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Two-Photon Spectroscopy of a Series of Platinum Acetylides: Conformation-Induced Ground-State Symmetry Breaking

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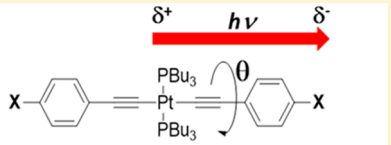
ABSTRACT: With the goal of elucidating electronic and conformational effects on structure−spectroscopic property relationships in platinum acetylides, we synthesized a series of nominally centrosymmetric chromophores *trans*-Pt$(PBu_3)_2$(C≡C-Phenyl-X)$_2$, where **X** = diphenylamino (**DPA**), **NH_2**, **OCH_3**, ***t*-Bu**, **CH_3**, **H**, **F**, benzothiazole (**BTH**), **CF_3**, **CN**, and **NO_2**. We collected one- and two-photon absorption spectra and also performed density functional theory (DFT) and time-dependent (TD) DFT calculations on the ground- and excited-state properties of these compounds. The DFT calculations revealed facile rotation between the two ligands, suggesting that the compounds exhibit nonplanar ground-state conformations in solution. TDDFT calculation of the S_1 state energy and transition dipole moment for a nonplanar conformation gave good agreement with experiment. Two-photon absorption spectra obtained from these compounds allowed estimation of the change of permanent electric dipole moment upon vertical excitation from ground state to S_1 state. The values are small $\Delta\mu < 1.0$ D for neutral substituents such as **CH_3**, **H**, and **F** but increase sharply to $\Delta\mu \approx 11$ D for electron-accepting **NO_2**. When in a nonplanar conformation, the corresponding calculated $\Delta\mu$ values showed good agreement with the experimental data indicating that the two-photon spectra result from nonplanar ground-state conformations. Previously studied related chromophores having extended conjugation (Rebane, A.; Drobizhev, M.; Makarov, N. S.; Wicks, G.; Wnuk, P.; Stepanenko, Y.; Haley, J. E.; Krein, D. M.; Fore, J. L.; Burke, A. R.; Slagle, J. E.; McLean, D. G.; Cooper, T. M. *J. Phys. Chem. A* **2014**, *118*, 3749−3759) show similar dependence of $\Delta\mu$ on the substituents, which allows us to conclude that the excited-state properties of these floppy chromophores are a function of the electronic properties of the substituents, ligand size, and nonplanar molecular conformation.



Broken ground state symmetry enables charge transfer excited states.

INTRODUCTION

Platinum acetylides are known to exhibit exceptional photophysical properties, which has stimulated continuing structure−property investigations.[1−9] Over the last two decades, there have been research published on excited-state phenomena including ground- and excited-state absorption, phosphorescence, intersystem crossing, triplet-state absorption, two-photon absorption (2PA),[10−13] three-photon absorption,[14] formation of excimers,[15] and two-beam coupling.[16] We recently reported on the synthesis and photophysical characterization of a series of platinum(II) *trans*-bis(tributylphosphine)-bis(4-((9,9-diethyl-7-ethynyl-9*H*-fluoren-2-yl)ethynyl)-X) complexes, **Pt-(FL-R-X)$_2$**, where **FL-R-X** stands for the ligand containing an end group **X** with a range of electron-donating and electron-accepting characteristics.[17−19] We found their ground- and excited-state behavior to be a strong function of conformation as well as electronic effects. In particular, we observed that even if the molecular structure is nominally close to centrosymmetric, the presence of potent electron-accepting end groups such as benzothiazole (**BTH**), **CN**, and **NO_2** imposes a behavior resembling that of strongly dipolar chromophores. While lowering of symmetry in molecular excited states is a rather common phenomenon, evidence supporting spontaneous symmetry-breaking in the ground state remains relatively scarce.[20] To understand how the conformation, ligand length, and electronic effects influence the spectroscopic behavior of platinum acetylides, we synthesized a parallel series of *trans*-Pt$(PBu_3)_2$(C≡C-Phenyl-X)$_2$ having the molecular formula shown in Scheme 1. In comparison to **Pt-(FL-R-X)$_2$** series, current **Pt-(R-X)$_2$** structures possess a compact (and presumably less complex) conjugation framework. This attribute was designed to provide a more clear indication of the symmetry-breaking effect and its underlying causes. We collected ground-state absorption as well as 2PA spectra, where the latter provided insight about molecular symmetry via alternative parity selection rule. We also performed density

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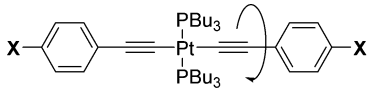
Scheme 1. Molecular Formula of Platinum Acetylide Pt-(R-X)$_2$ Series[a]



X=NH_2, OCH_3, DPA, t-Bu, CH_3, H, F, BTH, CF_3, CN, NO_2

[a]DPA = diphenyl amino, BTH = benzothiozole. The angle θ is the angle between the two phenyl ring planes. The compounds are identified by the names of the end caps (**X**).

functional theory (DFT) and time-dependent (TD) DFT calculations on the ground- and excited-state properties of **Pt-(R-X)$_2$** including identification of possible conformations. On the basis of good quantitative correspondence between calculations and experimental findings, we conclude that the spectroscopic behavior of platinum acetylides is a function of electronic effects from the substituent and conformational effects due to free rotation about the C≡C bond, and these compounds exhibit nonplanar conformation in solution.

EXPERIMENTAL SECTION

Compound **H** and all the other compounds were synthesized according to published methods.[1]

NH_2: *trans*-Bis(tributylphosphine)-bis(4-amino-phenylethynyl)platinum ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12(d, J = 9.0 Hz, 4H), 7.40(d, J = 9.0 Hz, 4H), 2.13(m, 12H), 1.62(m, 12H), 1.48(m, J = 7.2 Hz, 12H), 0.95(t, J = 7.2 Hz, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.99, 132.03, 119.77, 115.09, 108.78, 104.36("false t", J = 14.5 Hz), 26.62, 24.69(t, J = 7.1 Hz), 24.35(t, J = 17.1 Hz), 14.12; ^{31}P NMR (121 MHz, $CDCl_3$) δ 3.84 (J_{Pt-P} = 2375 Hz); IR (KBr) ν 2107.9 cm^{-1} Pt−C≡C; electron impact mass spectrometry (EIMS) calcd. [M+]831.43 ; found [M+]831.43; Anal. Calcd for $C_{40}H_{66}N_2P_2Pt$: C, 57.74%; H, 8.00%; N, 3.37%. Found: C, 57.94%; H, 7.78%; N, 3.46%.

OCH_3: *trans*-Bis(tributylphosphine)-bis(4-methoxy-phenylethynyl)platinum ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23(d, J = 8.7 Hz, 4H), 6.79(d, J = 8.7 Hz, 4H), 3.81(s, 6H), 2.19(m, 12H), 1.64(m, 12H), 1.49(m, J = 7.2 Hz, 12H), 0.95(t, J = 7.2 Hz, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.34, 132.09, 122.05, 113.71, 108.30, 105.62 ("false t", J = 14.6 Hz), 55.47, 26.62, 24.68 (t, J = 6.6 Hz), 24.14 (t, J = 17.1 Hz), 14.09; ^{31}P NMR (121 MHz, $CDCl_3$) δ 4.00 (J_{Pt-P} = 2370 Hz); IR (KBr) ν 2106.0 cm^{-1} Pt−C≡C; EIMS calcd. [M+] 862.01; found [M+] 862; Anal. Calcd for $C_{42}H_{68}O_2P_2Pt$: C, 58.52%; H, 7.95%; O, 3.71%. Found: C, 57.79%; H, 7.8%; O, 3.98%.

DPA: *trans*-Bis(tributylphosphine)-bis(4-*N*,*N*-diphenyl−phenylethynyl)platinum ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25(m, 10H), 7.14(m, 10H), 7.00(m, 8H), 2.2(m, 12H), 1.66(m, 12H), 1.50(m, J = 7.2 Hz, 12H), 0.97(t, J = 7.2 Hz, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.10, 144.94, 131.91, 129.39, 124.32, 124.20, 124.03, 122.67, 108.78, 107.63("false t", J = 14.6 Hz), 26.64, 24.72(t, J = 6.6 Hz), 24.14(t, J = 17.1 Hz), 14.14; ^{31}P NMR (121 MHz, $CDCl_3$) δ 3.94 (J_{Pt-P} = 2365 Hz); IR (KBr) ν 2098.0 cm^{-1} Pt−C≡C; EIMS calcd. [M+] 1136.37; found [M+] 1136; Anal. Calcd for $C_{64}H_{82}N_2P_2Pt$: C, 67.64%; H, 7.27%; N, 2.47%. Found: C, 67.64%; H, 7.35%; N, 2.33%.

***t*-Bu**: *trans*-Bis(tributylphosphine)-bis(4-*t*-butyl-phenylethynyl)platinum ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26(s, 8H), 2.18(m, 12H), 1.65(m, 12H), 1.60(m, J = 7.2 Hz, 12H0), 1.34(s, 9H), 0.98(t, J = 7.2 Hz, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −147.82, 130.68, 126.56, 125.02, 108.80, 107.17-("false t", J = 14.6 Hz), 34.72, 31.58, 26.65, 24.70(t, J = 6.6 Hz), 24.09(t, J = 17.1 Hz), 14.15; ^{31}P NMR (121 MHz, $CDCl_3$) δ 4.11 (J_{Pt-P} = 2369 Hz); IR (KBr) ν 2101.7 cm^{-1} Pt−C≡C; EIMS calcd. [M+] 914.17; found [M+] 914; Anal. Calcd for $C_{48}H_{80}P_2Pt$: C, 63.06%. Found: C, 63.1%.

CH_3: *trans*-Bis(tributylphosphine)-bis(4-methyl-phenylethynyl)platinum ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.22(d, J = 7.8 Hz, 4H), 7.05(d, J = 7.8 Hz, 4H), 2.34(s, 6H), 2.18(m, 12H), 1.66(m, 12H), 1.50(m, J = 7.2 Hz, 12H), 0.97(t, J = 7.2 Hz, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.60, 130.90, 128.85, 126.44, 108.91, 107.00("false t", J = 14.5 Hz), 26.64, 24.69(t, J = 7.1 Hz), 24.15(t, J = 17.1 Hz), 21.56, 14.11; ^{31}P NMR (121 MHz, $CDCl_3$) δ 4.11 (J_{Pt-P} = 2366 Hz); IR (KBr) ν 2101.0 cm^{-1} Pt−C≡C; EIMS calcd. [M+]830.01 ; found [M+] 830; Anal. Calcd for $C_{42}H_{68}P_2Pt$: C, 60.78%; H, 8.26%. Found: C, 60.53%; H, 7.96%.

F: *trans*-Bis(tributylphosphine)-bis(4-fluoro-phenylethynyl) platinum ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28(d, J = 5.7 Hz, 2H), 7.25(d, J = 5.7 Hz, 2H), 6.93(t, J = 5.7 Hz, 4H), 2.18(m, 12H), 1.66(m, 12H), 1.50(m, J = 7.2 Hz, 12H), 0.97(t, J = 7.2 Hz, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.80(d, J = 244.6 Hz), 132.32(d, J = 7.5 Hz), 125.40(d, J = 3.0 Hz), 115.07(d, J = 21.6 Hz), 107.86, 107.35("false t", J = 14.7 Hz), 26.63, 24.68(t, J = 6.6 Hz), 24.21(t, J = 17.1 Hz), 14.03; ^{31}P NMR (121 MHz, $CDCl_3$) δ 4.29 (J_{Pt-P} = 2357 Hz); IR (KBr) ν 2107.9 cm^{-1} Pt−C≡C; EIMS calcd. [M+] 837.94; found [M+] 838; Anal. Calcd for: $C_{40}H_{62}F_2P_2Pt$: C, 57.33%; H, 7.46%; F, 4.53%. Found: C, 57.2%; H, 7.35%; F, 4.29%.

BTH: *trans*-Bis(tributylphosphine)-bis(4-(2-benzo[*d*]-thiazole)-phenylethynyl))platinum ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00(m, 8H), 7.50(m, 2H), 7.39(m, 6H), 2.18(m, 12H), 1.66(m, 12H), 1.50(m, J = 7.2 Hz, 12H), 0.98(t, J = 7.2 Hz, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.47, 154.54, 135.24, 132.23, 131.46, 130.12, 127.46, 126.49, 125.16, 123.22, 121.78, 113.78("false t", J = 14.6 Hz), 109.82, 26.65, 24.69(t, J = 6.6 Hz), 24.27(t, J = 17.1 Hz), 14.09; ^{31}P NMR (121 MHz, $CDCl_3$) δ 4.43 (J_{Pt-P} = 2338 Hz); IR (KBr) ν 2095.4 cm^{-1} Pt−C≡C; EIMS calcd. [M+] 1068.3; found [M+] 1068; Anal. Calcd for $C_{54}H_{70}N_2P_2S_2Pt$: C, 60.71%; H, 6.48%; N, 2.62%; S, 6.00%. Found: C, 60.53%; H, 6.51%; N, 2.71%; S, 5.78%.

CF_3: *trans*-Bis(tributylphosphine)-bis(4-trifluoromethyl-phenylethynyl)platinum ^{1}H NMR (300 MHz, $CDCl_3$) δ7.48(m, J = 8.1 Hz, 4H), 7.36(m, J = 8.1 Hz, 4H), 2.15(m, 12H), 1.64(m, 12H), 1.48(m, J = 7.5 Hz, 12H), 0.96(t, J = 7.5 Hz, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 132.85(q, J = 1.1 Hz), 130.95,126.70(q, J = 32.3 Hz), 125.09(q, J = 3.5 Hz), 124.80(q, J = 271.4 Hz), 112.84("false t", J = 14.6 Hz), 108.72, 26.61, 24.64(t, J = 7.1 Hz), 24.21(t, J = 17.1 Hz), 14.02; ^{31}P NMR (121 MHz, $CDCl_3$) δ 4.50 (J_{Pt-P} = 2337 Hz); IR (KBr) ν 2099.0 cm^{-1} Pt−C≡C; EIMS calcd. [M+] 937.39; found [M+] 937; Anal. Calcd for $C_{42}H_{62}F_6P_2Pt$: C, 53.78%; H, 6.66%. Found: C, 53.92%; H, 5.56%.

CN: *trans*-Bis(tributylphosphine)-bis(4-cyano-phenylethynyl)platinum ^{1}H NMR (300 MHz, $CDCl_3$) δ7.51(d, J = 8.4 Hz, 4H), 7.31(d, J = 8.4 Hz, 4H), 2.10(m, 12H), 1.60(m, 12H), 1.46(m, J = 7.2 Hz, 12H), 0.93(t, J = 7.2 Hz, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 133.88, 132.03, 131.32, 119.80, 116.79-("false t", J = 14.6 Hz), 109.34, 107.89, 26.59, 24.63(t, J = 6.8 Hz), 24.22(t, J = 17.1 Hz), 14.03; ^{31}P NMR (121 MHz, $CDCl_3$) δ 4.63 (J_{Pt-P} = 2322 Hz); IR (KBr) ν 2098.0 cm^{-1} Pt−C≡C; EIMS calcd. [M+] 851.98; found [M+] 852; Anal.

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J. Phys. Chem. A XXXX, XXX, XXX−XXX

Calcd for $C_{42}H_{62}N_2P_2Pt$: C, 59.21%; H, 7.33%; N, 3.29%. Found: C, 59.17%; H, 7.16%; N, 3.13%.

NO_2: *trans*-Bis(tributylphosphine)-bis(4-nitro-phenylethynyl)platinum ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12(d, J = 9.0 Hz, 4H), 7.40(d, J = 9.0 Hz, 4H), 2.13(m, 12H), 1.62(m, 12H), 1.48(m, J = 7.2 Hz, 12H), 0.95(t, J = 7.2 Hz, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.84, 136.15, 131.18, 123.84, 119.35-("false t", J = 14.6 Hz), 109.87, 26.61, 24.62(t, J = 6.6 Hz), 24.29(t, J = 17.1 Hz), 14.01; ^{31}P NMR (121 MHz, $CDCl_3$) δ 4.78 (J_{Pt-P} = 2314 Hz); IR (KBr) ν 2096.0 cm^{-1} Pt−C≡C; EIMS calcd. [M+] 891.96; found [M+] 892; Anal. Calcd for $C_{40}H_{62}N_2O_4P_2Pt$: C, 53.86%; H, 7.01%; N, 3.14%. Found: C, 53.83%; H, 6.70%; N, 3.14%.

Extinction coefficients were measured from samples dissolved in methyl-tetrahydrofuran. A detailed study of linear, emission, and time-resolved spectroscopy will be published elsewhere. For two-photon absorption spectroscopy, all samples were prepared in tetrahydrofuran (THF) solution at chromophore concentration values in the range of 1−10 mM in standard 1 cm spectroscopic cuvettes. Degenerate instantaneous 2PA cross-section spectra were measured in the wavelength range of 550−900 nm utilizing a femtosecond optical parametric amplifier (OPERA, Coherent) pumped by a Ti:sapphire regenerative oscillator/amplifier (Libra, Coherent, Inc.). Because Pt-$(R\text{-}X)_2$ compounds studied here emit virtually no fluorescence, the 2PA measurements were performed using nonlinear transmission (NLT) method previously described.[18] Briefly, the optical parametric amplifier (OPA) provided pulse energy up to 5−100 μJ per pulse (depending on wavelength) at 100 Hz pulse repetition rate. A thermoelectric optical power meter (Nova II, Ophir Inc.) was used to measure the average power. A diffraction grating spectrometer (USB4000, Ocean Optics) was used to measure the OPA spectrum, and a custom second harmonic generation autocorrelator was used to determine the pulse duration. The average spectral bandwidth and pulse duration were, respectively, $\Delta\lambda$ = 15−35 nm and 120−150 fs, depending on the wavelength. A linear polarizer along with a stack of color glass filters was used to block residual wavelengths in the OPA output. The OPA beam was slightly focused using long focal length lenses (f = 500−1500 mm) to provide a spot size on the sample 300−1000 μm, again depending on wavelength. Two pick-off glass plates were placed at a distance of ∼10 cm before and after the sample. The reflected light was directed to two integrating spheres equipped with silicon photodetectors (DET100A, Thorlabs). The OPA wavelength was tuned in 2 nm steps, and at each wavelength the incident pulse energy was varied in the range of P_{in} = 0.2−20 μJ by using a personal computer (PC)-controlled variable reflective ND filter (Thorlabs). At each wavelength, the output signal of the two detectors was digitized using a DAQ card (PCI-6011, National Instruments, Inc.), and the data were analyzed using custom LabView routine, which evaluated the relative transmittance (defined as the ratio between the two integrated-over-the-pulse photodetector signals) as a function of the pulse energy. The intensity-dependent transmittance was fitted with a linear function, whereas to ensure validity of the linear fits, the maximum transmittance change was kept well below 5−10%. The two-photon absorption cross-section spectrum was obtained by comparing the slope of the fit function with respect to the slope obtained under the same excitation conditions using a known 2PA reference standard fluorescein in pH 11 H_2O. Estimated experimental uncertainty of the 2PA values is ∼20%.

Calculations were done using Gaussian 09W, Version 7.0.[21] The chromophores were modeled as *trans*-$Pt(PMe_3)_2(C{\equiv}C\text{-}Phenyl\text{-}X)_2$ in THF through use of polarizable continuum model (PCM). We performed DFT energy minimizations for the ground state using B3LYP/6-311g(2d,p) and TDDFT calculations using CAM-B3LYP/6-311g(2d,p). The basis set for the central Pt atom was SDD.

RESULTS AND DISCUSSION

Figure 1 shows ground-state absorption spectra of the compounds dissolved in methyl-tetrahydrofuran. Oscillator

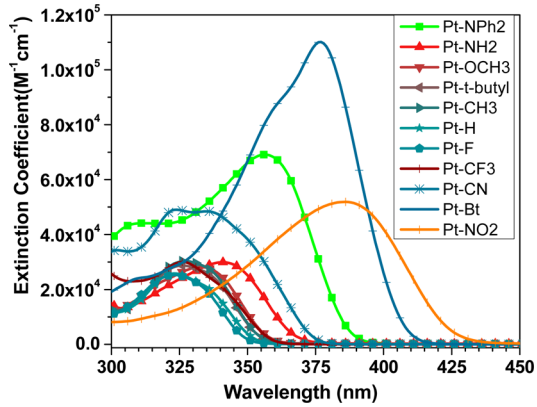

Figure 1. Ground-state absorption spectra of complexes dissolved in benzene.

strengths for the $S_0 \rightarrow S_1$ transition were calculated from a Gaussian fit to the low-lying ground-state spectra, and transition dipole moments were calculated from the relation

$$f_{01} = 4.701\,67 \times 10^{-7} \nu_{01} \mu_{01}^2 \quad (1)$$

where the transition frequency ν_{01} is in inverse centimeters, and the transition dipole moment μ_{01} is in debyes. The corresponding values are collected in Table 1.

Table 1. Summary of Ground-State Absorption Spectra

X	λ_{max} [a]	ε_m [b]	μ_{01} [c]
NH_2	341	2.99	5.83
OCH_3	332	2.81	4.85
DPA	356	6.91	8.41
***t*-Bu**	326	2.87	5.12
CH_3	327	3.04	5.31
H	323	2.58	4.37
F	323	2.53	4.57
BTH	377	11.0	10.9
CF_3	326	3.00	5.40
CN	335	4.84	7.71
NO_2	386	5.19	8.71

[a]Absorption maximum (nm). [b]Extinction coefficient ($(M^{-1}\ cm^{-1}) \times 10^{-4}$). [c]Transition dipole moment (D) obtained from Equation 1.

Figure 2 shows the 2PA cross-section spectra of the 11 compounds in THF solution. The 2PA cross section, σ_{2PA}, is expressed in Goeppert−Mayer units (1 GM = 1×10^{-50} cm^4 photon^{-1} s). Corresponding linear absorption spectra are also shown for comparison. With notable exception of **NO_2**, the 2PA cross section of all compounds increases with decreasing excitation wavelength, λ_{2PA}, with maximum values reached at

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J. Phys. Chem. A XXXX, XXX, XXX−XXX

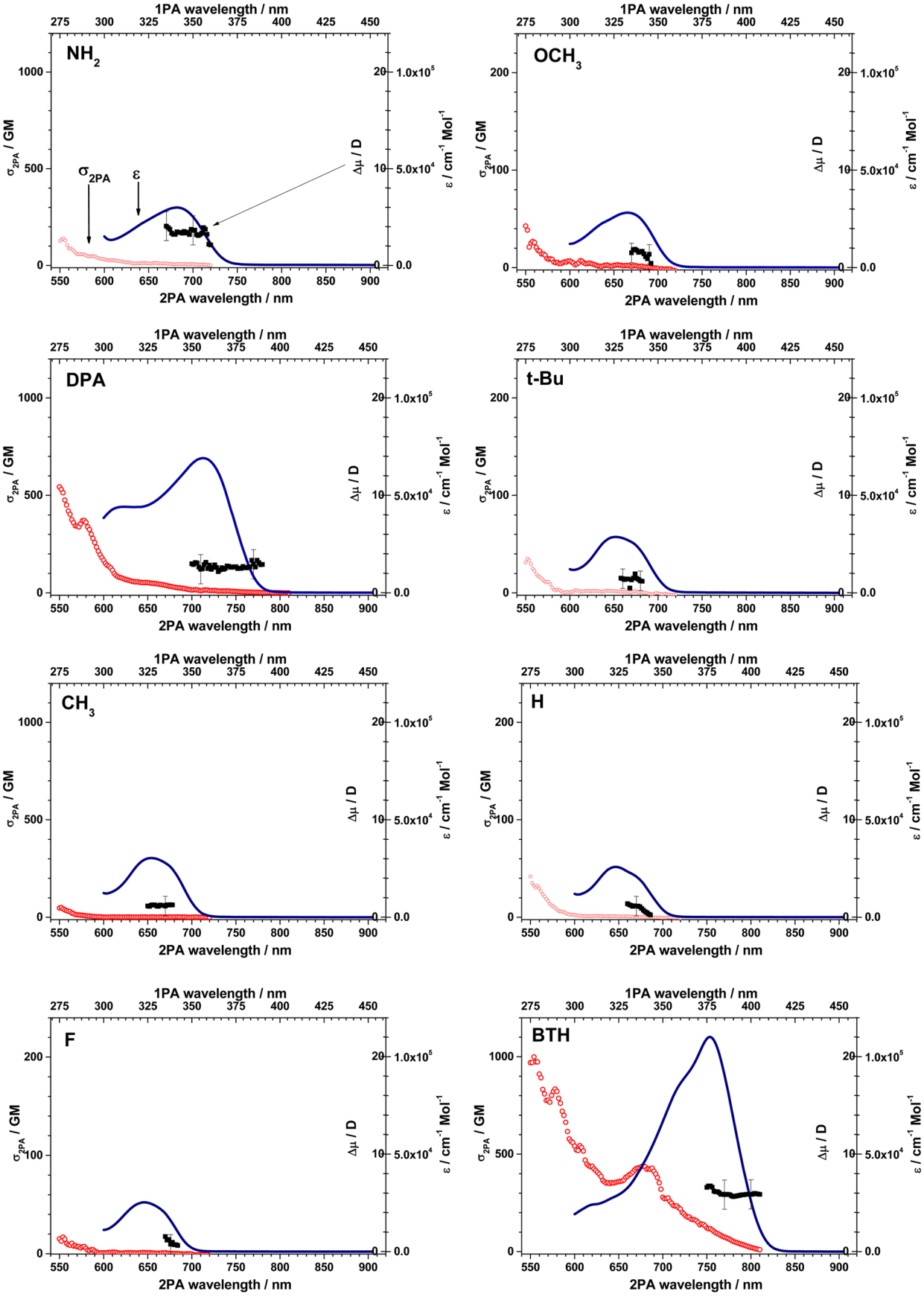

Figure 2. continued

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J. Phys. Chem. A XXXX, XXX, XXX−XXX

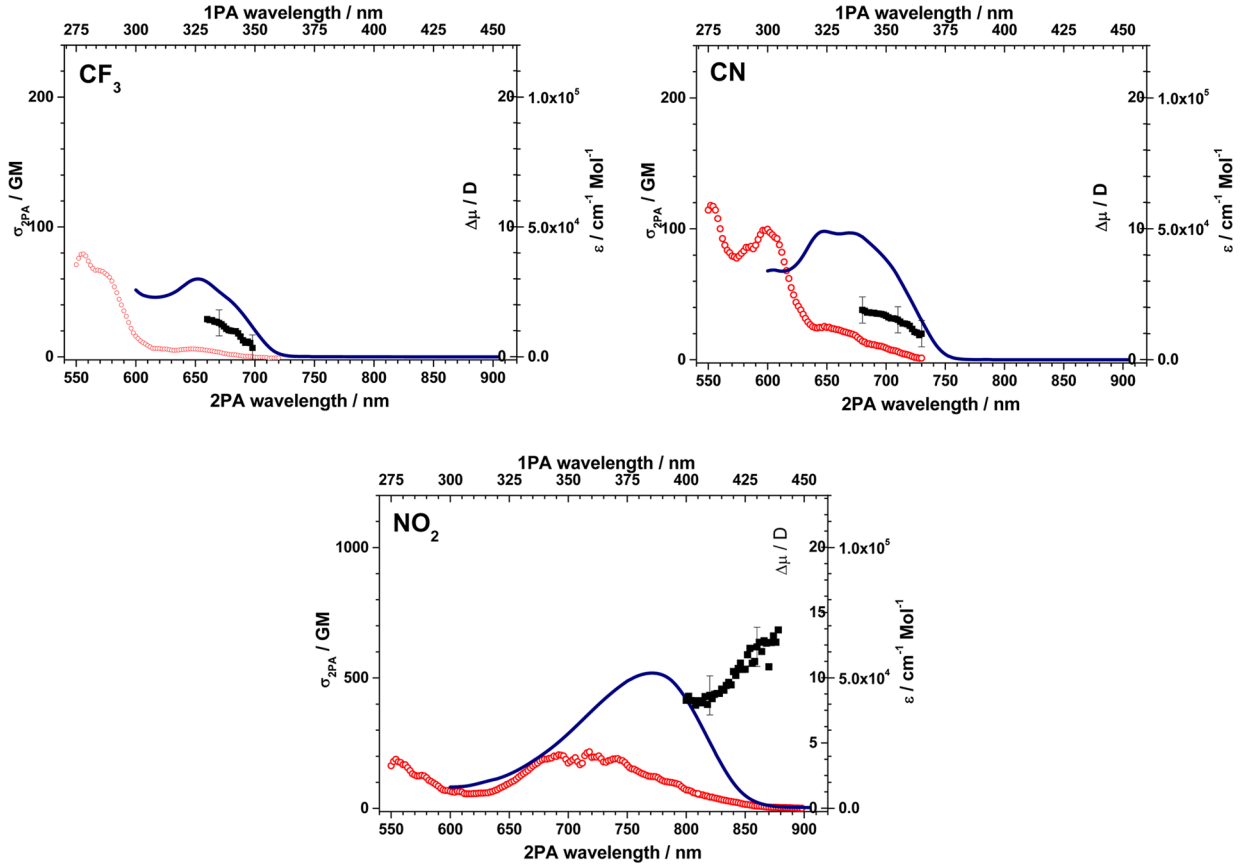

Figure 2. 2PA cross-section spectrum (red ○, left vertical axis) of the 11 **Pt-(R-X)$_2$** compounds in THF studied by the NLT method (left vertical axis). The ground-state extinction spectrum (blue line, right outside vertical axis) is shown for comparison. The lower and upper horizontal axes are calibrated in 2PA and 1PA wavelengths, respectively. (■) $\Delta\mu$ values (inner right vertical axis) evaluated according to eq 2. As an example the spectra for compound **NH$_2$** were labeled to help interpret the axis labels.

the shortest excitation wavelength, λ_{2PA}< 650 nm. This behavior may be attributed, in part, to conjugated organic chromophores often exhibiting the strongest two-photon transitions at energies, well above the $S_0 \rightarrow S_1$ band, and resonance enhancement effect via the lowest-energy dipole-allowed transition.[16] From this perspective, the fact that the highest 2PA values in the whole series are observed in **BTH** ($\sigma_{2PA} \approx$ 1000 GM) and in **DPA** ($\sigma_{2PA} \approx$ 600 GM) at λ_{2PA} = 550 nm, correlates with higher-than-average transition dipole moments μ_{01} = 10.9 and 8.4 D, respectively (Table 1). The resonance contribution to 2PA is likely further augmented because both chromophores exhibit a red-shifted $S_0 \rightarrow S_1$ band. In the remaining nine compounds, the maximum 2PA in the short wavelength region is substantially lower, σ_{2PA} < 20−200 GM, indicating that pronounced 2PA may occur at still higher energy that lies beyond current lower limit of 550 nm. We previously studied these effects in detail with the analogous **Pt-(Fl-R-X)$_2$** series, where we measured the 2PA spectra of the platinum complexes and the ligands.[18,19] We also previously collected ultrafast transient absorption spectra of the **Pt-(Fl-R-X)$_2$** compounds.[17] At higher transition energy corresponding to $S_0 \rightarrow S_n$ transition region, we find strong correlation between 2PA measured by the NLT method with excited state absorption (ESA) measured by pump−probe techniques. Because of weak ground-state absorption at 400 nm, we were unable to collect ESA spectra for the entire **Pt-(R-X)$_2$** series. Ultrafast ESA spectra were measured for **H**, which was excited by femtosecond pulses at 340 nm.[22] The intersystem crossing time measured by fluorescence upconversion was estimated to be 70 fs. The ESA spectrum of **H** has broad absorption centered at 640 nm. In Figure 2, we observe increasing 2PA absorption from **H** at λ < 600 nm, which certainly includes ESA contribution.

Because the symmetry effects manifest most clearly in the lowest-energy transitions, especially in the 0−0 component of $S_0 \rightarrow S_1$ band, we will focus on the longest-wavelength portion of the 2PA spectrum. The σ_{2PA} of the 0−0 component of the $S_0 \rightarrow S_1$ transition, along with the corresponding wavelength, are shown in Table 2. These data show that σ_{2PA} corresponding to the 0−0 component of $S_0 \rightarrow S_1$ varies between 11 and 1 GM, whereas the latter value is most likely determined by upper accuracy limit of our experiment. If the angle θ between the two phenyl ring planes of **Pt-(R-X)$_2$** is small, then the structure (Scheme 1) is nominally centrosymmetric, and one might expect that alternative parity selection rule must apply for one- and two-photon absorption spectra. Indeed, in case of **H**, **F**, and **CH$_3$**, 0−0 component of $S_0 \rightarrow S_1$ band that is strongly allowed in the linear absorption, is rather weak or even vanishing in the 2PA spectrum. However, in compounds decorated with potent electron-donating end groups and, in particular, those with strong electron-withdrawing substituents, the parity selection rule appears to be violated. This is especially evident in case of **NO$_2$**, where the one-photon and two-photon spectral profiles virtually coincide (Figure 2). Such behavior is common for strongly dipolar chromophores but not normally expected from systems possessing inversion symmetry. We evaluated the

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J. Phys. Chem. A XXXX, XXX, XXX−XXX

Table 2. Summary of 2PA Cross Sections

X	Pt-(R-X)$_2$ [$S_0 \rightarrow S_1(0-0)$]			Pt-(FL-R-X)$_2$ [$S_0 \rightarrow S_1$ (0–0)]		
	λ_{2PA}[a]	σ_{2PA}[b]	$\Delta\mu$[c]	λ_{2PA}[d]	σ_{2PA}[d]	$\Delta\mu$[d]
DPA	712	16	3	810	33	3.5
NH$_2$	682	15	3.5	782	93	6.4
OCH$_3$	668	10	1.5	774	57	5.5
***t*-butyl**	672	1	1	772	73	6
CH$_3$	670	1	1	774	61	5.3
H	672	1	1	774	92	7.5
F	668	1	1	772	53	5.5
CF$_3$	684	2	1.5	792	120	7.5
CN	702	8	2	814	190	12
BT	752	120	6	826	270	12
NO$_2$	774	120	11	862	700	25

[a]Two-photon absorption maximum (nm). [b]Two-photon cross section (GM). [c]Measured dipole moment change $\mu_1 - \mu_0$ (D) for S_1 state. [d]Published two-photon absorption maximum, two-photon cross section, and dipole moment change for **Pt-(FL-R-X)$_2$** system.[18]

change of permanent electric dipole in vertical $S_0 \rightarrow S_1$ transition using the relation[23,24]

$$\Delta\mu = 4550\left(\frac{3}{n^2+2}\right)\sqrt{\frac{n\sigma_{2PA}(2\lambda)}{\lambda\varepsilon_m(\lambda)}} \quad (2)$$

where n is the index of refraction of the solvent, λ is the wavelength of 0–0 component of $S_0 \rightarrow S_1$ transition, and ε_m is the corresponding molar extinction (cm^{-1} M^{-1}). Figure 2 shows $\Delta\mu$ (square symbols, right inner vertical axis) calculated according to eq 2 for 0–0 transition region in all 11 **Pt-(R-X)$_2$** chromophores. In **NH$_2$**, **OCH$_3$**, **DPA**, ***t*-Bu**, **CH$_3$**, and **BTH**, $\Delta\mu$ is nearly constant, which is expected in case of a static electric dipole. But in some cases such as **CF$_3$**, **CN**, and **NO$_2$**, the value appears to change with the wavelength. There may be solvent complexes with the highly polar trifluoromethyl, nitrile, and nitro groups, which red-shift the 0–0 transition of a proportion of the solutes and change $\Delta\mu$. To further understand these interactions, molecular dynamics simulations with explicit solvent–solute interactions followed by TDDFT calculations of properly sampled molecular conformations would need to be performed.[25] The average dipole moment values are summarized in Table 2. **BTH** and **NO$_2$** exhibit the largest dipole moment change, 6 and 11 D, respectively. Also **NH$_2$** and **DPA** show a pronounced dipole moment change $\Delta\mu \approx 3$ D. It is significant that the nonvanishing $\Delta\mu$ appears in vertical transitions from the electronic ground state. Since both one- and two-photon absorption are instantaneous quantum transition events with no time for any conformational changes, we conclude that inversion symmetry must be broken already in the ground state, that is, before the chromophore reaches the excited state. It is worth reminding that once in the excited-state manifold, changes of chromophore intrinsic symmetry are quite common, induced, for example, by vibrational relaxation, intersystem crossing, solvent rearrangement, etc. In the ground state, where the chromophore and its surrounding solvent are in equilibrium, spontaneous symmetry breaking is not so well-understood.

A qualitatively similar dependence of $\Delta\mu$ on the end-cap substituent structure was previously observed in the related series of **Pt-(FL-R-X)$_2$**.[18] The corresponding data for of 0–0 component of $S_0 \rightarrow S_1$ transition is reproduced in Table 2 for comparison. In both cases, **NO$_2$** substituent appears to cause the most pronounced symmetry-breaking effect, on the one hand because the corresponding values are the largest, and on the other hand because the shape of the 2PA spectrum switches to a distinctly dipolar character.

An explanation for the observed loss of inversion symmetry is nonplanar ground-state conformations. If the angle between the two phenyl ring planes is $\theta = 0°$, then, by definition, $\Delta\mu = 0$. However, if the rings are mutually rotated, then a finite electric dipole may occur. Table 3 summarizes the TDDFT calculations

Table 3. Summary of TDDFT Calculations[a]

X	ΔE[b]	μ_{01}[c]	$\mu_1-\mu_0$[d]	ΔE[e]
NH$_2$	3.99	8.59	2.98	0.03
OCH$_3$	4.07	8.32	1.3	0.13
DPA	3.76	11.2	4.45	0.26
***t*-Bu**	4.09	8.64	0.53	0.33
CH$_3$	4.1	8.28	0.74	0.17
H	4.12	7.92	−0.07	0.22
F	4.14	7.73	0.5	0.17
BTH	3.53	14.9	3.69	0.34
CF$_3$	4.06	8.87	2.69	0.34
CN	3.88	10.7	5.24	0.28
NO$_2$	3.53	11.4	10.05	0.29

[a]For $\theta = 90°$. [b]Transition energy in electronvolts for state 1. [c]Transition dipole in debyes for state 1. [d]Dipole moment difference in debyes between S_1 state and ground state when $\theta = 90°$. [e]Ground-state energy difference $\Delta E = E_{gs}(\theta = 90°) - E_{gs}(\theta = 0°)$ in kilocalories per mole.

results regarding the transition energy, $S_0 \rightarrow S_1$ transition dipole moment and $\Delta\mu$ in the case of $\theta = 90°$. The S_1 state in all the calculations has predominantly highest occupied molecular orbital (HOMO) → lowest unoccupied molecular orbital (LUMO) character. The last column in Table 3 shows the calculated ground-state energy differences between $\theta = 0°$ and 90° conformations (in kcal mol^{-1} units). Because the energy difference is much less than kT (0.6 kcal/mol) at room temperature, the calculations suggest that there is free rotation between the ligands, which means that statistically the chromophores are predominantly out-of-plane in solution, justifying our assumed rotation angle value, $\theta = 90°$.

Figure 3 shows plots of calculated versus experimental S_1 state energies and transition dipole moments. The S_1 state energies and transition dipole moments obtained from the absorption spectra correlate very well with the calculations. The slopes are near unity, showing the calculations successfully describe the variation in energy and transition moment with substituent.

Figure 4 shows the effect of ligand length on $\Delta\mu$. The left-hand portion of Figure 4 shows the experimental dipole moment change in the **Pt-(R-X)$_2$** series (vertical axis) plotted as a function of $\Delta\mu$ values obtained previously in the **Pt-(FL-R-X)$_2$** series (horizontal axis) with the same Pt core and the same 11 end-caps.[18] The right-hand portion shows calculated $\Delta\mu$ values from **Pt-(R-X)$_2$** vs **Pt-(FL-R-X)$_2$**. The linear fit to the data for both experimental and calculated dipole moment changes (red line) has the slope ~0.5 because the absolute dipole moment values are ~2 times larger in the **Pt-(FL-R-X)$_2$** compounds, which may be related to the conjugation, and intramolecular charge transfer extends over a larger distance compared to the shorter **Pt-(R-X)$_2$** series. Aside from the difference in absolute values, there is good correlation between

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J. Phys. Chem. A XXXX, XXX, XXX–XXX

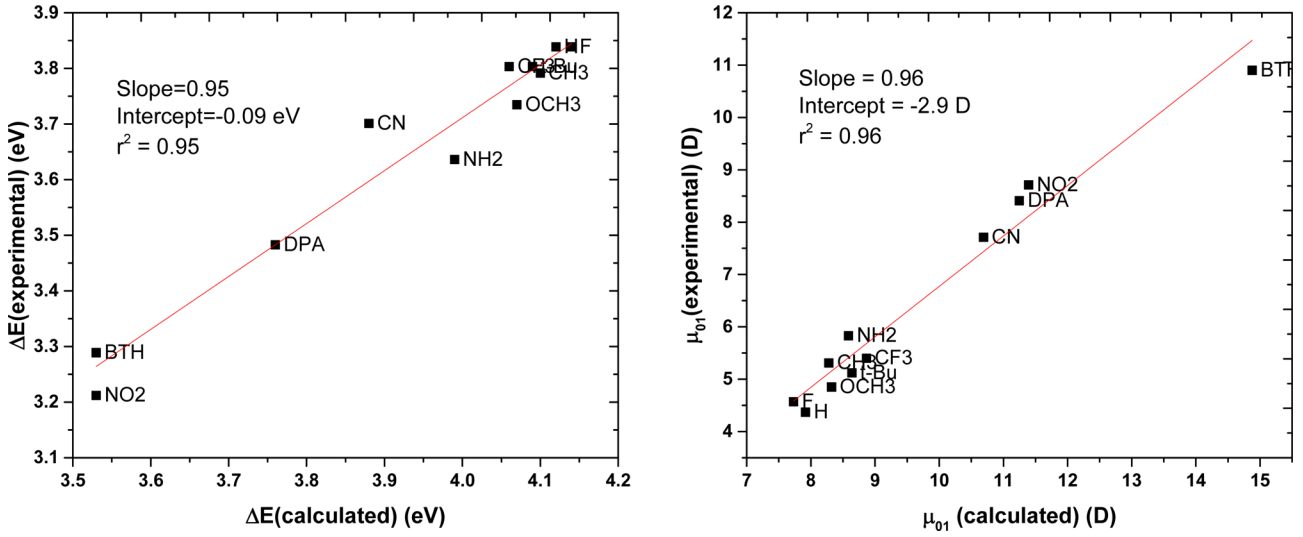

Figure 3. (left) Plot of calculated vs experimental S_1 state transition energies. (right) Plot of calculated vs experimental transition dipole moments.

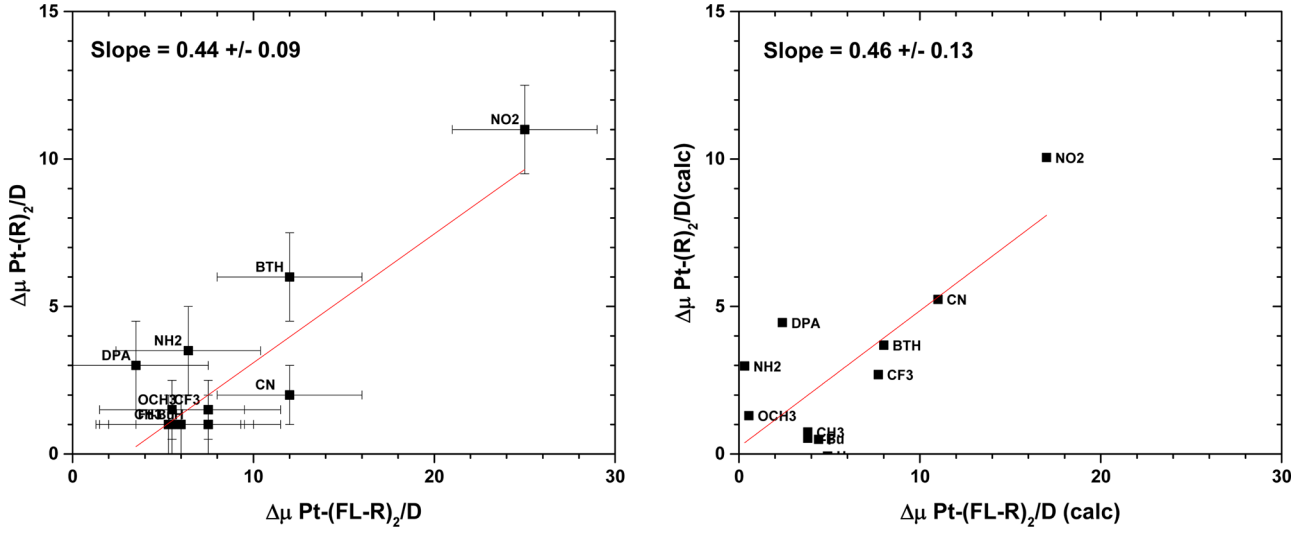

Figure 4. (left) Experimental $\Delta\mu$ in the **Pt-(R-X)$_2$** series (vertical axis) plotted as a function of $\Delta\mu$ values obtained previously in the **Pt-(FL-R-X)$_2$** series[18] with the same Pt core and the same 11 end-caps, but additional fluorenyl linker inserted between the core and the end-caps; (right) calculated $\Delta\mu$ values from **Pt-(R-X)$_2$** vs **Pt-(FL-R-X)$_2$**.[18]

dipole moments for the same end cap. From these observations we can conclude that in both series $\Delta\mu$ is determined by the nonplanar molecular conformation, the electronic properties of the end caps, and the length of the spacer group. There is recent literature describing systems in which, upon excitation, a nominally quadrupolar chromophore behaves like an excited-state dipole.[26−29] Provided the ground-state conformation is rigid, the time-resolved spectroscopic data can be interpreted as relaxation to a dipolar excited state. In the current system, the centrosymmetric chromophores have a floppy ground-state conformation, which gives then dipolar excited-state behavior.

CONCLUSIONS

In this work we synthesized a series of chromophores *trans*-Pt(PBu$_3$)$_2$(C≡C-Phenyl-X)$_2$, where **X** = **NH$_2$**, **OCH$_3$**, **DPA**, ***t*-Bu**, **CH$_3$**, **H**, **F**, **BTH**, **CF$_3$**, **CN**, and **NO$_2$**. We collected ground-state absorption and two-photon spectra. We also performed DFT and TDDFT calculations on the ground and excited-state properties of these compounds. The calculations show the energy difference between the $\theta = 90°$ versus $\theta = 0°$ is less than kT, suggesting the compounds in solution have a statistical mix of out-of-plane conformations. When $\theta = 90°$, there is good agreement between calculated and experimental S_1 state energies, transition dipole moments, and excited-state dipole moments. The spectroscopy and calculation results suggest these chromophores have very flexible structure, and out-of-plane conformation predominates in solution. The ground-state and 2PA absorption spectra result from symmetry-broken ground-state out-of-plane conformations.

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Notes

The authors declare no competing financial interest.

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J. Phys. Chem. A XXXX, XXX, XXX−XXX

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J. Phys. Chem. A XXXX, XXX, XXX−XXX