Quadratic and Cubic Optical Nonlinearities of Y-Shaped and Distorted-H-Shaped Arylalkynylruthenium Complexes**

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Abstract: Straightforward syntheses of bis[bis{1,2bis(diphenylphosphino)ethane}ruthenium]-functionalized 1,3,5triethynylbenzene-cored complexes via a methodology employing "steric control" permit facile formation of Y-shaped Sonogashira coupling products and distorted-H-shaped homo-coupled guadrupolar products. Cvclic voltammetric data from these products reveal two reversible metal alkynyl-localized oxidation processes for all complexes. The wavelengths of the linear optical absorption maxima are dominated by the nature of the peripheral alkynyl ligand rather than the substituent at the unique arm of the "Y" or at the quadrupolar complex "core". The quadratic optical nonlinearities of the Y-shaped complexes were assessed by the hyper-Rayleigh scattering technique at 800 nm and employing 100 fs light pulses; introduction of donor NEt₂ and/or acceptor NO₂ to the wedge periphery resulted in non-zero nonlinearities, with the largest $\beta_{\text{HRS},800}$ values being observed for the complexes containing the 4-nitrophenylalkynyl ligands. Depolarization ratios are consistent with substantial offdiagonal first hyperpolarizability tensor components and 2D nonlinear character. Computational studies employing time-dependent density functional theory have been employed to assign the key low-energy transitions in the linear optical spectra and to compute the quadratic nonlinear optical tensorial components. Cubic optical nonlinearities of the quadrupolar complexes were assessed by the Z-scan technique

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over the range 500-1600 nm and employing 130 fs light pulses; twophoton absorption cross-sections for these distorted-H-shaped complexes are moderate to large in value (up to 5500 GM at 880 nm), while one example displays significant three-photon absorption (1300 x 10^{-80} cm⁶ s² at 1200 nm).

Introduction

The continuing interest in nonlinear optical (NLO) materials that can modify the propagation characteristics of light (e.g. phase, frequency, path, etc.) has resulted in studies of a diverse array of molecules, both organic and inorganic in composition.^[1] The NLO efficiencies displayed by certain organic molecules and coordination complexes have demonstrated that both the purely organic and the transition metal coordination complex environment can promote desirable NLO behavior. Not surprisingly, therefore, organometallic complexes, pairing organic moieties with ligated metal centres, have also come under scrutiny as potential NLO materials.^[2] Amongst the panoply of organometallic complexes, extensive studies have identified metallocenyl and metal alkynyl complexes as exhibiting the potentially useful combination of strong NLO efficiencies and sufficient stability to withstand the processing conditions and environmental exposure that is needed in putative applications (see, for example, reference [3]). However, the key metal-tocyclopentadienyl charge-transfer interaction in metallocenyl complexes is orthogonal to the π -system of the cyclopentadienyl substituent organic chromophore, which may deleteriously impact NLO merit.^[4] In contrast, alkynyl complexes contain metal atoms located in the plane of the π -system of the alkynyl ligands, a potentially more favorable location for influencing π -electrondependent phenomena such as molecular NLO properties. Metal alkynyl complexes have consequently attracted considerable attention, with certain examples displaying record or near-record values of key molecular NLO coefficients (see, for example, references [5]).

The majority of studies exploring the NLO properties of molecules have focused on linear or quasi-linear dipolar examples with a donor- π -bridge-acceptor composition, and this is also true of organometallic NLO-active complexes. Nevertheless, pioneering work has revealed the potential of compounds with other multipolar charge distributions such as quadrupoles or octupoles (see, for example, references [6]), which prompted us to explore the NLO potential of metal alkynyl complexes with unusual charge distributions. We report herein studies directed towards this goal, with specific targets including unusual "Y-shaped" and "distorted-H-shaped" complexes. The syntheses of



Scheme 1. Preparation of **2c-e** and **3a-m**. Complexes **2a,b** were prepared using NH₄PF₆ instead of NaPF₆ and have been reported elsewhere.^[7] [Ru] = *trans*-Ru(dppe)₂.

the target compounds exploit an unusual "steric control" methodology to rapidly afford key intermediates.^[7] We report comprehensive studies of linear optical and cyclic voltammetric behavior, quadratic NLO studies of the Y-shaped complexes employing the hyper-Rayleigh scattering technique, and cubic NLO studies of the formally quadrupolar distorted H-shaped complexes utilizing the Z-scan technique. Computational studies of models of the Y-shaped complexes have also been undertaken within the framework of time-dependent density functional theory (TD-DFT) to shed light on the experimental linear optical and quadratic NLO behavior.

Results and Discussion

Synthesis and Characterization. The target Y-shaped complexes and branched quadrupolar H-shaped complexes were synthesized via the intermediacy of key diruthenium "wedge" complexes. The new alkynyl wedge complexes **2c-e**, the Y-shaped complexes **3a-m**, and the quadrupolar distorted-H-shaped complexes **4**, **5a-c** and **6a-b** were prepared as shown in Schemes 1 and 2. We have previously described the "steric control" reaction of 1,3,5-triethynylbenzene with excess *cis*-[RuCl₂(dppe)₂]^[8] that proceeds to afford the bis-metallated product 1,3-{*trans*-[(dppe)₂ClRuC=C]}₂-5-HC=CC₆H₃ (**1**), the steric bulk of the [Ru(dppe)₂] unit precluding formation of a trismetallated derivative.^[7] Complex **1** features the 1,3,5-C₆H₃A₂B "wedge" composition that is the prototypical branching unit in

 π -delocalizable dendrimers, and we have used **1** to construct homometallic^[5b, 7b, 9] and heterometallic examples.^[10] The present studies show that complex 1 can also serve as precursor to Yshaped dipolar complexes (Scheme 1) and distorted-H-shaped quadrupolar complexes (Scheme 2). Reactions of 1 with phenylacetylene or 4-nitrophenylacetylene have been shown to afford $1,3-\{trans-[(dppe)_2(4-RC_6H_4C=C)RuC=C]\}_2-5-C_6H_3C=CH$ $(R = H 2a, R = NO_2 2b)$, the ethynyl group in 1 being sterically shielded from reaction at a further ruthenium center.^[7b] Similar reactions with other 4-aryl functionalized phenylacetylenes 4- $HC=CC_6H_4R$ (R = NEt₂, C=CPh, C=C-4-C₆H₄NO₂) afforded the new wedge complexes 2c-e in 60 - 79% yields (Scheme 1). Although the ethynyl group in 2a-e is sterically protected from reaction with Ru(dppe)₂ units, it can accommodate a palladium center and thereby undergo Pd-catalyzed C-C coupling. Thus, Sonogashira coupling of 2a-e with iodobenzene and 4-substituted analogues gave the Y-shaped complexes 3a-i in 41 - 81% yields. Complexes 3h-i contain pendant trimethylsilylethynyl groups and undergo smooth desilvlation on reaction with NBuⁿ₄F to give the ethynyl derivatives 3k-m in yields of around 80% in each case. Complexes 1. 2a-c and 3I-m contain ethynyl functionalities that undergo homocoupling under standard Hay coupling conditions to give the quadrupolar complexes 4, 5a-c and 6a-b (Scheme 2), respectively, in 47 - 90% yields.

The new complexes (2c-e, 3a-m, 4, 5a-c, 6a-b) were characterized using a combination of IR, ¹H and ³¹P NMR, and UV-vis spectroscopies, and ESI mass spectrometry. The IR spectra contain characteristic v(C=C) bands at 2059 - 2046 cm⁻¹, with the lower energy bands corresponding to complexes with a 4-nitrophenylethynyl unit directly attached to the metal centers. The ³¹P NMR spectra contain singlets, consistent with *trans*-ligated metal centers, in the narrow range of 54.4 - 54.7 ppm, with the notable exception of 5b (53.4 ppm). The ESI mass spectra contain molecular ions (2c, 3b, 3c, 3e, 3g-h, 3k, 6c), sodium adducts of molecular ions (2d-e, 3a, 3d-e, 3i-j), or a dication (3f). The UV-vis spectra (Table 1) feature maxima at long wavelengths whose location depends on the peripheral ethynyl ligand. Phenylethynyl, 4-tolylethynyl and 4-diethylaminophenylethynyl



Scheme 2. Preparation of **4,5a-c** and **6a-b**. [Ru] = *trans*-[Ru(dppe)₂], TMEDA = 1,2-bis(dimethylamino)ethane.

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Table 1. Cyclic voltammetric and UV-vis data.^a

	Compo	ound R	R'	$E_{1/2}Ru^{\text{II/III}}V$ ($\DeltaE_{c})$	E _{1/2} NO ₂ (V)	λ_{max} nm (ϵ 10 ⁴ M ⁻¹ cm ⁻¹)
	1 ^{b,c}	-	-	0.53, 0.72 (0.19)	-	334 (3.8) (thf)
	2a ^{b,c}	н	-	0.47, 0.60 (0.13)		335 (8.0) (thf)
R _Y → H → A	2b ^c	NO ₂	-	0.67, 0.81 (0.14)	-1.10	475 (4.8) (thf)
[Ru] [Ru]	2c	NEt ₂	-	0.20, 0.74 (0.54)	•	339 (10.7)
2a-e	2d	C≡CPh	-	0.54, 0.65 (0.11)	-	385 (12.5)
	2e	$4-C=CC_6H_4NO_2$	-	0.55, 0.64 (0.11)	-0.92	466 (7.6)
(Bu) (Du)	3a	Н	н	0.48, 0.63 (0.15)	-	338 (7.8), 378 (sh, 1.5)
3a-m	3b	Н	NO ₂	0.53, 0.66 (0.14)	-0.91	342 (15.), 443 (sh, 0.4)
	3c	Н	Me	0.53 br (-)	-	331 (5.5), 388 (sh, 0.4)
	3d	NO ₂	н	0.64, 0.79 (0.15)	-1.16	329 (5.8), 488 (4.0)
[Hu] [Hu]	3e	NO ₂	NO ₂	0.63, 0.75 (0.12)	-0.91, -1.08	336 (4.3), 485 (2.6)
4	3f	NEt ₂	н	0.21, 0.74 (0.52)		336 (6.2), 387 (sh, 0.9)
	3g	NEt ₂	NO ₂	0.25, 0.76 (0.49)	-0.92	342 (11.6)
 R	3h	н	C≡CSiMe₃	0.49, 0.61 (0.12)	-	335 (9.5) (thf)
	3i	C≡CPh	C≡CSiMe₃	0.54, 0.65 (0.11)	-	383 (14.1)
[Ru] [Ru]	3j	4-C≡CC ₆ H ₄ NO ₂	C≡CSiMe₃	0.57, 0.69 (0.10)	-0.87	464 (8.3)
5 a-c	3k ^b	н	C≡CH	0.50, 0.62 (0.12)	-	330 (9.9) (thf)
[Ru] [Ru]	31	C≡CPh	C≡CH	0.52, 0.65 (0.13)	-	383 (16.1)
R R	3m	4-C≡CC ₆ H ₄ NO ₂	C≡CH	0.53, 0.65 (0.12)	-0.94	464 (9.8)
R R	3n °	NO ₂	C≡CH	0.68, 0.81 (0.11)	-1.08	474 (4.1) (thf)
	4			0.47. 0.63 (0.15)	-	335 (13.9)
	5a ^b	H		0.50, 0.62 (0.12)	_	335 (14 1) (thf)
[Ru] [Ru]	5b	NO ₂		0.67, 0.77 (0.10)	-1 12	342 (12.2) 481 (8.1)
	5c	NEt ₂		0.75, 0.26 (0.49)	-	342 (16.2)
Ŕ R	6a	C≡CPh	-	0.53, 0.67 (0.13)	-	367 (18.8)
	6b	4-C≡CC ₆ H₄NO ₂	-	0.57. 0.69 (0.12)	-0.92	462 (4.2)
				,		× /

[a] Voltammetric measurements were carried out in CH₂Cl₂ using the ferrocene/ferrocenium couple (located at 0.56 V) as the internal reference; UV-vis were measured as CH₂Cl₂ solutions unless otherwise noted. [Ru] = *trans*-Ru(dppe)₂. [b] Reference ^[7b].

complexes have maxima at 330-342 nm (**2c**, **3a-c**, **3f**, **3h**, **3k**, **5a**, **5c**), those with 4-phenylethynylphenylethynyl ligands (and thereby a more extended π -system) have maxima at 367-385 nm (**2d**, **3i**, **3l**, **6a**), while complexes with 4-nitrophenylethynyl ligands (incorporating the strongly electron-withdrawing nitro substituent) have maxima at much longer wavelengths, 474-488 nm (**2b**, **3d-e**, **3n**, **5b**); the effect of the nitro substituent is attenuated in proceeding to complexes with a longer π -system, the 4-nitrophenylethynyl-4-phenylethynyl complexes displaying maxima at 462-466 nm (**2e**, **3j**, **3m**, **6b**). These observations are consistent with the low-energy bands being primarily MLCT (to the alkynyl ligand) in character.

Cyclic voltammetric data are listed in Table 1. Note that in Table 1 and in the following discussion, the oxidation processes

are listed as Ru^{II/III}; we emphasize that this is a convenient description, but that rather than being strongly localized at the metal, the HOMO is instead delocalized over the adjacent ethynyl group with contributions from the contiguous ligands, and the reader should bear this in mind in the subsequent discussion. Due to the fact that such "metal-centered" oxidation processes in complexes of this type are usually fully reversible, the electrochemical properties of a large number of bis(bidentate diphosphine)ruthenium alkynyl complexes have been studied,^{17b, 9b, 12b, d, e, 13}] All complexes from the present study display two reversible oxidation processes, assigned to sequential Ru^{II/III} events at the ruthenium atoms separated by the 1,3-diethynylarene units. Differences in the potentials for the two

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processes of ca. 0.1 - 0.2 V are seen for all complexes except those containing the 4-diethylaminophenylethynyl groups, for which the potential differences are significantly larger (0.49 - 0.54 V).

Quadratic Nonlinear Optical Studies. Before proceeding to discuss the results of the second-order NLO studies (Table 2), it is useful to examine the composition of the Y-shaped complexes, which can be considered to possess three 'internal dipole components' of the total dipole, two formed by the arms terminated with R and with a ca. 120° angle between them, while the third is the dipole along the major axis of the molecule, in the same direction as the total dipole. The two dipoles due to the Rterminated arms may be deconvoluted into components orthogonal to the C2 axis of the molecule (which cancel each other out) and components along the C2 axis (which are additive and which contribute to the overall molecular dipole) (note that these axes are defined as the x and z axes, respectively, in the computational studies - see Figure in Table 2). The molecular dipole is also influenced by the group in the R' position: for example, the electron withdrawing 4-nitrophenyl group increases the magnitude of the dipole, while the phenyl and tolyl groups have less of an effect. The largest molecular dipoles are expected from compounds where R and R' have the greatest electrondonating and withdrawing character, respectively. Depending upon the nature of the excited-state dipole moments, these larger ground-state dipole moments can potentially lead to larger values of B.

Quadratic optical nonlinearities were assessed by the HRS technique at 800 nm employing ca. 100 fs pulses (Table 2). The complexes lacking polarizing substituents (3a,c) did not display measurable HRS activity. Introduction of a strongly electronwithdrawing nitro group at the unique arm of the "Y", on proceeding to 3b (and thereby affording a significant molecular dipole along the C₂ axis), resulted in a $\beta_{\text{HRS},800}$ value of (112 ± 10) x 10⁻³⁰ esu, whereas introducing nitro groups at the rutheniumcontaining arms, on proceeding to 3e (and thereby with a molecular dipole in the reverse direction), afforded a significantly higher $\beta_{\text{HRS},800}$ response (221 \pm 35 x 10⁻³⁰ esu). Introduction of nitro groups at all three peripheral sites (on proceeding to 3d, and thereby partially cancelling the dipolar contributions) resulted in a diminished, but still significant, HRS activity; the observed nonlinearity is consistent with the *p*-nitrophenylalkynylruthenium units being the predominant contributors to quadratic NLO activity in these complexes. Replacing the nitro substituents on the ruthenium-containing arms by diethylamino groups (proceeding from 3e to 3g) resulted in a significant reduction in optical nonlinearity, although 3g is substantially more transparent than 3e. Undertaking the same compositional modification, on proceeding from 3d to 3f, affords the most strongly dipolar molecule in the present study and resulted in a small increase in quadratic nonlinearity that is within the error margins of the experiment, but it is noteworthy that 3f is significantly less efficient than **3e**. We conclude from these data that the strong $Ru \rightarrow NO_2$ charge transfer in 3d and 3e is the key contributor to quadratic NLO merit in these complexes.

Computational Studies. Density functional theory (DFT) and time-dependent density functional theory (TD-DFT) calculations were then undertaken, to shed further light on the linear optical and quadratic nonlinear optical properties of the Y-shaped complexes. Our calculations employed the model complexes 3a'g', which possess the same structures as 3a-g, but with H₂PCH₂CH₂PH₂ ligands instead of the experimental dppe ligands (Figure 1 (top)). Table 3 shows the calculated UV-vis results corresponding to the main transitions in the low-energy region of the spectra. Note that the TD-DFT data suggest that the experimental low-energy UV-vis spectral band(s) of all complexes comprise several intense excitations; however, to simplify the analysis only a few transitions from the TD-PBE1PBE data are discussed below. Isodensity plots of frontier molecular orbitals (FMOs) involved in the main transitions are shown in Figure S1. Energy levels of the molecular orbitals are displayed in Figure S2.

The introduction of the strongly electron-accepting NO₂ group, on proceeding from **3a'** (R = R' = H) to **3b'** (R = H, $R' = NO_2$), results in a red-shift in the low-energy transitions (Table 3), consistent with a significant contribution of the nitro group to the LUMO (Figure S1), and the stabilization of the LUMO following nitration (Figure S2). Replacing H with the weakly electrondonating methyl group, on proceeding from **3a'** (R = R' = H) to **3c'** (R = H, R' = Me), has a minor effect on the low-energy optical behaviour; it seems that the contribution of the Me group to the low-lying CT processes is also moderate (Figure S1). Replacing



Comp	olex ^b	R R′	λmax (nm)	βhrs °	σ		
3a	н	н	338	no signal	no signal		
3b	н	NO ₂	342	112 ± 10	2.63 ± 0.04		
3c	н	Ме	331	no signal	no signal		
3d	NO_2	NO ₂	485	135 ± 25	2.13 ± 0.07		
3e	NO ₂	Н	488	221 ± 35	2.64 ± 0.04		
3f	NEt ₂	NO ₂	342	48 ± 14	2.49 ± 0.08		
3g	NEt ₂	н	336	91 ± 5	2.29 ± 0.05		

[a] Measured in CH₂Cl₂; reference β_{XXX} (crystal violet) = 338 x 10⁻³⁰ esu in MeOH. Local field correction factors have been used to correct for solvent differences; no interfering multi-photon fluorescence has been observed. β values are analyzed as β_{HRS} , independent of the molecular symmetry. Depolarization ratios σ indicate that the molecular structures cannot be analyzed as purely dipolar or octupolar in nature. x and z axis defined for computational studies. [b] [Ru] = *trans*-Ru(dppe)_2. [c] 10⁻³⁰ esu.

the H atoms with the strongly electron accepting NO₂ groups, in moving from **3a'** (R = R' = H) to **3d'** (R = NO₂, R' = H), results in a substantial red-shift in the lowest-energy band. For **3d'**, the composition of the LUMO+1 (Figure S1), the acceptor orbital involved in the lowest-energy transition, confirms the significant contributions of the nitro groups to the transition.

Conceptually nitrating the third terminal phenyl group, on proceeding from **3d'** to **3e'**, has a minor effect on the lowestenergy band position and character (Table 3 and Figure S1). The LUMO of **3e'** is stabilized due to the nitration and comprised largely of the π -system of the 4-nitrophenyl group in the on- C_2 axis arm, while the LUMO of **3d'** is primarily the nitrophenyl groups of the off- C_2 -axis arms. Increasing the acceptor strength of the on- C_2 -axis arm leads to a sharp reduction in the LUMO energy. Replacing the terminal Hs in going from **3a'** (R = R' = H)



Figure 1. Model complexes used in the DFT study (top). Diagonal (center) and off-diagonal (bottom) tensors calculated using the CPKS scheme and a three-level model (TLM). Values in 10^{-30} esu.

to **3f'** ($R = NEt_2$, R' = H) does not lead to a dramatic change in the observed or calculated optical properties. The experimental spectral band for **3f** (the laboratory analogue of **3f'**) is somewhat broad, probably due to the presence of several transitions close in energy as suggested by the TD-DFT data. The calculations reveal three intense CT transitions (oscillator strengths > 0.6) in the region 25,000 – 35,000 cm⁻¹ for **3g'**, with the transition calculated at ca. 34,300 cm⁻¹ being the most intense (Table 3). The broad experimental band for **3g** (the laboratory analogue of **3g'**) may thus be due to the overlap of these individual bands. The HOMO-6 to LUMO transition in **3g'** is significantly red-shifted compared to that in **3f'** because the LUMO of the former is stabilized significantly following conceptual nitration (Figure S2).

First hyperpolarizability tensors were calculated using the coupled-perturbed Kohn-Sham (CPKS) approach, in order to investigate the 2D NLO character of these complexes. Because of Kleinman symmetry,^[14] ten independent tensor components were calculated using the PBE1PBE functional in the static limit. The key calculated first hyperpolarizability (!) data are collected in Table 3. We also undertook the $_{\bullet}$ calculations using the long-range corrected CAM-B3LYP functional (Table S1). Both functionals yield the same relative trend in on-diagonal β_{zzz} and off-diagonal β_{zxx} components of ! (Table 3 and S1), i.e. $\beta_{zzz} > \beta_{zxx}$ for 3a'-c', 3e', and 3g' and $\beta_{zzz} < \beta_{zxx}$ for 3d' and 3f'. To simplify the computational analysis, we have therefore limited the subsequent discussion to the PBE1PBE results. The calculations of accurate absolute hyperpolarizability values for such complexes is beyond the scope of the present work.

In addition to the CPKS approach, the contributions from the parallel (z-polarized) and perpendicular (x-polarized) transitions to the diagonal and off-diagonal components, respectively, were calculated using a three-level model (TLM, Table S2), the calculated results from both methods being contrasted in Figure 1. Although the three-level model-derived data are somewhat larger than the CPKS values for all complexes, there are similar variations in the two tensor components as a function of the nature of the R and R' substituents for both approaches. The decrease in the three-level-derived β_{zxx} value on proceeding from 3f' to 3g' (in contrast to the corresponding CPKS data) is a clear exception (Figure 1). The discrepancies may arise because the three-level model only includes contributions from the first z- and x-polarized transitions; contributions from other z- and x-polarized transitions are ignored (Table S2). From the CPKS data (Table 3 and Figure 1), introduction of NO2 at the R' site (e.g. on proceeding from 3f' to 3g' or 3a' to 3b') results in a significant increase in the $|\beta_{\tau\tau\tau}|$ component compared to β_{zxx} , consistent with the experimental data. Three-level data also show that nitrating the R' position results in a significant increase in the ondiagonal element (Table S2 and Figure 3). According to the data in Table S2, the exceptionally large dipole moment difference between the ground state and excited state $(\Delta \mu_{e\sigma})$ associated with the parallel (z-polarized) low-energy transitions in the complexes **3b'**, **3e'**, and **3g'** contribute significantly to the β_{zzz} data, indicating that the β_{zzz} element may be modified by varying the acceptor capability of the R' group and increasing/decreasing the on-C₂-axis arm length. However, a considerable decrease in the

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Complex	E _{eg} ªE	$v_{\max} \left[f\right]^{b}$	% Contribution	Character		$\mu_{\text{eg}^{c}}$		βzzz ^d	βzxx ^e	k ^f
					x	у	z			
3a'	3.93	31730 [0.475]	H−1 → L+4 (33) ⁹ ; H → L+6 (39)	MLCT; MLCT; LLCT	2.2	0.0	0.0	-15.69	-6.12	0.39
	4.01	32345 [0.884]	H–5 → L (33)	LLCT	0.0	0.0	3.0			
	4.07	32830 [0.705]	H–4 → L (54)	LLCT	2.7	0.0	0.0			
3b'	2.98	24010 [0.260]	H–5 → L (98)	LLCT	0.0	0.0	-1.9	-140.34	-9.38	0.07
	3.49	28145 [0.855]	H–7 → L (93)	LLCT; MLCT	0.0	0.0	-3.2			
	3.94	31770 [1.082]	H–1 → L+6 (65)	MLCT	3.3	-0.1	0.0			
3c'	3.99	32200 [0.726]	H–1 → L+4 (35)	MLCT	-2.7	0.1	0.0	-10.26	-6.13	0.60
	4.00	32285 [0.985]	H–5 → L (33)	LLCT	0.0	0.0	3.2			
3d'	2.89	23350 [0.767]	H → L+1 (76)	MLCT; LLCT	3.3	-0.1	0.0	10.98	98.77	9.00
	3.59	28930 [0.453]	H–4 → L (56)	LLCT; MLCT	-2.3	0.1	0.0			
	4.14	33355 [0.988]	H–4 → L+2 (57)	LLCT; MLCT	0.0	0.0	3.1			
3e'	2.96	23885 [0.855]	H → L+2 (71)	MLCT; LLCT	-3.4	0.1	0.0	-101.25	91.74	-0.91
	3.64	29340 [0.652]	H–6 → L (86)	LLCT; MLCT	0.0	0.0	-2.7			
	3.68	29655 [0.546]	H–4 → L+2 (58)	LLCT; ILCT	-2.5	0.0	0.0			
3f'	3.86	31095 [1.316]	H–1 → L+5 (70)	MLCT; LLCT	3.7	-0.2	0.0	-19.27	-35.48	1.84
	4.23	34155 [0.882]	H–6 → L (57)	MLCT; LLCT	0.0	0.1	-2.9			
3g'	3.33	26840 [0.816]	H–6 → L (81)	MLCT; LLCT; ILCT	0.0	0.0	3.2	-155.52	-41.38	0.27
	3.76	30360 [0.680]	H–1 → L+6 (64)	LLCT; MLCT	-2.7	0.1	0.0			
	4.26	34330 [0.822]	H–1 →L+18 (30)	LLCT; MLCT	-2.8	0.1	0.0			

Table 3. Calculated linear optical and static quadratic nonlinear optical data of the model complexes.

[a] Excitation energies (eV). [b] Wavenumbers (cm⁻¹). [f] = oscillator strength. [c] Transition electric dip<u>cle moments</u> (au). [d] Diagonal β components (10⁻³⁰ esu). [e] Off-diagonal β components (10⁻³⁰ esu). [f] Calculated static in-plane anisotropy values (Cartesian). $k_{cal} = \beta_{zxx}/\beta_{zzz}$, [g] H, HOMO; L, LUMO.

experimental diagonal element was observed on moving from **3d** to **3e** (Table S4).

The CPKS results indicate relatively large off-diagonal β_{zxx} components for **3d'** and **3e'** (Table 3). Indeed, dominance of β_{zxx} over β_{zzz} is predicted for **3d'** employing both CPKS and the three-level model. However, in contrast to the CPKS calculations, the three-level model indicates that $|\beta_{zxx}| > |\beta_{zzz}|$ for **3e'**; this is to some extent because the TLM involves non-dipolar contributions. It seems that the red-shifted bands (i.e. those with lower excitation energy E_{eg}) in **3d'** and **3e'** contribute to the β_{zxx} values, according to the three-level model parameters. Although the experimental

HRS studies show that β_{zzz} is dominant for all complexes, the calculated β_{zxx} value may differ from the β_{zxx} obtained from HRS measurements due to Kleinman symmetry breaking (as mentioned below), and an averaged value for the off-diagonal element is likely to have been obtained experimentally. [^{15}]

Third-Order Nonlinear Optical Studies. The nonlinear absorption and nonlinear refraction properties of 4, 5a-c and 6ab were assessed by the Z-scan technique over the spectral range



Figure 2. (Left): Plot of σ_2 (red) and σ_3 (blue) for **6b** overlaid on the UV-visible spectrum (black), and including plots of the UV-visible spectrum at twice (red) and three times (blue) the wavelength. (Right) The real (red) and imaginary (blue) parts of the third-order hyperpolarizability of **6b** overlaid on the UV-visible spectrum (black), and including plots of the UV-visible spectrum at twice (red) and three times (blue) the wavelength.

6,500-17,000 cm⁻¹, and employing ca. 130 femtosecond pulses at low repetition rates to minimize contributions to nonlinear absorption from excited-state absorption and avoid thermal effects. Closed- and open-aperture Z-scans were recorded, affording simultaneous evaluation of the absorptive and refractive components of the hyperpolarizability. The results from these studies are displayed in Figure 2 and Figures S4-S8 and the key data are collected in Table 4. For all complexes, the real part of the nonlinearity γ_{real} is negative or near zero over the spectral range surveyed, with negative maximal values of γ_{real} at approximately coincident wavelengths to positive maximal values of γ_{real} on all nonlinear absorption processes through a nonlinear Kramers-Kronig relationship.^[16]

The 2PA maximal values for these complexes are found in the wavelength range 840-920 nm. Compounds 4 and 5 exhibit the lowest σ_2 values of this group, consistent with the smaller molecular size (4) and lack of polarizing substituents (5a). Introduction of electron-donating or withdrawing substituents at the periphery of 5a, in proceeding to 5b and 5c, significantly improves nonlinear absorption merit. Being mindful of the significant error margins with these studies, the data suggest that the electron-withdrawing nitro substituent is more effective in increasing σ_2 value than the electron-donating diethylamino substituent. Conceptual extension of the π -system in **5a** and **5b**, to afford 6a and 6b respectively, results in complexes with significantly enhanced 2PA cross-sections. These structureproperty observations are consistent with σ_2 merit increasing onperipheral acceptor group installation or on π -system lengthening; consistent with this, the complex with the largest maximal value of 2PA cross-section is 6b.

In two cases, we observed measurable nonlinear absorption activity at longer wavelengths. The intensity dependence of the Zscan traces revealed that this was three-photon absorption (3PA), the key data for which are summarized in Table 4. The limited measurable σ_3 data for these complexes are insufficient to establish conclusions, but are suggestive of an increase in 3PA maximal value on π -system extension; **6b**, the most efficient complex for 3PA, is also the most efficient complex for 3PA, with a maximal value (ca. 10^{-77} cm⁶ s² at 1300 nm) that is large in absolute terms.^[5b, 9b, 17]





Con	npound R	$2\text{PA}\lambda_{\text{max}}$	σ_2 (GM)	$3\text{PA}\;\lambda_{\text{max}}$	σ_3		
4		920	0 ± 7				
5a	н	840	40 ± 40				
5b	NO ₂	880	1400 ± 300				
5c	NEt ₂	880	900 ± 300	1480	300 ± 50		
6a	C≡CPh	920	480 ± 40				
6b	$4-C \equiv CC_6H_4NO_2$	880	5500 ± 1500	1300	1200 ± 100		
[a] [Ru] = trans-Ru(dppe) ₂ , CH ₂ Cl ₂ solvent, λ_{max} in nm, σ_2 in GM, σ_3 in 10 ⁻⁸⁰							

[a] [Ru] = *trans*-Ru(dppe)₂, CH₂Cl₂ solvent, λ_{max} in nm, σ_2 in GM, σ_3 in 10⁻⁸⁰ cm⁶ s².

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Discussion. The studies summarized above have demonstrated that the bis[bis{1,2-bis(diphenylphosphino)ethane}ruthenium]functionalized 1,3,5-triethynylbenzene-cored complex 1, which we have previously shown is readily available by employing a "steric control" synthetic methodology, permits the facile syntheses of Y-shaped Sonogashira coupling products 3a-n and distorted-H-shaped homo-coupled quadrupolar products 4, 5a-c, and 6a-b. Cyclic voltammograms of all products reveal two reversible metal alkynyl-localized complexes with 4diethylaminophenylethynyl groups (0.49 - 0.54 V) sufficiently large that one could contemplate their use in multi-state molecular (nonlinear) optical switches^[18] if the changes in oxidation states are accompanied by distinctly different optical properties. Electronic spectra of these highly soluble species reveal that the wavelengths of the linear optical absorption maxima are dominated by the nature of the peripheral alkynyl groups. The differences in the potentials stem from these ligands rather than the substituent at the unique arm of the "Y" or at the guadrupolar complex "core".

The quadratic optical nonlinearities of the Y-shaped complexes were assessed by the hyper-Rayleigh scattering technique at 800 nm and employing 100 fs light pulses; introduction of donor NEt₂ and/or acceptor NO₂ to the wedge periphery resulted in non-zero nonlinearities, with the largest $\beta_{HRS,800}$ values being observed for the complexes containing the 4-nitrophenylalkynyl ligands. Depolarization ratios are consistent with substantial off-diagonal first hyperpolarizability tensor components and 2D nonlinear character.

Computational studies employing time-dependent density functional theory were employed to assign the key low-energy transitions in the linear optical spectra and to compute the static quadratic nonlinear optical (NLO) tensorial components. The agreement between the CPKS calculations and the experimental data for *k* (= β_{zxx}/β_{zzz} : Table 3 and S4) is not good. For example, for **3d'** and **3f'**, the β_{zxx} value is significantly larger than the β_{zxx} for the calculated data, particularly in the case of 3d' (k = 9.00), whilst the experimental HRS measurements show that the β_{zzz} is always the dominant component (Table S4). There are several possible reasons for a lack of correspondence between computational and experimental data. Firstly, HRS data may be resonance enhanced, and this is the case for 3a-g. The wavelength dependences of the quadratic NLO parameters are unknown and are likely to be highly complicated for complex twodimensional charge-transfer molecules (in related work, some of us have recently analysed the dominant role of dispersion rather than charge-transfer in the magnitude of experimentally determined quadratic nonlinearity for octupolar triindoles).^[19] In the present study, the experimental data were collected at 400 nm, and 3d and 3e have absorption maxima to low-energy of the measurement wavelength, but the other complexes have λ_{max} to higher energy, so an analysis based on simple charge-transfer arguments is unlikely to be applicable to the experimental data. Secondly, although Kleinman symmetry is obeyed for the calculations which were performed in the static limit ($\beta_{zxx} = \beta_{xxz} =$ β_{xzx}), it may not be valid under the conditions that the HRS measurements were performed ($\beta_{zxx} \neq \beta_{xxz} = \beta_{xzx}$), and thus the β_{zxx} (and ρ and k) values obtained from the HRS experiment (Table

S4) should be used with caution (see references [15, 20] for further details). Thirdly, the theoretical studies were performed in a vacuum, whereas the HRS measurements were performed in tetrahydrofuran. Fourthly, all four phenyl rings in the computational complexes were assumed to be co-planar for the sake of computational expediency, but this planar geometry almost certainly does not correspond to the experimental geometry.

We have addressed the fourth point above (the possible lack of correspondence in molecular geometry in the experimental and computation studies) by examining the effect on the on-diagonal and off-diagonal tensor components of the reduction in π delocalization due to the phenyl rings twisting out of coplanarity. For the purposes of this study, the representative complexes 3b' and 3d' were sampled. For 3d', the in-plane anisotropy k suggested by the DFT studies is particularly large, while for 3b' the anisotropy is quite small compared to the experimental data (Table S4). Four extreme cases were considered, via rotating terminal phenyl groups by 90 degrees with respect to the core phenyl ring, as shown in Figure S3. In the most stable conformations of 3b' and 3d', all phenyl rings are coplanar, resulting in an extended π -delocalizable system. It appears that the least stable conformer for both 3b' and 3d' is only ca. 5 kJ/mol less stable than the planar structure, so distortions from the ideal coplanar structure can be expected for these species, suggesting that the experimental data from the HRS measurements result from an averaging of all conformations in solution. It also appears that the relative orientation of the phenyl groups in the complex has a significant effect on the β_{zzz} and β_{zxx} tensors (Table S3). For example, rotating the nitrophenyl group of 3b' results in a substantial decrease in the on-diagonal β_{zzz} element in **3b'(2)** and **3b'(3)**, and thus the anisotropy dramatically increases (k = 0.07 to 0.24), in good agreement with the absolute value from the experimental data (|k| = 0.30: Table S4). In contrast, the anisotropy decreases in proceeding from 3d' to 3d'(2) and 3d'(3), but data for the latter two conformers exhibit better agreement with the experimental data (Table S4) than does data for the fully planar structure 3d'. For the reasons explained above, we do not anticipate correspondence in the experimental and computational data, but the computational data have afforded some insight into the experimental outcomes.

Finally, cubic optical nonlinearities of the H-shaped complexes were assessed by the Z-scan technique over the range 500-1600 nm and employing 130 fs light pulses. Two-photon absorption cross-sections for the distorted-H-shaped complexes in the present study are large (up to 5500 GM at 880 nm), while one example displays significant three-photon absorption (1200 x 10^{-80} cm⁶ s² at 1300 nm); complex **6b** is amongst the best molecular materials assessed under fs conditions thus far.^[5b,17g,h,k,I]

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Facile syntheses of Y-shaped Sonogashira coupling products and distorted-H-shaped homocoupled quadrupolar products are demonstrated, exploiting the ready synthesis of precursor wedge using "steric control". Strongly dipolar examples of the former exhibit significant quadratic optical nonlinearity, while the largest example of the latter displays significant nonlinear absorption behavior.



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Quadratic and Cubic Optical Nonlinearities of Y-Shaped and Distorted-H-Shaped Arylalkynylruthenium Complexes