and the α-acetylene carbon to be 3.035 Å while that to the *β* carbon is 3.521 Å. The corresponding distances from the sydnone hydrogen are 2.736 and 3.073 Å, respectively. The C−C distances are in the range (3−4 Å) for strong electrostatic interaction between a polar C−H group and nearby atoms.[22] Does resonance between the sydnone and the phenyl contribute to the observed effects? A small twist angle will lead to large resonance effects while a larger angle will have smaller effects. The large angle (45°) between the sydnone group and the attached phenyl group suggests resonance effects make a small contribution to the shifts.

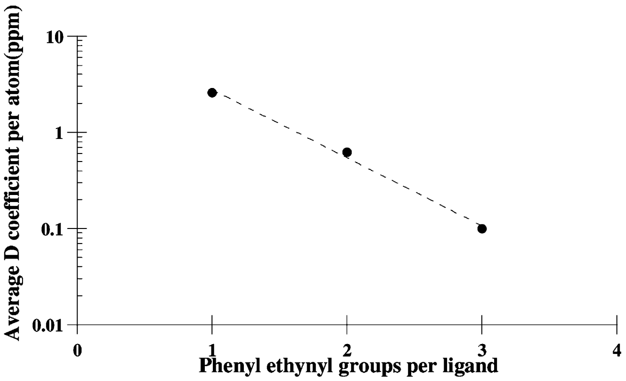

Figure 4. Plot of the average *D* coefficient per acetylene carbon vs the number of phenyl ethynyl groups per ligand.

The *D* coefficient measures platinum−sydnone interaction effects on the acetylenic carbon chemical shift. The *Syd*-PE1-Pt acetylenic carbons show significant evidence for platinum−sydnone interaction, with a downfield shift of 5 ppm in C_1 and a smaller shift in C_2. The *Syd*-PE2-Pt acetylenic carbons show a moderate sydnone shift in carbons 3 and 4 and a smaller shift in carbons 1 and 2. The *Syd*-PE3-Pt acetylenic carbons show a small shift in carbons 5 and 6 and no shift in carbons 1−4. A plot of the average *D* coefficient per atom (Figure 4) shows an exponential decrease with the increase in the number of ligand phenyl ethynyl groups. The trend suggests a platinum−sydnone interaction that decreases with increasing platinum−sydnone distance. A positive value of *D* suggests a decrease in electron density on the acetylene carbons due to a platinum−sydnone interaction. The trend implies a charge-transfer interaction between the central platinum atom, the acetylenic carbons, and the sydnone group.

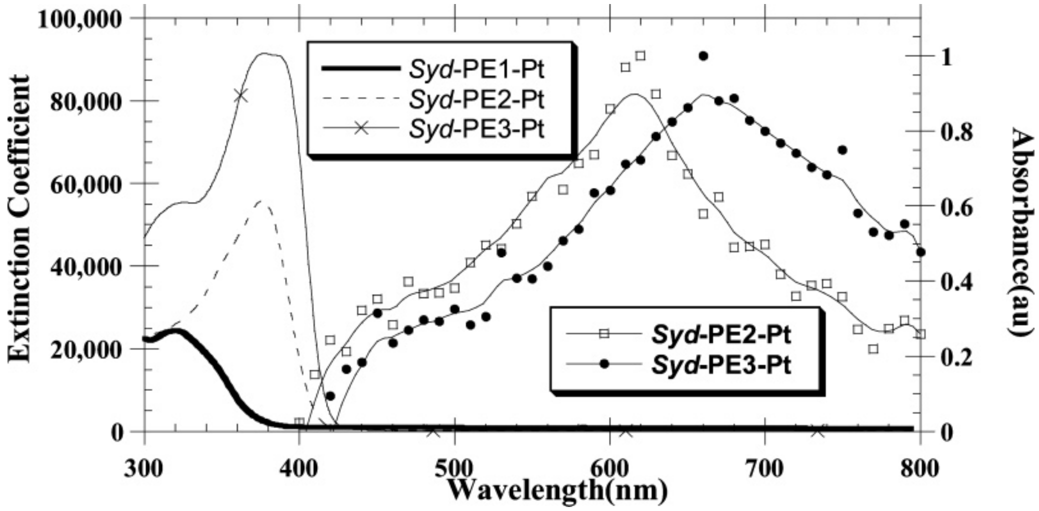

Figure 5. Ground-state and triplet-state absorption spectra of the three compounds dissolved in benzene.

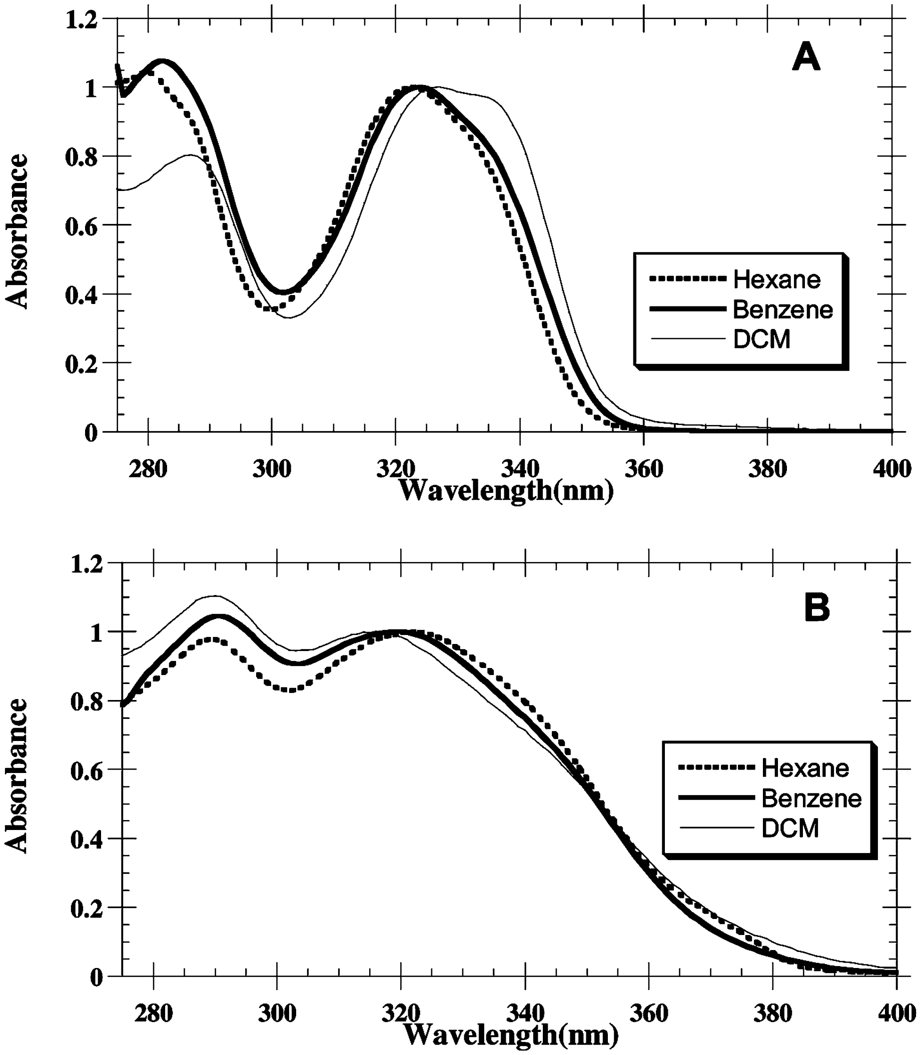

Figure 6. (a) Absorption spectra of PE1-Pt in various solvents. (b) Absorption spectra of *Syd*-PE1-Pt in various solvents.

The ground-state absorption spectra ($S_0 \rightarrow S_1$transition) of the Pt complexes arise from a mixture of transitions having metal-to-ligand charge transfer (MLCT) and intraligand $\pi\pi^*$ character.[8] The ground-state spectra of *Syd*-PEn-Pt (Figure 5) are very similar to those collected from PEn-Pt.[10,23] In both cases, there are no absorption bands in the visible region and an increase in extinction coefficient with increasing oligomer length. When compared to PE2-Pt and PE3-Pt, the absorption maxima of the ground-state spectra of *Syd*-PE2-Pt and *Syd*-PE3-Pt are red shifted 20 and 5 nm, respectively, but have a similar band shape. The absorption spectrum of *Syd*-PE1-Pt appears to have a broader band shape than PE1-Pt. To compare dipole moment changes upon excitation, we measured the solvatochromism of the sydnones and the unmodified complexes. Solvatochromism has been reviewed in detail.[24] The ground-state transition energy shifts with increasing solvent polarity.

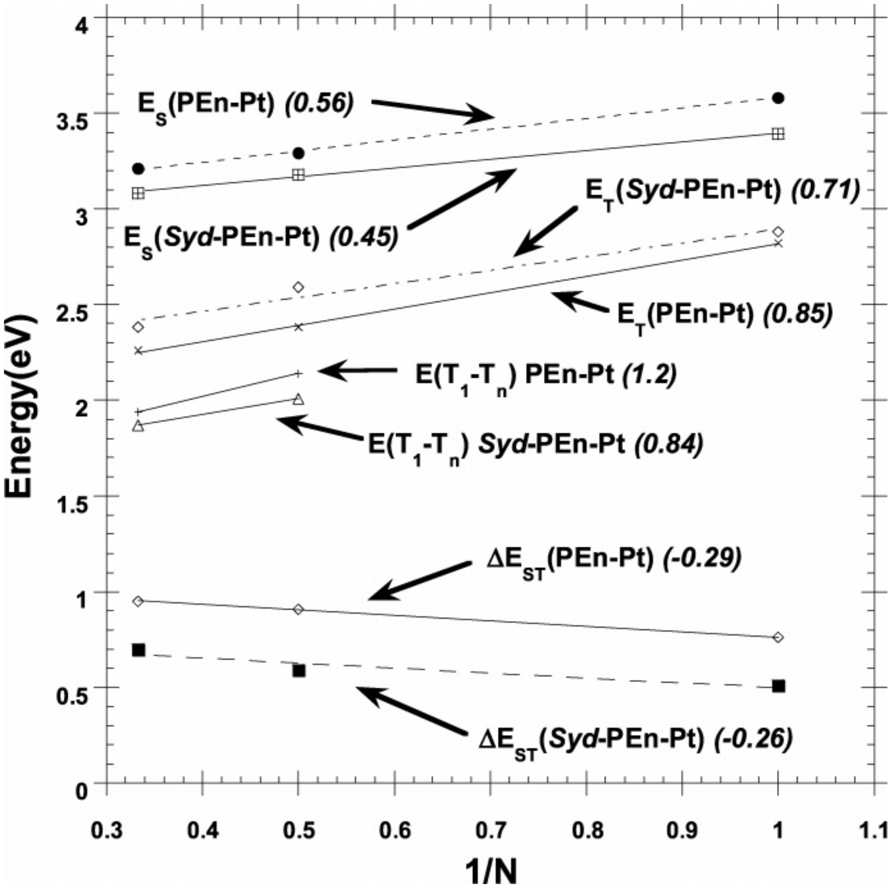

Figure 7. Plot of E_S and E_T for the sydnones and baseline compounds. N is the number of phenyl ethynyl units in the ligand. E_S and E_T for the unmodified platinum complexes were published previously.[10] The number adjacent to each label is the slope of the plot of E_S or E_T vs 1/*N*.

The sign and magnitude of the shift is a function of the molecular dipole moment change upon conversion to the excited state. When the excited-state dipole moment is larger than the ground-state dipole moment, the transition energy decreases with increasing solvent polarity. When the excited-state dipole moment is less than the ground-state dipole moment, the transition energy increases with increasing solvent polarity. Figure 6A shows absorption spectra of PE1-Pt in hexane, benzene, and dichloromethane (DCM). As the solvent changes from hexane to DCM, the absorption maximum red shifts from 323 to 327 nm, suggesting the excited state is more polar than the ground state. Opposite behavior is observed in *Syd*-PE1-Pt (Figure 6B). As the solvent changes from hexane to DCM, the absorption maximum blue shifts from 322 to 316 nm, suggesting the excited state is less polar than the ground state. The spectra in Figure 6B also show isosbestic points, indicating a possible solvent-dependent conformation equilibrium. Literature reports suggest the excited-state dipole moment of sydnones is less than the ground-state dipole moment.[25] These effects are not observed in *Syd*-PE2-Pt. In PE2-Pt, the absorption maximum shifts from 347 to 363 nm as the solvent changes from hexane to DBM. A smaller red shift (376 nm to 383 nm) occurs in *Syd*-PE2-Pt. Because of poor solubility in hexane, a comparison between PE3-Pt and *Syd*-PE3-Pt was not made. The anomalous behavior of *Syd*-PE1-Pt gives evidence the sydnone group has a dominant contribution to the absorption spectra, while in *Syd*-PE2-Pt and *Syd*-PE3-Pt, the effect of the sydnone group is smaller. The ground-state absorption spectra of *Syd*-PE1-Pt may include ligand-centered transitions as well as MLCT transitions.

Figure 5 shows triplet-state absorption spectra of *Syd*-PE2-Pt and *Syd*-PE3-Pt. As the lifetime of the *Syd*-PE1-Pt triplet state is less than the response time of our flash photolysis experiment, we were unable to collect its triplet state absorption spectrum. The triplet-state lifetimes of *Syd*-PE2-Pt and *Syd*-PE3-Pt dissolved in air-saturated benzene are 280 and 290 ns, respectively. The triplet state absorption spectra of *Syd*-PE2-Pt and *Syd*-PE3-Pt show broad absorption throughout the visible and near-IR regions. Compared to the published triplet-state absorption spectra of PE2-Pt and PE3-Pt, *Syd*-PE2-Pt red shifted 19 nm and *Syd*-PE3-Pt 30 nm, showing delocalization effects of the sydnone group.

All three *Syd*-PEn-Pt complexes have weak room-temperature fluorescence with emission maxima around 400 nm (Figures S25, S30, and S35 in Supporting Information). The fluorescence quantum yields referenced to quinine sulfate are $<10^{-3}$, 10^{-3}, and 1.6×10^{-2} for *Syd*-PE1-Pt, *Syd*-PE2-Pt, and *Syd*-PE3-Pt, respectively. The quantum yield behavior is very similar to published behavior of the PEn-Pt compounds, where the quantum yield trend is attributed to increased $\pi\pi^*$ and decreased MLCT character of the excited state.[10] When dissolved in 2-Me-THF, cooled, and irradiated, the *Syd*-PEn-Pt complexes exhibit intense phosphorescence. Published results show the phosphorescence spectra of platinum acetylides having an intense 0−0 band and well-defined vibronic satellites.[29] The T_g of 2-Me-THF is between 90 and 100 K.[26−28] When the solvent temperature is below T_g, the phosphorescence of *Syd*-PEn-Pt and the PEn-Pt compounds exhibit site selectivity, where the 0−0 band energy and the band shape is a function of excitation wavelength (Figures S28, S33, and S38 of Supporting Information). Site selectivity results from formation of a distribution of ground-state solute conformations and solvent environments in a glass. When the solvent temperature is above T_g, there is less site selectivity, although a distribution of molecular conformations

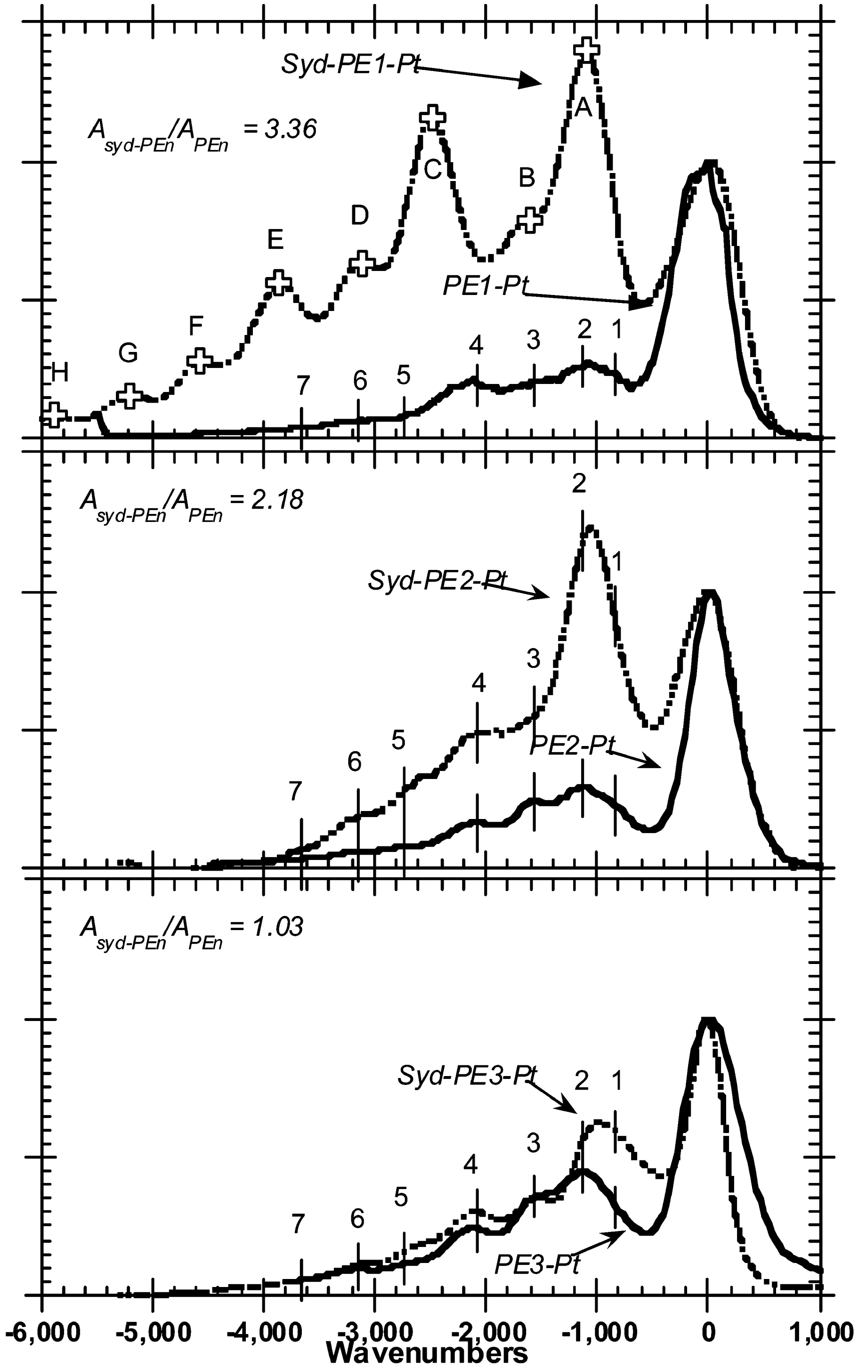

Figure 8. Comparison of representative phosphorescence band shapes for *Syd*-PEn-Pt and PEn-Pt series. Spectra are normalized to the 0−0 band. Vibronic bands (in cm^{-1} from the 0−0 band) observed in the phosphorescence spectrum of syd-PE1 are labeled as letters. (A) 1085, (B) 1600, (C) 2470, (D) 3114, (E) 3855, (F) 4572, (G) 5207, (H) 5878. The numbered vibronic bands (in cm^{-1} from the 0−0 band) use assignments obtained from the literature:[29] 1,839 (ν_1); 2, 1137 (ν_2); 3, 1565 (ν_3); 4, 2081 (ν_4); 5, 2742 (ν_2+ν_3); 6, 3146 (2ν_3); 7, 3662 ($\nu_3 + \nu_4$). The excitation wavelengths (nm) are: PE1-Pt, 324; *Syd*-PE1-Pt, 348; PE2-Pt, 360; *Syd*-PE2-Pt, 390; PE3-Pt, 360; *Syd*-PE3-Pt, 381. The spectra were obtained from 2-Me-THF glasses and selected for easily identifiable 0−0 bands.

complicates the spectra (Figures S26, S31, and S36 of Supporting Information).

We used the absorption and emission spectra of the sydnones to measure the singlet- and triplet-state energies E_S and E_T. E_S was measured from the intersection of the normalized ground state and fluorescence spectra (Figures S25, S30, and S35 of Supporting Information). E_T was measured from the onset of the phosphorescence spectrum of a 2-Me-THF solution above T_g (Figures S28, S31, and S36 of Supporting Information). Figure 7 is a plot of E_S, E_T, $E(T_1 - T_n)$, and ΔE_{ST} vs the reciprocal of the number of phenyl ethynyl groups per ligand. The slope of the line measures change in exciton dimension as the ligand increases in size.[29] A larger slope implies a more delocalized exciton. The lines for the sydnones vs the unmodified complexes are parallel, with attachment of the sydnone displacing the line by a constant energy. The sydnone group lowers E_S and $E(T_1 - T_n)$ by ~0.1 eV but raises E_T by approximately the same amount. As a result, the sydnone group lowers ΔE_{ST} by ~0.2 eV. The trend in ΔE_{ST} contains information about the singly occupied molecular orbitals (SOMO) of the triplet state. ΔE_{ST} is proportional to the overlap integral between SOMO$_1$ and SOMO$_2$.[30] The sydnone effect implies either SOMO$_1$ or SOMO$_2$ is more localized on the sydnone group. This effect also appears in the NMR data described above. The trend in the D coefficient (Figure 4) suggests a charge-transfer interaction between the sydnone group and the central platinum atom. The values of the slopes in Figure 7 suggest the singlet exciton is more localized than the triplet exciton. In our bidentate compounds, increasing the size of the ligand delocalizes the triplet exciton more than the singlet exciton. For example, when the number of phenyl ethynyl units of *Syd*-PEn-Pt goes from one to three, E_S decreases 0.3 eV, while E_T decreases 0.5 eV. This behavior is different from the polymer $[Pt(PBu_3)_2C{\equiv}C(C_6H_5)C{\equiv}C]_n$, where the spectral shift of the 0−0 band from the monomer to the polymer is less than 0.1 eV.[29] A similar small shift is observed in a systematic examination of the oligomer length dependence on phosphorescence.[1] In these papers, the authors conclude the triplet exciton is confined by the platinum centers. In the current work, we have one platinum center with variation of the conjugation length of the ligands, while in the published investigations of the oligomers, the ligand remains constant and the number of platinum centers varied. A symmetry explanation can account for this difference.[31,32] As the chromophore has a center of symmetry, the molecular orbitals have either g or u symmetry. The ground state, having g symmetry, contains contributions from the platinum d orbitals and a centrosymmetric combination of ligand π orbitals. For allowed transitions, the S_1 (and T_1) states have u symmetry. As d orbitals have g symmetry, they cannot contribute to S_1 or T_1 states. As a result, all the excited-state electron density is primarily confined to the ligand with small contributions from platinum and phosphorus p orbitals.[33] The effect inhibits conjugation across the metal. In polymeric systems, this will confine the exciton between a few monomer units. Increasing the oligomer length will therefore not change the phosphorescence electronic energy. In the present work, we have one platinum center and two ligands. Increasing ligand length delocalizes the triplet exciton.

The vibronic lines in the phosphorescence spectra contain information about which bond lengths and angles are distorted upon conversion to the triplet state. Figure 8 shows representative phosphorescence spectra of the sydnones and unmodified complexes where the 0−0 bands have been overlayed so the band shapes can be directly compared. Does the phosphorescence spectrum contain contributions from one group or the combined effects of the phenyl acetylide group and the sydnone group? If there are significant differences between the areas and vibronic peaks of the two spectra, then the sydnone group has a large contribution to the emission spectrum. The area of the emission band of *Syd*-PE1-Pt is about three times that of PE1-Pt, that of *Syd*-PE2-Pt is about twice that of PE2-Pt, and that of *Syd*-PE3-Pt is about the same as PE3-Pt. This trend indicates the sydnone contribution to phosphorescence decreases as the number of phenyl ethynyl groups in the ligand increases. We analyzed the vibronic bands using published assignments.[29] The PEn-Pt compounds show vibronic bands corresponding to out-of-plane C−H bend, C−C stretch, aromatic C−C stretch, and acetylenic C≡C stretch vibrations, overtones and combination bands. The vibronic progression in *Syd*-PE1-Pt's phosphorescence spectrum(labeled A−H in Figure 8) is significantly different from PE1-Pt. Bands C through H have a 687 cm^{-1} spacing, assigned as an in-plane aromatic C−H bend vibration. Many of the vibronic lines observed in the emission spectra of PE2-Pt and PE3-Pt appear in that of *Syd*-PE2-Pt and *Syd*-PE3-Pt, in particular bands numbered 3−7 in Figure 8. However, the difference between the vibronic lines of PE1-Pt and *Syd*-PE1-Pt shows the sydnone group contributes significantly to *Syd*-PE1-Pt's phosphorescence spectrum.

Conclusions

We have investigated the effect of attachment of a mesoionic sydnone group on the spectroscopic properties of a series of platinum acetylide oligomers. The ^{13}C NMR data show the sydnone group has an effect on the charge distribution of the proximal C≡C bond. There is also evidence for a platinum−sydnone interaction that diminishes with increasing oligomer length. Solvent effect experiments on the ground-state absorption spectra show the excited state of *Syd*-PE1-Pt is less polar than the ground state, while the excited state of *Syd*-PE2-Pt has a larger dipole moment. The phosphorescence spectrum of *Syd*-PE1-Pt has a unique band shape compared to PE1-Pt, while those of *Syd*-PE2-Pt and *Syd*-PE3-Pt are similar to PE2-Pt and PE3-Pt. Trends in the singlet-state energy E_S, triplet-state energy E_T, and the singlet−triplet splitting ΔE_{ST} suggest one of the triplet state SOMOs is localized on the sydnone group, while the other is localized on the rest of the ligand. All the spectroscopic data presented in this paper show the sydnone group has the largest effect in a small system.

Supporting Information Available: Complete synthesis procedures, analytical data, proton-coupled and proton-decoupled ^{13}C NMR spectra of all the compounds, absorption, emission, and excitation spectra as well as an X-ray crystallographic file (CIF) of *Syd*-PE1-Pt. This material is available free of charge via the Internet at http://pubs.acs.org.

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