

Symmetry Breaking in Platinum Acetylide Chromophores Studied by Femtosecond Two-Photon Absorption Spectroscopy

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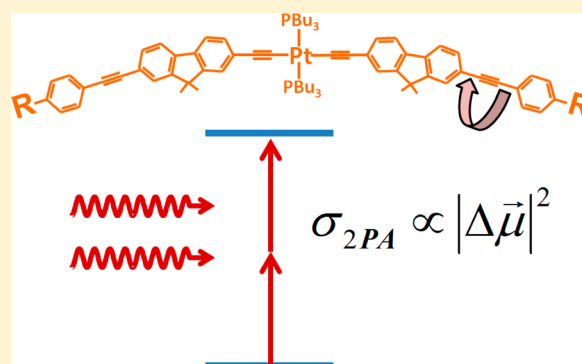
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ABSTRACT: We study instantaneous two-photon absorption (2PA) in a series of nominally quasi-centrosymmetric *trans*-bis(tributylphosphine)-bis-(4-(9,9-diethyl-7-ethynyl-9*H*-fluoren-2-yl)ethynyl)-*R*-platinum complexes, where 11 different substituents, *R* = N(phenyl)₂(NPh₂), NH₂, OCH₃, *t*-butyl, CH₃, H, F, CF₃, CN, benzothiazole, and NO₂, represent a range of electron-donating (ED) and electron-withdrawing (EW) strengths, while the Pt core acts as a weak ED group. We measure the 2PA cross section in the 540–810 nm excitation wavelength range by complementary femtosecond two-photon excited fluorescence (2PEF) and nonlinear transmission (NLT) methods and compare the obtained values to those of the Pt-core chromophore and the corresponding noncentrosymmetric side group (ligand) chromophores. Peak 2PA cross sections of neutral

and ED-substituted Pt complexes occur at $S_0 \rightarrow S_n$ transitions to higher energy states, above the lowest-energy $S_0 \rightarrow S_1$ transition, and the corresponding values increase systematically with increasing ED strength, reaching maximum value, $\sigma_2 \sim 300$ GM (1 GM = 10^{-50} cm⁴ s), for *R* = NPh₂. At transition energies overlapping with the lowest-energy $S_0 \rightarrow S_1$ transition in the one-photon absorption (1PA) spectrum, the same neutral and ED-substituted Pt complexes show weak 2PA, $\sigma_2 < 30$ –100 GM, which is in agreement with the nearly quadrupolar structure of these systems. Surprisingly, EW-substituted Pt complexes display a very different behavior, where the peak 2PA of the $S_0 \rightarrow S_1$ transition gradually increases with increasing EW strength, reaching values $\sigma_2 = 700$ GM for *R* = NO₂, while in the $S_0 \rightarrow S_n$ transition region the peak 2PEF cross section decreases. We explained this effect by breaking of inversion symmetry due to conformational distortions associated with low energy barrier for ground-state rotation of the ligands. Our findings are corroborated by theoretical calculations that show large increase of the permanent electric dipole moment change in the $S_0 \rightarrow S_1$ transition when ligands with strong EW substituents are twisted by 90° relative to the planar chromophore. Our NLT results in the $S_0 \rightarrow S_1$ transition region are quantitatively similar to those obtained from the 2PEF measurement. However, at higher transition energy corresponding to $S_0 \rightarrow S_n$ transition region, the NLT method yields effective multiphoton absorption stronger than the 2PEF measurement in the same systems. Such enhancement is observed in all Pt complexes as well as in all ligand chromophores studied, and we tentatively attribute this effect to nearly saturated excited-state absorption (ESA), which may occur if 2PA from the ground state is immediately followed by strongly allowed 1PA to higher excited states.



1. INTRODUCTION

Organoplatinum chromophores exhibit promising nonlinear-optical properties making them attractive for a variety of applications in photonics and photomedicine.^{1–31} Bis(phenylethynyl) bis(tributylphosphine) platinum(II) complexes have been shown to possess efficient multiphoton absorption that combines instantaneous two-photon absorption (2PA) and a slower, albeit

often more efficient, excited-state absorption (ESA).^{1,7,9,10,18,23,29–33}

Because the probability of 2PA increases as the square of the photon flux density, the transmittance of a light pulse propagating through a

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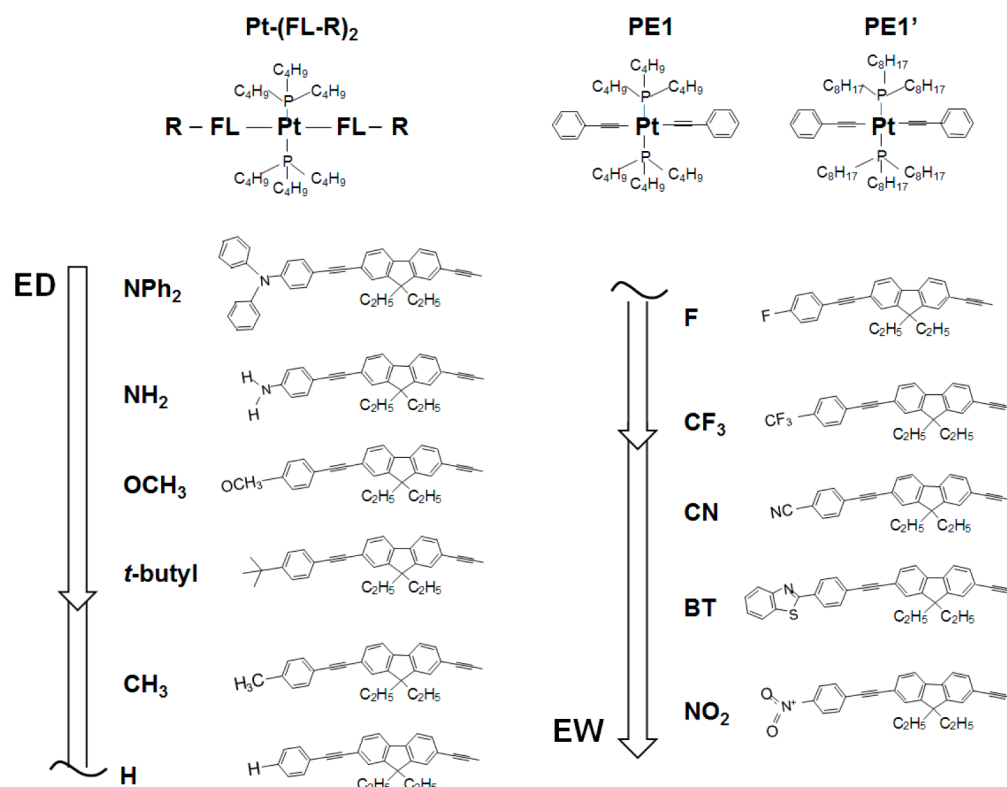


Figure 1. Chemical structures of the Pt complexes $\text{Pt}-(\text{FL-R})_2$, corresponding ligand chromophores FL-R, and Pt-core model chromophores PE1 and PE1'. Arrows indicate increase of EW ability.

medium comprising 2PA-active chromophores decreases with increasing intensity. Furthermore, if the chromophores also possess a large one-photon absorption (1PA) cross section from excited singlet and/or triplet states, then a combined 2PA + ESA nonlinear absorption mechanism is observed.^{14,23,24,29,31}

Recently, we have reported on the synthesis and photophysical characterization of a series of platinum(II) *trans*-bis(tributylphosphine)-bis(4-((9,9-diethyl-7-ethynyl-9H-fluoren-2-yl)ethynyl)-R)-complexes, where R represents one of the different end groups N(phenyl)₂(NPh₂), NH₂, OCH₃, *t*-butyl, CH₃, H, F, CF₃, CN, benzothiazole (BT), or NO₂.³⁴ The previous study showed that the series exhibits broad spectral bandwidth femtosecond ESA as well as efficient nanosecond ESA, where the latter is attributed to long triplet lifetime and rapid singlet-to-triplet intersystem crossing that is characteristic of Pt complexes.³⁴ The same study also concluded that in the triplet manifold the conjugation through the Pt core is terminated, thus localizing the triplet exciton of the nominally quasi-centrosymmetric complex only on one ligand.³⁴ We have recently reported³⁵ on the femtosecond 2PA cross sections and the 2PA spectra of the 11 chromophores used here as the side groups (ligands), with the structure 4-((9,9-diethyl-7-ethynyl-9H-fluoren-2-yl)ethynyl)-R. By using a femtosecond two-photon excited fluorescence (2PEF) technique we showed that increasing either electron-donating (ED) or electron-withdrawing (EW) strength of the end group R significantly enhances the peak σ_2 value in the $S_0 \rightarrow S_1$ transition, up to $\sigma_2 = 60\text{--}80 \text{ GM}$ ($1 \text{ GM} = 10^{-50} \text{ cm}^4 \text{ s}$), relative to that in the neutral substituents, $\sigma_2 < 10 \text{ GM}$. It was also previously shown that the value of the permanent electric dipole moment change in the $S_0 \rightarrow S_1$ transition $\Delta\mu$, determined from the 2PA measurements by applying two-level model, is in good quantitative agreement with theoretically calculated values obtained for these noncentrosymmetric chromophores.³⁵

We investigate the femtosecond 2PA spectra and the 2PA cross sections of the aforementioned 11 Pt complexes using femtosecond two-photon excited fluorescence (2PEF) method. We complement our 2PEF measurements with femtosecond nonlinear transmission (NLT) measurement,³⁰ which utilizes a nearly collimated laser beam and allows for evaluation of the 2PA cross sections of weakly fluorescent Pt-core chromophores.

The previously observed symmetry breaking in the triplet exciton raises an interesting question about permanent electric dipole moment change in vertically excited singlet states of the Pt complexes and, in particular, its dependence on different substituents R. Indeed, if all 11 Pt complexes possess quasi inversion symmetry, then the value of the dipole as well as its change would be expected to remain small in the entire series. By the same token, the 1PA and 2PA spectral shapes should always show mutually exclusive transitions. On the other hand, studies performed in conjugated dendrimers have pointed out the importance of conformational changes that may strongly influence the 2PA properties.³⁶ Nguyen et al. recently calculated 2PA cross sections and spectra of ED- or EW-substituted Pt acetylide complexes with structures related to the series studies here and showed that low barriers for rotations of the alkylphosphinyl and phenylene groups may lead to multiple low-lying conformers with different (lower) symmetries; however, no substantial effects of the conformational changes on the 2PA properties were predicted.²² Leng et al. used hyper-Raman and hyper-Rayleigh scattering to show that in some nominally centrosymmetric metal-free chromophores the inversion symmetry could be broken in vertical transitions by interactions with solvent, even though the 2PA spectra indicated mostly quadrupolar behavior.³⁷

Here we use femtosecond 2PEF and NLT measurements in the $S_0 \rightarrow S_1$ transition region to show that the effective symmetry of the Pt complexes strongly depends on the substitutions, where

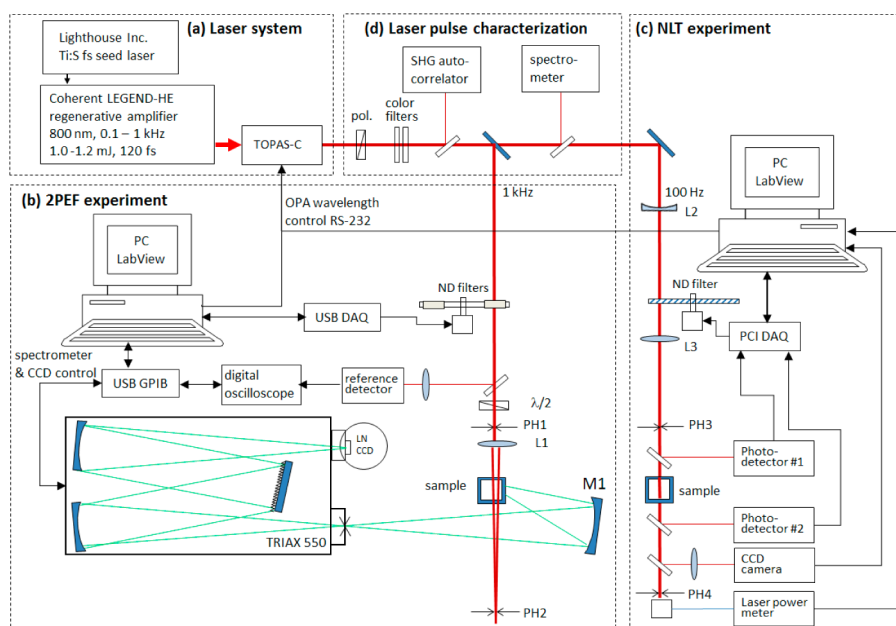


Figure 2. Experimental setup. (a) Laser system comprising femtosecond Ti:sapphire seed oscillator (Lighthouse Photonics), regenerative amplifier (Legend-HE, Coherent) and femtosecond TOPAS-C OPA (Light Conversion). (b) 2PEF experiment: PH1 and PH2, pinholes to guide the excitation beam; L1, focusing lens; M1, spherical mirror to collect the fluorescence. (c) NLT experiment: L2, diverging lens; L3, focusing lens; PH3 and PH4, pinholes to guide the excitation beam. (d) Laser pulse characterization system.

only ED or neutral substituents exhibit the 2PA spectra consistent with centrosymmetric or nearly centrosymmetric structure, whereas strong EW substituents lead to a complete breaking of the inversion symmetry. The resulting dipolar behavior of the EW-substituted complexes is clearly manifested in the appearance of the $S_0 \rightarrow S_1$ transition in the 2PA spectrum, large peak 2PA cross section values up to $\sigma_2 \sim 700$ GM, and large permanent electric dipole moment changes up to ~ 10 – 20 D, all corresponding to this transition. We present theoretical calculations indicating that this effect can be due to large twisting angle of the ligand's phenyl rings relative to the Pt core. Finally, we observe that NLT measurements performed at shorter wavelengths corresponding to 2PA transitions to higher-energy excited singlet states yield effective multiphoton absorption stronger than the 2PEF measurement in the same spectral range, which we tentatively attribute to femtosecond ESA involving even higher excited states.

The structures of the Pt complexes Pt-(FL-R)₂ and the corresponding ligand chromophores FL-R are shown in Figure 1. The compounds are named in boldface by their substituent, R. For example, the complex containing end-caps H is designated as Pt-(FL-H)₂ and the corresponding ligand is FL-H. Two model compounds, *trans*-bis(tributylphosphine) bis(phenylethynyl) platinum(II) PE1 and *trans*-bis(trioctylphosphine)bis(phenylethynyl) platinum(II) PE1', representing the Pt-core chromophore, are also shown. We note that PE1' has a glass-transition temperature $T_g = -91$ °C and that upon heating the supercooled liquid spontaneously crystallizes at -47 °C followed by melting at $T_m = -6$ °C.^{38,39} The low T_m allowed us to study this compound by NLT at room temperature as a neat liquid.

2. METHODS

2.1. Experimental Section. Synthesis of the Pt complexes and of the corresponding ligands, along with the techniques for measuring linear absorption spectra were described previously.³⁴ Our femtosecond laser setup used for 2PEF and NLT measurements

is shown in Figure 2. The system comprised a Ti:sapphire regenerative amplifier (Legend-HP, Coherent, Inc.) that was seeded by a Ti:sapphire femtosecond oscillator (Lighthouse Photonics, Inc.). The output of the amplifier (pulse energy, 1.1–1.2 mJ; pulse duration, ~ 120 fs; wavelength, $\lambda \sim 792$ nm) was used to pump an optical parametric amplifier (OPA; TOPAS-C, Light Conversion). The OPA wavelength was tuned in 2 nm steps in the range $\lambda_{\text{SHS}} = 540$ – 810 nm (second harmonic of signal) and $\lambda_{\text{SHI}} = 790$ – 950 nm (second harmonic of idler). The OPA output pulse energy was 20–30 μJ for λ_{SHS} and 5–10 μJ for λ_{SHI} . A linear polarizer along with a stack of color glass filters blocked residual wavelengths in the OPA output beam. A diffraction grating spectrometer (USB4000, Ocean Optics) was used to measure the OPA spectrum. The spectral bandwidth of the OPA output pulses varied in the range $\Delta\lambda = 15$ – 30 nm, depending on the wavelength. A second harmonic generation autocorrelator (AC-1, Clark MXR) was used to measure the temporal autocorrelation width of the pulses. Assuming sech^2 pulse shape, the pulse duration was 100–120 fs full-width at half max (fwhm). Data collection, including scanning of the OPA wavelength, was automated using the LabVIEW (National Instruments, Inc.) programming environment.

All samples were prepared in toluene solution in standard 1 cm spectroscopic cuvettes. The 2PEF measurements were performed at dye concentrations of $\sim 3.0 \times 10^{-5}$ M for the Pt complexes and $\sim 10^{-5}$ M for the ligands. The NLT measurements were performed at higher dye concentration, 0.7–7.0 $\times 10^{-3}$ M and 5.0–10 $\times 10^{-3}$ M for the Pt complexes and the ligands, respectively. The 2PEF experiments were performed at 1 kHz pulse repetition rate; for the NLT, the repetition rate was lowered to 100 Hz to reduce possible thermal effects.

The principle of the 2PEF measurement has been described previously⁴⁰ and consists in acquiring the 2PEF excitation spectrum and calibrating its shape and the absolute value relative to appropriately selected reference standards. Fluorescein in (pH 11) H₂O solution and Rhodamine B in methanol were used

to calibrate the 2PEF spectral shapes, and Coumarin 485 in methanol was used to determine absolute cross sections.

The principle of the NLT measurement was described in ref 30. Briefly, the OPA beam was passed through the sample and the transmittance T , defined as the ratio of the relative pulse energy after and before the sample was measured with two photodetectors (Photodetectors #1 and #2 in Figure 2, DET100A, Thorlabs) and a DAQ board (PCI-6110, National Instruments). The incident pulse energy on the sample was varied in the range $P_{in} = 0.2\text{--}20\ \mu\text{J}$ by using a PC-controlled continuously variable reflective ND filter (Thorlabs). A combination of positive and negative long focal length lenses ($f = 500\text{--}1500\ \text{mm}$) was used to adjust the beam spot size on the sample to about $w = 300\text{--}1000\ \mu\text{m}$. A digital CCD camera (Stingray, Allied) was used to monitor the spatial beam shape, and a laser energy meter (Nova II, Ophir) with pyroelectric probe (PE9-SH) was used to measure the pulse energy. The OPA wavelength was tuned in 2 nm steps in the range $\lambda_{SHS} = 540\text{--}810\ \text{nm}$. The intensity-dependent transmittance $T(P_{in})$ was measured at each wavelength and was fitted with a linear function. Total transmission changes were kept to $<10\%$ to ensure the validity of the linear fits. The NLT spectrum was obtained by plotting the negative slope as a function of the wavelength and by calibrating the result relative to the slope obtained in reference standard samples (Fluorescein in pH 11 H_2O) under the same excitation conditions.

2.2. Quantum Calculations. Calculations were carried out using Gaussian 09W, version 7.0.⁴¹ The chromophores were modeled as platinum(II) *trans*-bis(trimethylphosphine)-bis(4-((9,9-diethyl-7-ethynyl-9H-fluoren-2-yl)ethynyl)-R)-complexes. The basis set for all calculations was LANL2DZ for the platinum atom and 6-31G(d) for the other atoms. We performed density functional theory (DFT) energy minimizations for the ground state using the B3LYP functional. When we performed time-dependent density functional theory (TDDFT) calculations, the excited states of these chromophores were assumed to have charge-transfer character, so we used the long-range corrected version of B3LYP, coulomb-attenuating method (CAM-B3LYP).⁴² We included solvent effects by running ground-state energy minimization and TDDFT calculations with the polarizable continuum model.⁴³

3. RESULTS AND DISCUSSION

We start with the analysis of nonlinear spectra of the model core chromophores PE1 and PE1'. Because these systems exhibit very low fluorescence quantum yield, $\Phi < 0.6 \times 10^{-3}$,³⁸ using the 2PEF method is not practical. Figure 3 shows the NLT spectra in air-saturated toluene solution of PE1 at a concentration of 9.0 mM and PE1' as a neat liquid. In the last case the concentration was estimated to be $\sim 1.4\ \text{M}$ based on the density, and a 1 mm path-length spectroscopic quartz cuvette was used. Linear extinction of PE1 in toluene along with the experimental background signal obtained with blank sample is shown for comparison.

The molecules PE1 and PE1' differ only by the size of the peripheral groups, and their toluene solutions show nearly identical linear extinction spectra. Both PE1 and PE1' show a 2PA peak near 560 nm with the maximum value $\sigma_2 = 35\text{--}40\ \text{GM}$. This result agrees well with the previously calculated gas phase 2PA spectrum of PE1²² with maximum value 88 GM at 503 nm. The remaining discrepancy in the peak 2PA is most likely due to the fact that, according to the calculation,²² the molecule has different conformations exhibiting rather different peak 2PA cross sections, and the slightly higher $\sim 0.5\ \text{eV}$ theoretical 2PA

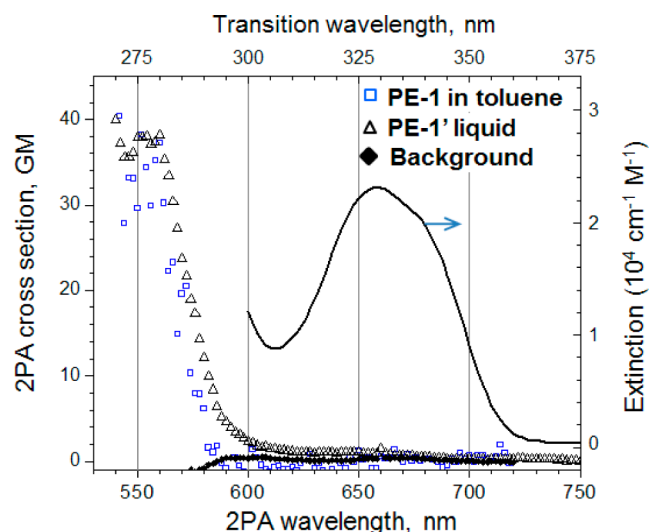


Figure 3. 2PA of model core Pt-chromophores PE1 in toluene (empty blue squares) and PE1' neat liquid (empty black triangles). The 1PA spectrum in toluene (solid line, top and right axes) and NLT of blank sample (filled black diamonds) are shown for comparison.

transition energy can likely be explained as due to interaction with the solvent.

Figure 4 shows the 2PA spectra of Pt-(FL-R)₂ complexes (right column) and the corresponding FL-R ligands (left column) in toluene solution. Red circles correspond to 2PEF measurement, and blue squares show NLT experimental data. The 1PA spectra are shown for comparison (solid line). The ligand 2PEF spectra were published previously³⁵ and are reproduced here for comparison.

The 2PA spectra may be divided into the longer- and shorter-wavelength regions, where the first corresponds roughly to the $S_0 \rightarrow S_1$ transition in the 1PA spectrum and the latter belongs to transitions to higher-energy states, denoted here as $S_0 \rightarrow S_n$. In the $S_0 \rightarrow S_1$ transition region, the spectral shapes and the cross-sectional values obtained by 2PEF and NLT method are both qualitatively and quantitatively similar. In the shorter-wavelength region, the NLT method gives similar band shapes yet the peak values are systematically higher. In part this discrepancy may be explained by low fluorescence yield of the Pt-(FL-R)₂ series compounds, which complicated the 2PEF measurements. However, the systematic increase of the NLT signal most likely has a distinct physical origin, as will be discussed below. For this reason, the NLT 2PA cross sections in the $S_0 \rightarrow S_n$ transition range are to be treated as effective values. Table 1 summarizes the peak 2PA cross sections and the corresponding wavelengths. In the $S_0 \rightarrow S_1$ range, the 2PA peak is obtained by a procedure described previously,³⁵ which consists of fitting the corresponding 1PA spectrum with a sum of Gaussians and using the shape of the longest-wavelength component to fit the lowest-energy transition in the 2PA spectrum. In addition, the NLT spectrum of Pt-(FL-R)₂ series in the $S_0 \rightarrow S_n$ transition range shows distinct peaks. The wavelengths of these peaks are indicated by arrows in Figure 4 and shown in Table 1, as λ_1 and λ_2 , along with the corresponding effective peak 2PA values.

Let us compare the 2PA spectra of the Pt complexes with the corresponding ligand chromophores. Initially, one may assume that if two identical FL-R chromophores are joined together into one conjugated and nominally centrosymmetric Pt-(FL-R)₂ structure, then that should decrease the 2PA in the lowest-energy $S_0 \rightarrow S_1$ transition, compared to twice the value in FL-R

taken separately. Such behavior is indeed manifest in case of $R = \text{NPh}_2$, where the peak σ_2 decreases from 60–90 GM in FL-NPh₂ to 30–70 GM in Pt-(FL-NPh₂)₂. At the same time, the peak 2PA in the higher-energy transition region experiences an increase from $\sigma_2 = 75$ GM in FL-NPh₂ to 320 GM in Pt-(FL-NPh₂)₂. The modest increase of the peak 2PA in the nominally quadrupolar systems is consistent with the notion that the Pt core acts as a weak ED unit. Absence of strong 1PA bands in the most 2PA-active spectral region is equally consistent with the alternate 1PA versus 2PA transition selection rule that is

characteristic of inversion symmetry. NH₂, along with other ED-active and neutral R, lead to the same kind of changes in the 2PA spectral shape, even though quantitatively the lowering of the 2PA in the $S_0 \rightarrow S_1$ transition is less evident. We conclude that ED- and neutral substituted Pt-(FL-R)₂ show features that are characteristic of expected quadrupolar structure.

EW-substituted Pt-(FL-R)₂ show 2PA spectra that are more consistent with dipolar chromophores. In particular, Pt-(FL-NO₂)₂ has the strongest 2PA in the 0–0 component of the $S_0 \rightarrow S_1$ transition, with a peak value $\sigma_2 = 700$ GM. Pt-(FL-BT)₂

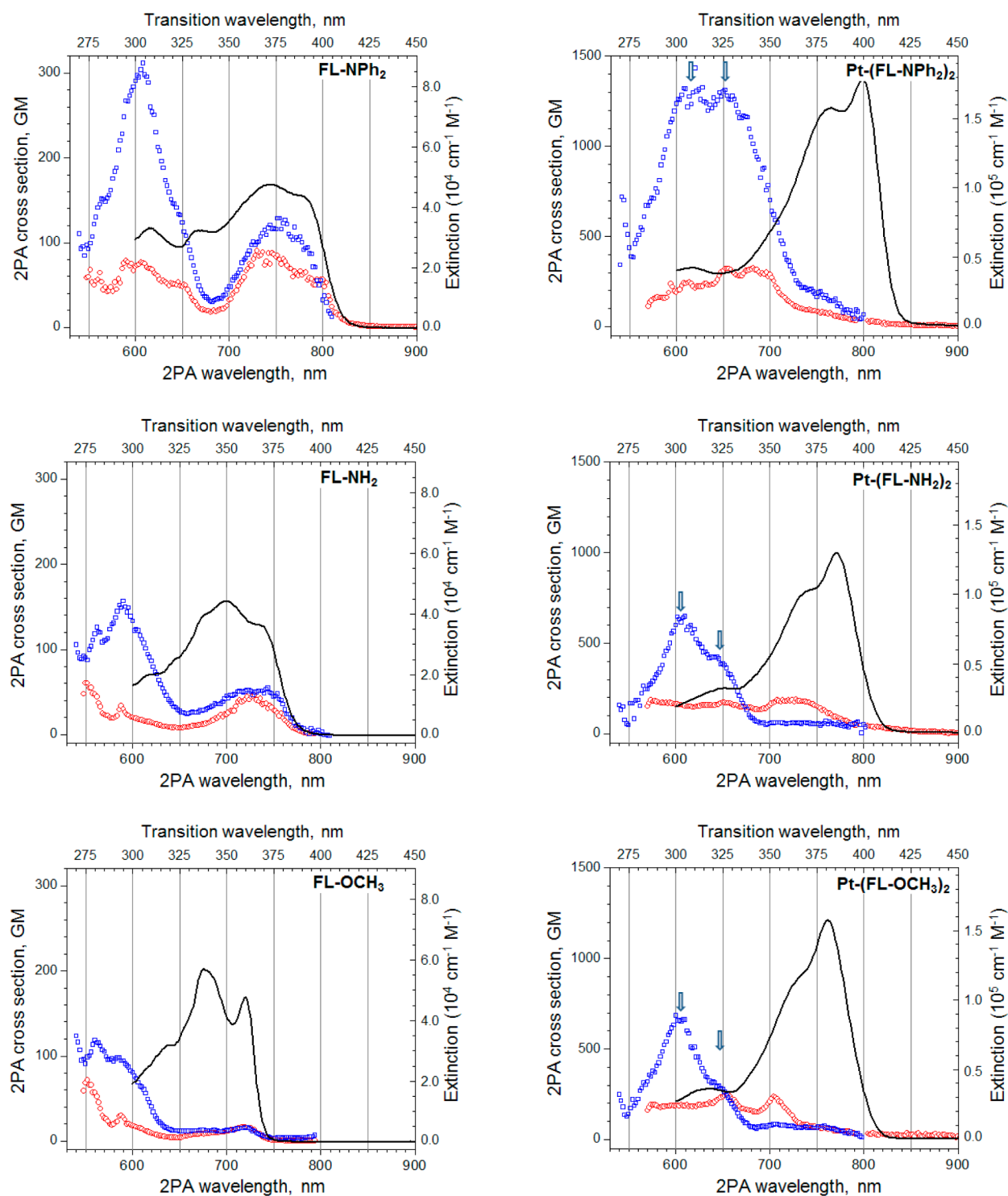


Figure 4. continued

and Pt-(FL-CN)₂ also show characteristic dipolar behavior. With this assumption in mind, we may try to gain better quantitative insight by evaluating the permanent electric dipole moment change of the S₀ → S₁ transition from the measured 2PA cross section according to the relation^{44–47}

$$\Delta\mu = \left(\frac{5}{12} \frac{hcN_A}{\pi 10^3 \ln 10} \frac{n}{f_{\text{opt}}^2} \frac{\nu_{\text{max}}(0-0)}{\epsilon_{\text{max}}(0-0)} \sigma_2(0-0) \right)^{1/2} \quad (1)$$

where $\nu_{\text{max}}(0-0)$ is the peak frequency of the 0–0 transition, ϵ_{max} the 0–0 peak extinction coefficient, $\sigma_2(0-0)$ the corresponding peak 2PA cross section, N_A the Avogadro number, f_{opt} the optical local field factor, and n the refractive index of the solvent. In eq 1 we assume that the direction of the permanent dipole moment difference vector is aligned parallel to the transition dipole moment vector. This seems to be a reasonable assumption for a quasilinear molecule. Table 2 summarizes the experimental $\Delta\mu$ values for Pt-(FL-R)₂ series in toluene solution. For ED and neutral R, the dipole change is in the range $\Delta\mu = 3.5\text{--}7.5$ D,

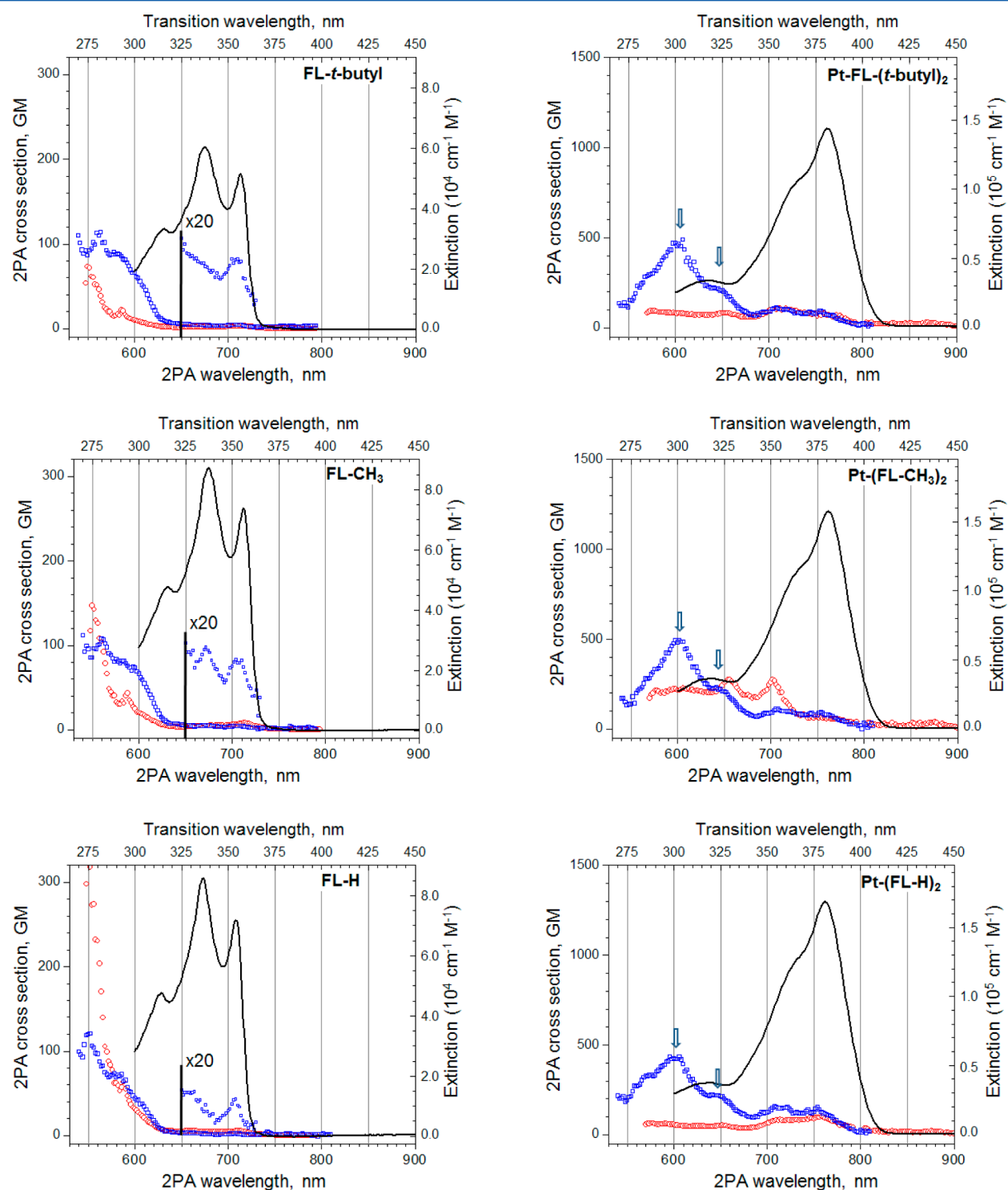


Figure 4. continued

but for the strongest EW groups, the value increases to $\Delta\mu = 12\text{--}25$ D.

One possible explanation for the large increase of the dipole moment difference and associated lowering of the intrinsic symmetry could be the solute–solvent interaction. Terenzi et al. used solvent-induced symmetry breaking to explain anomalously large solvent shifts in some nominally quadrupolar metal-free organic chromophores.⁴⁸ It was suggested that the large solvent shifts are due to an excited-state dipole moment that is generated after rearrangement of the solvent dipoles.⁴⁸ While

such solvent reorganization typically occurs on the time scale of the lifetime of the excited state, in our 2PA experiments we are probing strictly only the instantaneous (vertical) excited states (also, there has to be a dipole moment change to induce solvent reorientation). This suggests that the solvent is most likely not the main cause of the symmetry breaking in the Pt complexes.

Because previous studies indicated that platinum(II) acetylides may be quite flexible,^{22,49} we hypothesize that symmetry breaking in some Pt-(FL-R)₂ may be caused by facile conformational changes. Potential involved twisting degrees of

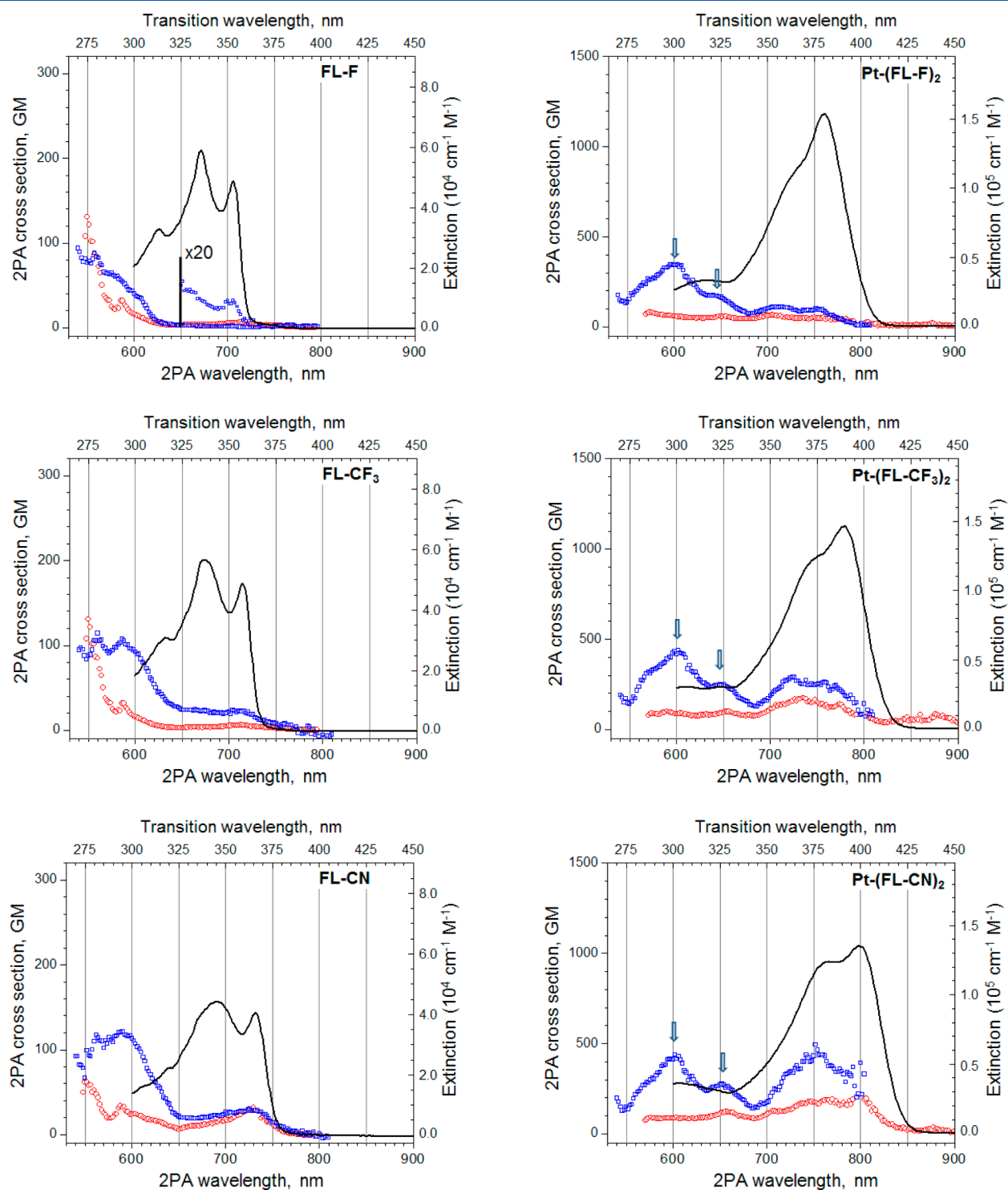


Figure 4. continued

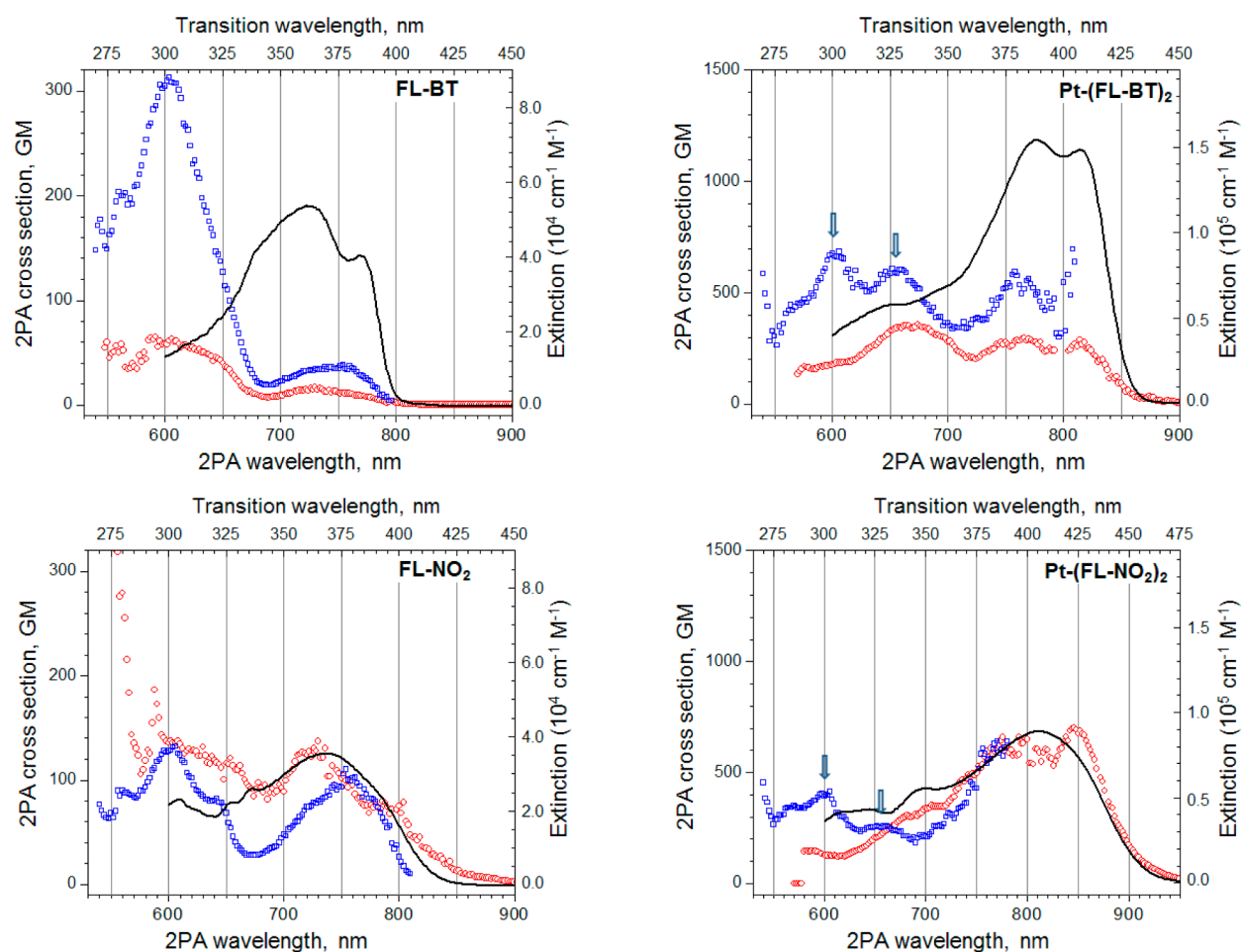


Figure 4. 2PA spectra (left vertical axis) of ligand chromophores (left column) and the corresponding Pt complexes (right column), as measured by 2PEF (red empty circles) and NLT (blue empty squares) methods. Bottom horizontal axes show 2PA laser wavelength. Upper horizontal axes show 1PA transition wavelength. 1PA spectra (black solid lines) are shown for comparison (right vertical axis). In the right column, the vertical arrows indicate the λ_1 and λ_2 peaks (see text for discussion).

Table 1. 2PA Properties of Pt-(FL-R)₂ and FL-R Obtained by 2PEF and NLT Measurements

R	FL-R						Pt-(FL-R) ₂							
	$\sigma_2 [S_0 \rightarrow S_1 (0-0)]$			$\sigma_2 [S_0 \rightarrow S_n]$			$\sigma_2 [S_0 \rightarrow S_1 (0-0)]$			$\sigma_2 [S_0 \rightarrow S_n]$				
	λ (nm)	2PEF (GM)	NLT (GM)	λ (nm)	2PEF (GM)	NLT ^a (GM)	λ (nm)	2PEF (GM)	NLT (GM)	λ_1 (nm)	2PEF (GM)	NLT ^a (GM)	λ_2 (nm)	NLT ^a (GM)
NPh ₂	784	63	94	608	76	310	810	33	67	618	320	1300	654	1300
NH ₂	742	18	53	590	30	160	782	93	51	602	160	650	644	420
OCH ₃	722	16	16	560	57	120	774	57	66	604	190	660	646	300
<i>t</i> -butyl	714	3.3	3.9	560	51	110	772	73	72	600	84	470	646	220
CH ₃	712	7.5	3.7	560	100	110	774	61	81	602	220	490	642	230
H	710	5.2	1.8	562	200	120	774	92	120	600	52	420	644	220
F	706	5.9	1.6	560	85	85	772	53	89	600	60	340	644	170
CF ₃	714	6.4	22	586	31	110	792	120	210	602	87	440	650	250
CN	732	29	28	590	32	120	814	190	350	602	88	440	652	280
BT	772	8.1	27	604	58	310	826	270	580	600	180	680	658	610
NO ₂	782	—	74	604	140	130	862	700	—	602	53	400	658	260

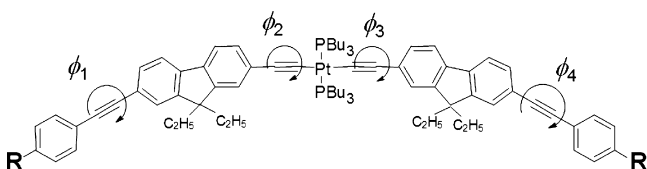
^aEffective 2PA cross section value, σ_2

freedom are shown in Figure 5. To verify this hypothesis, we calculated the dipole moment difference between the S_0 and S_1 states $\Delta\mu$ for different relative rotation angles ϕ_n ($n = 1, 2, 3, 4$). The calculated values, along with corresponding permanent dipole moments, are shown in Table 2. In the planar conformation ($\phi_1 = \phi_2 = \phi_3 = \phi_4 = 0^\circ$) all dipoles are vanishingly small, independent of R. Rotation of 90° of both terminal phenyls and

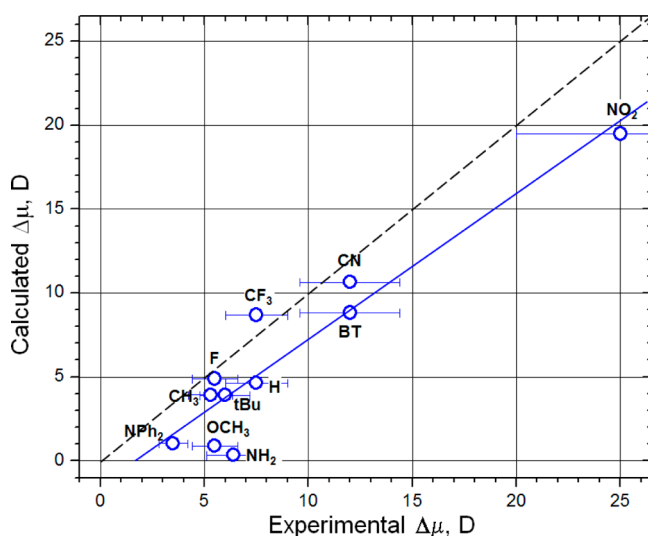
one of the fluorine groups ($\phi_1 = \phi_2 = \phi_4 = 90^\circ$; $\phi_3 = 0^\circ$) leads to a slight increase of the dipole change, $\Delta\mu < 2 D$, which is still small compared to the experiment. However, if only one phenyl is twisted perpendicular relative to the rest of the chromophore ($\phi_1 = \phi_2 = \phi_3 = 0^\circ$; $\phi_4 = 90^\circ$), then the dipole moment difference increases substantially and becomes comparable to the experimental values. Most importantly, the twisting has a much larger

Table 2. Experimentally Measured and Theoretically Calculated Dipole Moments and Dipole Moment Differences in the S_0 – S_1 Transition of Pt-(FL-R) $_2$ Complexes

	exptl	calcd in vacuum $\phi_1 = \phi_2 = \phi_4 = 90^\circ$			calcd in vacuum $\phi_1 = \phi_2 = \phi_3 = 0^\circ, \phi_4 = 90^\circ$			calcd in toluene $\phi_1 = \phi_2 = \phi_3 = 0^\circ, \phi_4 = 90^\circ$		
	$\Delta\mu$ (D)	μ_0 (D)	μ_1 (D)	$\Delta\mu$ (D)	μ_0 (D)	μ_1 (D)	$\Delta\mu$ (D)	μ_0 (D)	μ_1 (D)	$\Delta\mu$ (D)
NPh ₂	3.5	0.7	1.7	1.1	0.07	1.1	1.0	0.11	2.5	2.4
NH ₂	6.4	1.8	2.2	0.4	0.31	0.7	0.35	1.7	2.0	0.31
OCH ₃	5.5	1.1	2.4	1.3	1.9	2.80	0.89	2.0	2.6	0.55
<i>t</i> -butyl	6	0.7	1.7	1.1	0.04	4.0	3.9	0.04	3.8	3.8
CH ₃	5.3	0.7	2.0	1.3	0.06	4.0	3.9	0.05	3.8	3.8
H	7.5	0.7	2.0	1.4	0.08	4.7	4.6	0.07	5.0	4.9
F	5.5	0.4	2.1	1.7	0.06	5.0	4.9	0.02	4.4	4.4
CF ₃	7.5	1.9	3.6	1.8	0.43	9.1	8.7	0.32	8.0	7.7
CN	12	2.6	4.4	1.7	0.46	11	10.7	0.42	11	11
BT	12	0.5	2.2	1.8	0.66	9.5	8.8	1.2	9.1	8.0
NO ₂	25	3.0	2.9	0	0.67	20	19	1.0	18	17

**Figure 5.** Degrees of freedom corresponding to relative twisting in Pt-(FL-R) $_2$. ϕ_i ($i = 1, 2, 3, 4$): angles of rotation around one of the single bonds adjacent to triple bond.

effect in EW-substituted complexes and much less in the case of neutral and ED substituents. The calculation gives a quantitatively comparable result independent of whether the molecules are assumed to be in vacuum or if they are in solvent (toluene). Both vacuum and solvent results are shown in Table 2. Figure 6 correlates experimental and calculated (vacuum) $\Delta\mu$

**Figure 6.** Experimental (horizontal axis) and calculated vacuum (vertical axis) $\Delta\mu$ values for the lowest electronic transition of Pt complexes. Linear fit is shown with solid line. Dashed line corresponds to exact correlation.

values. Good correlation indicates that a twist around just one bond may be responsible for already introducing enough distortion to break quasi-inversion symmetry. Other conformations not considered here may be also contributing to dipolar behavior of Pt complexes with EW ligands. Our calculations, as well as

earlier results by Nguyen et al.,²² indicate that the energy difference between ground-state conformations may be rather small, $\Delta E = 0.3$ – 1.7 kcal mol⁻¹. This means that $\Delta\mu$ observed in the experiment is most likely an average over many different conformations present simultaneously.

Finally, we discuss the results shown in Figure 4, regarding the fact that in the $S_0 \rightarrow S_n$ transition region the NLT method gives effective 2PA values that are larger than those obtained by the 2PEF method. One possibility explaining this effect may be the strong simultaneous three-photon absorption (3PA) in platinum acetylide complexes,⁴⁹ which showed large 3PA cross sections, $\sigma_3 \sim 10^{-78}$ cm⁶ s².⁴⁹ However, instantaneous 3PA is most likely not a significant factor in our measurement because in order to match the enhancement of the NLT in our experimental conditions, the corresponding 3PA cross section should have a very large value, $\sigma_3 \sim 10^{-76}$ cm⁶ s². Furthermore, in our experiment, the transmission decreased linearly (within measurement accuracy) with increasing incident pulse energy, whereas in the case of 3PA the dependence is distinctly nonlinear (quadratic). Therefore, we assume that the enhanced NLT is most likely related to noninstantaneous transitions to higher excited states, where additional photons are absorbed from the same femto-second excitation pulse following the 2PA. One may argue, however, that even if the ESA occurs from a real intermediate state, then such a stepwise process should also lead to higher-than-linear intensity dependence. On the other hand, if the ESA responsible for the absorption of additional photons is saturated, then that could again manifest as a nearly linear dependence of the NLT signal on the pulse energy. We estimate that if the lifetime of higher excited states is comparable to or longer than the duration of the excitation pulse, then under our experimental conditions the ESA transition is at 50% of maximum saturation level if the absorption cross sections is $\sigma_{\text{ESA}} = 1.5 \times 10^{-16}$ cm². This value agrees well with the first singlet excited-state absorption cross section in Pt 2,2'-bipyridine complex determined by picosecond Z-scan method.²⁶ Indeed, Zhou et al. showed for similarly structured Pt(II) bis(aryleneethynylene)s that, in agreement with our results, the ESA strength decreased as the terminal moieties were varied from ED to EW character.^{23,29} Some further confirmation may also be obtained by comparison to our earlier femtosecond pump–probe ESA study,³⁴ which showed that the Pt-(FL-R) $_2$ series displays upon excitation with 400 nm, 100 fs pump pulse a strong transient absorption with a broad spectral peak varying from 570 to 645 nm. If the intrinsic 2PA spectrum $\sigma_2(\lambda)$ contains some features due to distinct $S_0 \rightarrow S_n$ transitions, then the same features will be

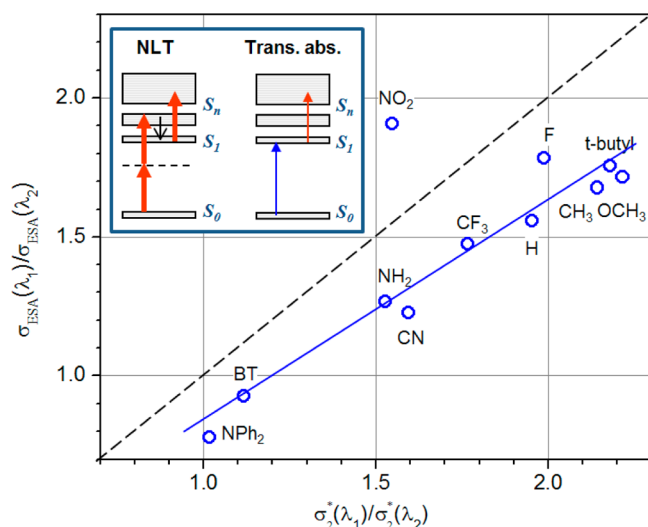


Figure 7. Correlation between relative NLT and relative ESA (data from ref 34) in Pt-(FL-R)₂. Solid line is linear fit (excluding NO₂). Dashed line corresponds to exact correlation. Inset shows tentative excitation pathways involved in NLT, compared to ESA measurement.

manifest in the NLT spectrum. To show such correlation between our NLT spectra and the earlier ESA measurement, we plot in Figure 7 the ratio $\sigma_2^*(\lambda_1)/\sigma_2^*(\lambda_2)$ versus the similar ratio derived from the pump–probe spectra. The figure inset illustrates the tentative excitation pathways involved in the NLT as compared to that in the ESA measurement. Figure 7 shows that both the wavelengths and the relative shape of the NLT spectra match previous ESA measurement.

4. SUMMARY AND CONCLUSIONS

We describe femtosecond two-photon absorption measurements in a series of platinum acetylide complexes Pt-(FL-R)₂ and corresponding ligands FL-R, substituted with systematically varying ED or EW end groups R. The 2PA spectra were measured in toluene solution in a broad spectral range, 540–810 nm, using two complementary methods: (i) two-photon excited fluorescence (2PEF) and (ii) nonlinear transmission (NLT). In the $S_0 \rightarrow S_1$ transition region, both methods give comparable 2PA spectra and cross sections, whereas in the region of higher-energy transitions $S_0 \rightarrow S_n$, the NLT method gives systematically higher values, likely due to absorption of additional photons from excited states. In the $S_0 \rightarrow S_1$ region, the peak 2PA cross sections of FL-R are consistent with their dipolar structure, and vary from $\sigma_2 \sim 2\text{--}6$ GM for the neutral substituents R = H, F to the maximum value $\sigma_2 \sim 70\text{--}90$ GM for the strongest ED and EW substituents, R = NPh₂, NO₂. In contrast, nominally centrosymmetric Pt-(FL-R)₂ demonstrate a dual behavior. The ED and neutral substitutions lead to the expected quadrupolar-like 2PA spectral shapes, whereas the higher-energy transitions $S_0 \rightarrow S_n$ dominate, with 2PEF peak values up to $\sigma_2 \sim 300$ GM for R = NPh₂. Surprisingly, EW substitutions result in distinctly dipolar 2PA spectral shapes, with Pt-(FL-NO₂)₂ showing the highest peak value $\sigma_2 = 700$ GM corresponding to the 0–0 component of the $S_0 \rightarrow S_1$ transition. We theoretically calculate the change of permanent electric dipole moments in $S_0 \rightarrow S_1$ transition and compare them to experimental values obtained from 2PA measurements using a two-level model. We find that in a certain conformation, where one of the phenyls is twisted 90° relative to the rest of the planar chromophore, the calculated values correlate well with those found in the experiment, which in the

case of Pt-(FL-NO₂)₂ are $\Delta\mu = 19$ and 25 D, respectively. We draw a tentative conclusion that breaking of inversion symmetry by conformational changes in the ground state are likely involved in giving rise to the dipolar behavior of Pt-(FL-R)₂ with strong EW ligands, even though further investigations are needed to elucidate the role of different conformations with similar ground-state energies. Further NLT experiments are also needed to investigate the enhanced excited-state absorption effect.

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Notes

The authors declare no competing financial interest.

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