

1 **Ruthenium Alkynyl Complexes in Nonlinear Optics***

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5

6 **Abstract**

7 Nonlinear optical (NLO) materials are able to modify the propagation characteristics of light.
8 Such materials have a range of potential applications in advanced technologies and are
9 therefore of considerable interest. This Account summarizes the development of one class of
10 organometallics as potential NLO materials, namely ruthenium alkynyl complexes. These are
11 available in high yields by straightforward synthetic procedures and have good thermal and
12 environmental stability. In studies ranging from small molecules (molecular weights ca. 1,000)
13 to second-generation dendrimers (with molecular weights of more than 20,000), the author's
14 group and collaborators have assayed the NLO effects in complexes with a variety of
15 "multipolar" charge distributions (dipolar, quadrupolar, octupolar), revealing that ruthenium
16 alkynyl complexes can be engineered to display record and near-record values of the
17 parameters responsible for various interesting NLO effects. In particular, recent studies driven
18 by the current focus on optimizing molecular multi-photon absorption cross-sections have
19 afforded several examples with world-record values of these key coefficients. The author's
20 group has also shown that the fully-reversible redox processes undergone by many ruthenium
21 alkynyl complexes are a distinctive feature that can be exploited to afford molecular NLO
22 switches, because the different and reversibly accessible redox forms of the complexes exhibit
23 measurably different NLO responses. This unique type of switching has been extended in two
24 ways to afford molecular switches with multiple accessible NLO states. Firstly, ruthenium
25 alkynyl complexes have been subjected to various "orthogonal" (independent) switching
26 stimuli (specifically oxidation/reduction, protonation/deprotonation, and photoisomerization),
27 affording complexes that function as NLO switches with up to six distinct NLO states.
28 Secondly, heterobimetallic complexes coupling ruthenium alkynyl and iron alkynyl centres
29 have been prepared that exhibit multiple redox-accessible NLO states.

30

31 **Introduction**

32 The field of nonlinear optics was launched following the development of the laser, which
33 afforded ready access to the high-intensity light needed to achieve observable nonlinear effects.
34 Materials that possess the requisite nonlinear optical (NLO) properties can modify the
35 propagation characteristics of light (frequency, amplitude, path, phase, polarization, etc.) and,
36 as a result, they are of significant interest for applications in laser technology, data storage,
37 telecommunications, optical signal and image processing, biological imaging, and
38 nanofabrication. Unlike electronics, where silicon is the material of choice for most
39 applications (excluding throwaway devices), there is thus far no broadly useful material for
40 photonics applications. A wide variety of materials have been assayed for NLO applications,

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41 including inorganic salts, organic molecules, polymers, liquid crystals, and composites, but
42 molecular organic, inorganic, and organometallic compounds have attracted especial interest
43 because of the ease in which their composition can be modified, and consequently structure-
44 property relationships established from which to optimize behaviour, as well as the large values
45 of the key molecular NLO parameters that have been obtained for some examples. This
46 Account summarizes some of our studies exploring the NLO properties of organometallics,
47 with a particular focus on ruthenium alkynyl complexes.

48 The theoretical background to the NLO materials field has been presented elsewhere,^[1] and
49 will not be reproduced in detail here; rather, a short introduction will be presented to clarify
50 the subsequent discussion. Briefly, an intense electric field \mathbf{E}_{loc} incident on a molecule can
51 distort its electron density distribution, and the resultant change in the dipole moment $\boldsymbol{\mu}_0$ is
52 given by:

$$53 \quad \boldsymbol{\mu} = \boldsymbol{\mu}_0 + \alpha \mathbf{E}_{\text{loc}} + \beta \mathbf{E}_{\text{loc}} \mathbf{E}_{\text{loc}} + \gamma \mathbf{E}_{\text{loc}} \mathbf{E}_{\text{loc}} \mathbf{E}_{\text{loc}} + \dots$$

54 where the tensors α , β , and γ are the linear polarizability (a 3 x 3 matrix), the quadratic
55 hyperpolarizability (a 3 x 3 x 3 matrix), and the cubic hyperpolarizability (a 3 x 3 x 3 x 3
56 matrix), respectively. This may seem complicated, but many tensor components are equivalent
57 by symmetry rules (or equal to zero), resulting in considerable simplification, while
58 polarizabilities are invariant with respect to all point group symmetry operations, so all the
59 components of β vanish in centrosymmetric point groups. A similar relation describes
60 polarization at the macroscopic level:

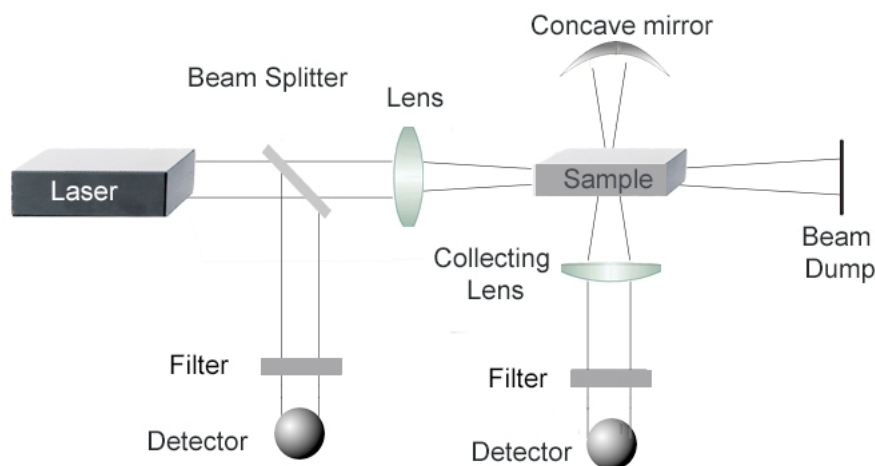
$$61 \quad \mathbf{P} = \mathbf{P}_0 + \chi^{(1)} \mathbf{E} + \chi^{(2)} \mathbf{E} \mathbf{E} + \chi^{(3)} \mathbf{E} \mathbf{E} \mathbf{E} + \dots$$

62 but the focus of this Account is on NLO effects at the molecular level.

63 Because the electric field of a light wave oscillates and can be written as $\mathbf{E}(t) = \mathbf{E}_0 \cos(\omega t)$, it is
64 immediately apparent from considering the trigonometric expansions $\cos^2(\omega t) = \frac{1}{2} +$
65 $\frac{1}{2} \cos(2\omega t)$ and $\cos^3(\omega t) = \frac{3}{4} \cos(\omega t) + \frac{1}{4} \cos^3(\omega t)$ that the nonlinear terms in the equation
66 above introduce contributions at double and triple the fundamental frequency (i.e. second-
67 harmonic generation (SHG) and third-harmonic generation (THG)), as well as a time-
68 independent (DC) contribution. A variety of other interesting effects are also possible; the key
69 requirement is to generate materials that have sufficiently large NLO coefficients, while being
70 stable to processing and device operating conditions.

71 A range of techniques has been employed to measure NLO properties of materials; detailed
72 descriptions can be found elsewhere.^[1d] Many of the early reports of NLO effects employed
73 the Kurtz powder technique, in which the second-harmonic light scattered from a
74 microcrystalline powder is assessed. This has the advantage of simplicity, and it has indeed
75 been deployed to assess the bulk material second-order NLO activity of vinylidene
76 complexes^[2] and alkynyl complexes^[3] relevant to the present Account, but it is generally just
77 a qualitative indication of NLO activity, and it has been largely supplanted by more quantitative
78 techniques measuring NLO performance at the molecular level. The quadratic NLO properties
79 of metal alkynyl complexes have mostly been assessed using the hyper-Rayleigh scattering
80 technique (HRS).^[4] HRS involves focussing an incident beam on a solution of the sample. A
81 concave mirror and collecting lens then collect the scattered light. The light is filtered to
82 remove the fundamental radiation, leaving the second-harmonic light (Figure 1). HRS replaced

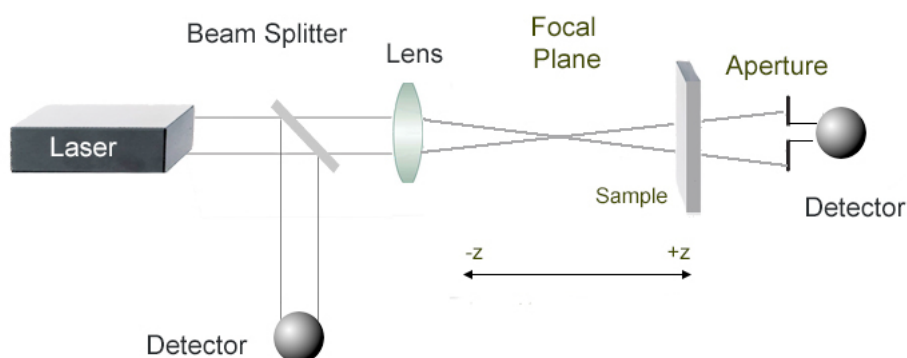
83 electric field-induced second-harmonic generation in the 1990s as the method of choice
84 because (i) it is simpler (a DC field is not needed, and there is no need to measure the dipole
85 moment or the cubic nonlinearity), (ii) it can sample the off-diagonal tensor components of the
86 quadratic nonlinearity, and (iii) it is applicable to a broader range of compounds (ionic
87 compounds, octupolar compounds). It has a couple of shortcomings: (i) it does not afford the
88 sign of β , but this is not a major problem because it is usually obvious, and (ii) any fluorescence
89 contributions need to be removed.



90

91 **Figure 1.** Schematic diagram of the HRS experiment.

92 Cubic NLO properties of metal alkynyl complexes have mostly been assessed using the Z-scan
93 technique,^[5] which largely displaced degenerate four-wave mixing and other procedures in the
94 1990s due to its experimental simplicity (a single-beam configuration giving both the real and
95 imaginary components of $\chi^{(3)}$ and consequently γ). Z-scan involves moving a solution of the
96 sample on a motorized stage through the focal plane of a laser. The self-focusing behaviour
97 and intensity-dependent absorption are thereby assessed (Figure 2). Z-scan has the
98 disadvantage of not affording temporal information about the NLO responses, but this has not
99 hindered its broad implementation.

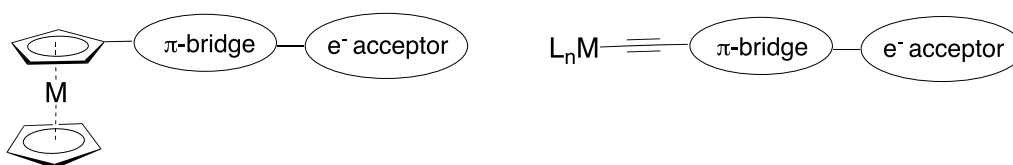


100 **Figure 2.** Schematic diagram of the Z-scan experiment.

101

102 While it was not the first report of the NLO properties of organometallic complexes,^[6] the
103 seminal study by Green et al. of second-harmonic generation effects exhibited by powders of

104 a certain ferrocenyl complex alerted the organometallic chemistry community to the potential
 105 of such complexes in this then-nascent field.^[7] A wide variety of organometallics (as well as
 106 organics and coordination complexes: see above) were assessed in the 1990s, affording some
 107 design rules for efficient NLO-active compounds.^[8] The need for both sufficient activity and
 108 sufficient stability for putative applications gradually focussed the organometallic field on
 109 metallocenyl (particularly ferrocenyl) and metal alkynyl complexes. An early report identified
 110 a potential shortcoming with metallocenyl complexes: the intra-chromophore charge transfer
 111 contributing to the NLO responses is orthogonal to the metal-to-cyclopentadienyl charge-
 112 transfer axis (Figure 3 (left)), a potentially unfavourable arrangement,^[9] although subsequent
 113 more-detailed studies have suggested that the key transitions in these metallocenyl complexes
 114 consist of a low-energy metal-to-acceptor transition and a higher-energy chromophore π -
 115 system-to-acceptor transition.^[10] In contrast, metal alkynyl complexes feature the ligated metal
 116 collinear with the intra-alkynyl ligand charge transfer (Figure 3 (right)), potentially affording
 117 the possibility of stronger coupling of the metal, and thereby enhanced optical nonlinearities.^[11]



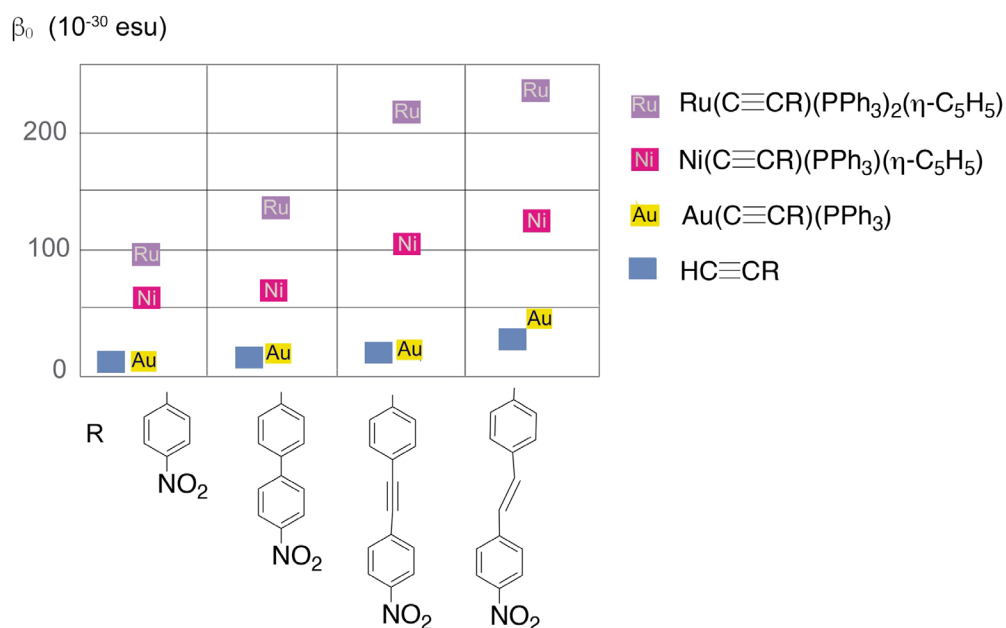
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119 **Figure 3.** MLCT and π - π^* charge transfer in metallocenyl and alkynyl complexes.

120 Metal alkynyl complexes have commanded significant attention from organometallic chemists
 121 since the initial report of nickel and copper alkynyls by Nast in 1953.^[12] Early studies of metal
 122 alkynyl complexes focussed on synthesis, structure, and bonding,^[13] and metal alkynyl
 123 complexes now exist for essentially all of the transition metals. Subsequently, the reactivity of
 124 these complexes came to the fore, with reports affording a plethora of derivative ligands
 125 (vinylidenes, carbenes, etc.),^[14] and with ensuing work extending these studies to applications
 126 in catalysis.^[15] More recently, materials applications of metal alkynyl complexes have been a
 127 focus, due to their electron-rich and π -delocalizable nature.^[16] In particular, in addition to the
 128 aforementioned interest in nonlinear optics, their potential use in molecular electronics has
 129 been actively pursued.^[17]

130 Ruthenium arguably sits in a Goldilocks Zone in the Periodic Table. Ruthenium's finely tuned
 131 balance of properties in catalysis applications led to Wilkinson describing it as "an element for
 132 the connoisseur".^[18] Ruthenium also possesses an optimal combination of properties for NLO
 133 applications.^[19] Early studies revealed that quadratic optical nonlinearities for metal alkynyl
 134 complexes increase on proceeding from 14 electron gold alkynyl complexes^[20] to 18 electron
 135 complexes, and increase further on replacing a less readily oxidized, less polarizable 3d metal
 136 such as nickel^[20b, 21] with a more readily oxidized, more readily polarizable 4d metal such as
 137 ruthenium (Figure 4).^[20b, 22] Consistent with these trends, the nonlinearities also increase on
 138 proceeding from 3d iron to 4d ruthenium and then 5d osmium in analogous complexes,^[23] but
 139 the relative kinetic inertness of the last-mentioned has stymied development of its chemistry
 140 and applications. Ruthenium is therefore the metal of choice in nonlinear optics, as it is in many
 141 other applications. This Account summarizes progress in the area of ruthenium alkynyl
 142 complexes in nonlinear optics, with a particular focus on research in the author's laboratory,
 143 and with an emphasis on molecular rather than bulk material studies. Computational studies of
 144 the NLO properties of ruthenium alkynyl complexes employing semi-empirical and density
 145 functional theory approaches have also been undertaken,^[22a-c, 24] but it remains the case that

146 benchmarking the computational data against experimental data is necessary, and so the focus
 147 of this Account is experimentally-derived NLO parameters.



148 **Figure 4.** The effect of varying the ligated metal upon the two-level-corrected quadratic
 149 nonlinearities for selected metal alkynyl complexes. (Note that dispersion of β for linear
 150 charge-transfer molecules can be described by a two-state model, and β values that have been
 151 corrected for resonance enhancement can be obtained from $\beta_0 = \beta[1 - (\lambda_{\text{max}}/\lambda)^2(1 - (2\lambda_{\text{max}}/\lambda)^2)]$,
 152 where β_0 are the corrected values, λ_{max} is the optical absorption maximum, and λ is the
 153 fundamental wavelength of the laser).

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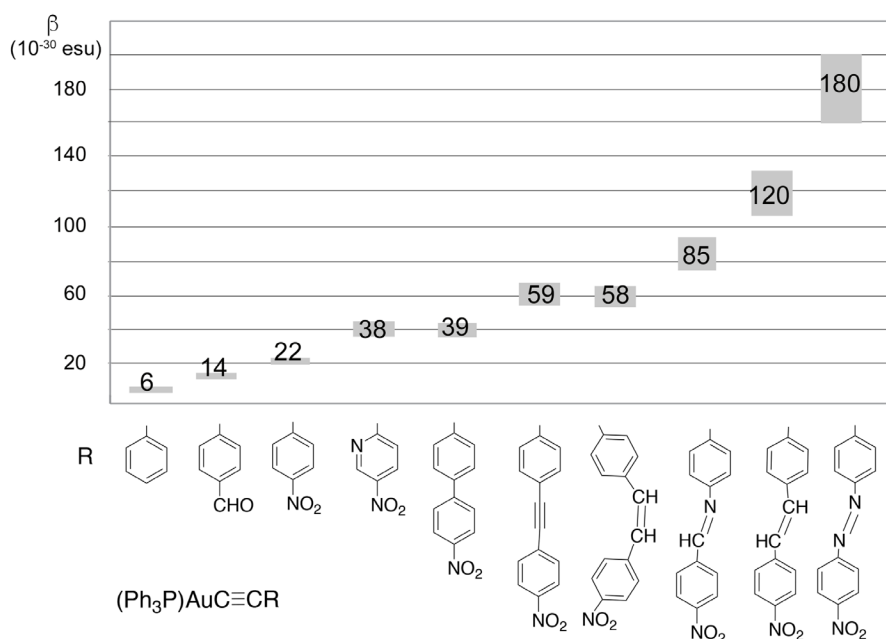
155 Quadratic NLO properties of ruthenium alkynyl complexes

156 Simple molecular design rules for efficient NLO-active materials were developed with small
 157 organic molecules and then propagated to the coordination, organometallic, and
 158 macromolecular realms. Studies correlating molecular structure with quadratic NLO properties
 159 of organic compounds have been summarized extensively elsewhere,^[25] so only relevant key
 160 outcomes will be mentioned here. One useful relationship derived from perturbation theory for
 161 molecules with a single charge-transfer excited state which dominates the quadratic
 162 hyperpolarizability is:

$$163 \quad \beta \approx 3(\mu_{ee} - \mu_{gg})(\mu_{ge}^2/E_{ge}^2)$$

164 This describes β in terms of the difference in excited-state and ground-state dipole moment μ_{ee}
 165 $-\mu_{gg}$, transition dipole moment μ_{ge} , and optical absorption energy E_{ge} of the key low-energy
 166 charge-transfer transition, so compounds exhibiting intense (large μ_{ge}) charge-transfer
 167 transitions (large $\mu_{ee} - \mu_{gg}$) at long wavelength (small E_{ge}) are suggested to possess large values
 168 of β . Not surprisingly, the most efficient purely organic quadratic NLO materials are dipolar
 169 with a donor-bridge-acceptor composition, and this is also true of organometallics. The most
 170 NLO-efficient dipolar metal alkynyl complexes have generally featured an electron rich ligated
 171 metal donor linked by an arylalkynyl bridge to an organic acceptor group, although the metal
 172 centre has also been employed in the bridge^[26] and as an acceptor group.^[27] With the ligated

173 metal unit as donor in a donor-bridge-acceptor composition, trends in the key coefficient β_{HRS}
 174 on varying the arylalkynyl ligand π -bridge length, solubilizing groups, aryl linking unit
 175 stereochemistry and composition, and acceptor group were established and rationalized in the
 176 1990s and 2000s, affording design rules for efficient metal alkynyl-based NLO molecular
 177 materials (see Figure 5 for examples of the structure-NLO property outcomes with certain gold
 178 complexes: β increases on incorporation of acceptor group, increasing the strength of the
 179 acceptor, progression from phenylene to heterocyclic unit, lengthening the π -system, and



180 progression from *Z*- to *E*-ene stereochemistry and progression from yne- to imino-, ene-, and
 181 azo-linkage in the bridge unit).^[20a, 28]

182 **Figure 5.** The effect of varying the alkynyl ligand upon quadratic nonlinearities of
 183 (triphenylphosphine)gold complexes. The width of the bars corresponds to the experimental
 184 uncertainty of the data.

185 Such changes involve the organic arylalkynyl ligand, but the greater interest with
 186 organometallics lies in the effect of structural modifications at the ligated metal centre. It is
 187 well established that the chemical and physical properties of transition metal complexes can
 188 usually be tuned by modifying the co-ligands comprising the coordination sphere. With
 189 organometallic complexes, this is a procedure with an enormous number of applications in
 190 catalysis,^[29] but it can also be employed as an attractive method to modify NLO properties,
 191 and this has been demonstrated with ruthenium alkynyl complexes. For example, with
 192 complexes in which the ligated metal functions as a donor group in a donor- π -bridge-acceptor
 193 construction, examples containing the comparatively electron-withdrawing co-ligand carbonyl,
 194 not surprisingly, have significantly lower nonlinearities than those possessing the electron-
 195 donating co-ligands PPh₃, 1,2-bis(diphenylphosphino)ethane (dppe), or 1,1'-
 196 bis(diphenylphosphino)ferrocene (dppf) (Table 1).^[22b, 22c, 23, 24c] π -Electron delocalization
 197 facilitated by the co-ligand is another important consideration, and in some cases this can prove
 198 more important than donor strength; progression from complexes incorporating the co-ligand

199 PMe_3 (a strong donor) to analogues with PPh_3 (with greater π -delocalization possibilities)
 200 resulted in an increase in quadratic NLO response (Table 1).^[22b, 22c]

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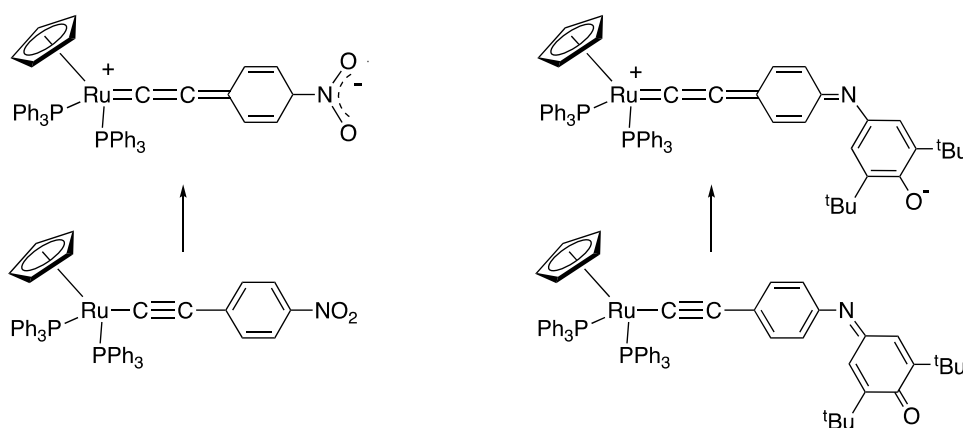
Table 1. Quadratic NLO data for selected (cyclopentadienyl)ruthenium alkynyl complexes.

Complex	λ_{max}^a (ϵ) ^b	β^c	$\beta_0^{c, d}$	Ref.
$\text{Ru}(\text{C}\equiv\text{C}-1,4\text{-C}_6\text{H}_4\text{NO}_2)(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)$	364 (1.6)	58	27	[23]
$\text{Ru}(\text{C}\equiv\text{C}-1,4\text{-C}_6\text{H}_4\text{NO}_2)(\text{PPh}_3)_2(\eta^5\text{-C}_5\text{H}_5)$	460 (1.1)	468	96	[22b, 22c]
$\text{Ru}(\text{C}\equiv\text{C}-1,4\text{-C}_6\text{H}_4\text{NO}_2)(\text{dppe})(\eta^5\text{-C}_5\text{H}_5)$	447 (1.8)	664	161	[23]
$\text{Ru}(\text{C}\equiv\text{C}-1,4\text{-C}_6\text{H}_4\text{NO}_2)(\text{dppf})(\eta^5\text{-C}_5\text{H}_5)$	469 (1.7)	770	165	[24c]
$\text{Ru}(\text{C}\equiv\text{C}-1,4\text{-C}_6\text{H}_4\text{NO}_2)(\text{PMe}_3)_2(\eta^5\text{-C}_5\text{H}_5)$	477 (4.0)	248	38	[22b, 22c]

[a] λ_{max} in nm; [b] ϵ in $10^4 \text{ M}^{-1} \text{ cm}^{-1}$; [c] β and β_0 in 10^{-30} esu ;

[d] $\beta_0 = \beta[1 - (2\lambda_{\text{max}}/1064)^2][1 - (\lambda_{\text{max}}/1064)^2]$.

202 NLO effects can be understood in terms of the polarizing electric fields modifying the ground
 203 state of a molecule and thereby generating a new state corresponding to the instantaneous
 204 mixing of excited states into the ground state.^[30] When the excited states involve substantial
 205 charge displacement from the ground state, such as with states resulting from charge transfer,
 206 the NLO effects can be significant. Metal arylalkynyl complexes exhibit strong charge transfer
 207 along the metal-alkynyl axis when excited, and such complexes are therefore of interest.
 208 However, while complexes possessing arylalkynyl ligands have been designed to exhibit
 209 significant optical nonlinearities, they lose aromatic stabilization energy when excited to the
 210 key charge-transfer state (Figure 6 (left)). To counter this deleterious outcome, complexes
 211 containing indoanilinoalkynyl ligands have been synthesized, because they possess a charge-
 212 transfer excited state that can be accessed without loss of aromatic stabilization energy (Figure
 213 6 (right)); pleasingly, these exhibit significant nonlinearities.^[31]



214

Figure 6. (left) Charge transfer at $\text{Ru}(\text{C}\equiv\text{C}-1,4\text{-C}_6\text{H}_4\text{NO}_2)(\text{PPh}_3)_2(\eta^5\text{-C}_5\text{H}_5)$
 [$\beta = 468 \times 10^{-30} \text{ esu}$; $\beta_0 = 96 \times 10^{-30} \text{ esu}$].

215

216

217

218 (right) Charge transfer at $\text{Ru}(\text{C}\equiv\text{C}-1,4\text{-C}_6\text{H}_4\text{N}=\text{CCH}=\text{C}\text{Bu}^+\text{C}(\text{O})\text{C}\text{Bu}^+=\text{CH})(\text{PPh}_3)_2(\eta^5\text{-C}_5\text{H}_5)$
 219 $[\beta = 658 \times 10^{-30} \text{ esu}, \beta_0 = 159 \times 10^{-30} \text{ esu}]$.
 220

221 The nonlinearities of metal alkynyl complexes with a donor- π -bridge-acceptor composition
 222 can be tuned by modification of any of the three components. The ligated metal has functioned
 223 as a donor in the vast majority of examples, with the nonlinearity being modified by metal
 224 replacement, co-ligand modification (see above), and acceptor group replacement (progressing
 225 from no acceptor (H) to a weak acceptor (CHO) and then to a strong acceptor (NO₂) at a 4-
 226 substituted arylalkynyl ligand results in increased quadratic optical nonlinearity: Figure 5).^{[20a,}
 227 ^{21, 22c, 28, 32]} The NLO merit has also been tuned by bridge modification. In addition to the
 228 various bridge modifications summarized above (Figure 5), bridge lengthening has attracted
 229 attention, and it has been shown that quadratic nonlinearities do not increase indefinitely, but
 230 instead they tend to saturate at a certain length (Table 2).^[24e, 33] Bridge “broadening” has also
 231 been explored, with nonlinearities increasing on proceeding from 1,4-phenylenyl to 1,4-
 232 naphthalenyl bridge.^[24h]

Table 2. Quadratic NLO data for selected bis(diphosphine)ruthenium alkynyl complexes.

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2				
3				
4				
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6				
7				
Complex	$\lambda_{\text{max}}^{\text{a}}$ (nm) ^b	β^{c}	$\beta_0^{\text{c, d}}$	Ref.
1	477 (2.0)	562	88	[33c]
2	468 (1.8)	1240	225	[33c]
3	429 (2.3)	1327	388	[33c]
4	426 (4.3)	515	160	[33b]
5	489 (2.6)	2310	283	[33d]
6	468 (1.6)	2570	470	[33d]
7	419 (7.7)	1355	435	[33d]

[a] λ_{max} in nm; [b] ϵ in $10^4 \text{ M}^{-1} \text{ cm}^{-1}$; [c] β and β_0 in 10^{-30} esu ;

[d] $\beta_0 = \beta[1 - (2\lambda_{\text{max}}/1064)^2][1 - (\lambda_{\text{max}}/1064)^2]$; [Ru] = *trans*-Ru(dppe)₂.

233 The aforementioned dipolar metal alkynyl complexes can be exceptionally NLO-efficient:
 234 quadratic nonlinearities (resonance-enhanced and two-level corrected) for some of these
 235 alkynyl complexes are amongst the largest for organometallic compounds thus far.^[33d, 34]
 236 However, dipolar molecules suffer from an NLO efficiency/optical transparency trade-off (i.e.,
 237 increasing nonlinearity is associated with a red-shift of the important linear optical absorption
 238 band corresponding to strong charge transfer, and this reduces the spectral range available to

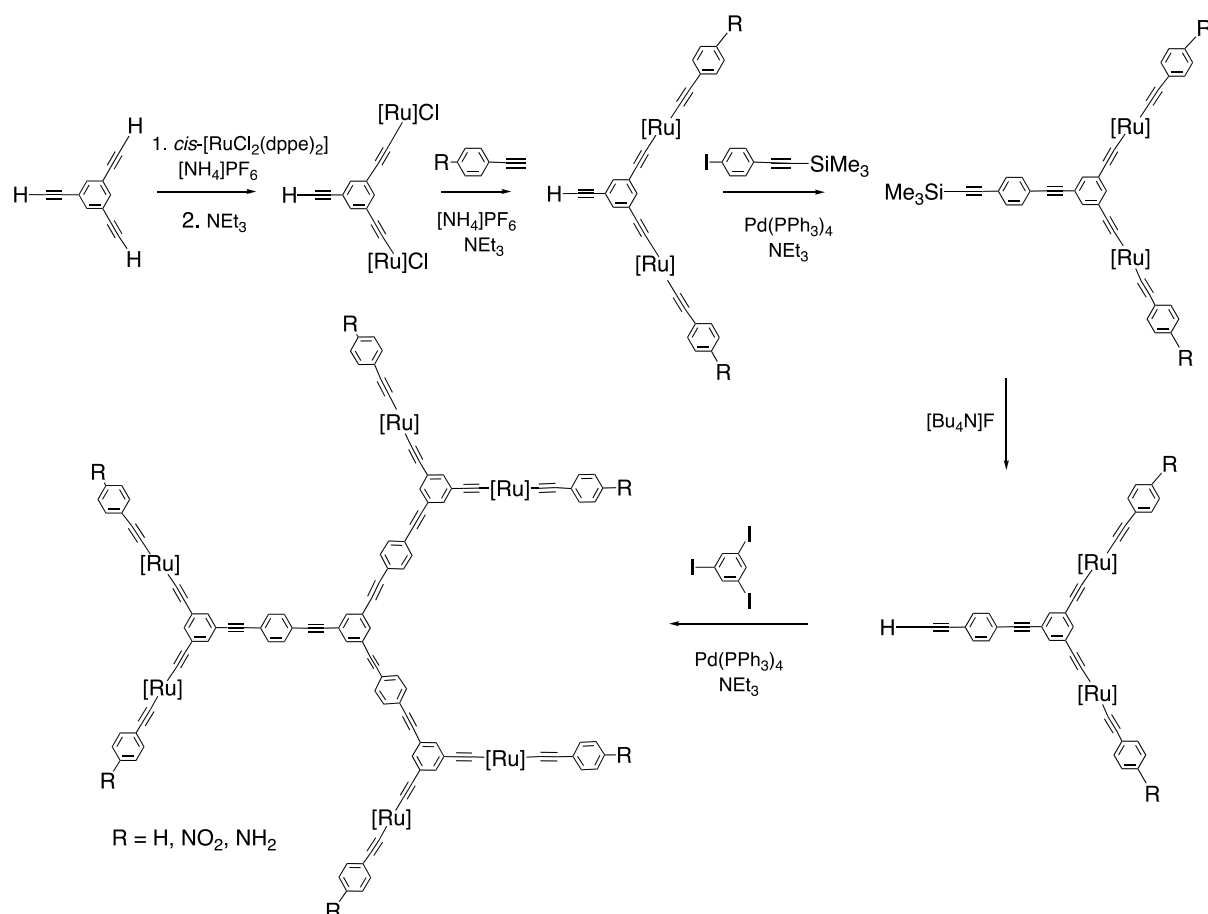
239 exploit the NLO properties). This problem has been met and addressed with organic molecules.
240 Zyss and co-workers showed that because higher-order multipoles may also contribute to
241 optical nonlinearities, octupolar organic compounds can possess significant NLO properties
242 while maintaining optimum transparency.^[35] Similarly, metal alkynyl complexes derived from
243 1,3,5-triethynylbenzene have a three-fold symmetry axis and are octupolar, and ruthenium-
244 containing examples have been studied.^[36] Examples thus far have lacked strongly polarizing
245 groups at the central arene ring and quadratic nonlinearities are consequently small, but are
246 non-zero, demonstrating the potential of this approach. In some instances, complexes
247 corresponding to an “arm” of the octupolar star complexes have also been examined, and the
248 data contrasted with those from the octupolar examples to demonstrate a “dimensional
249 evolution” of NLO properties (progressing from the one-dimensional linear “arm” complex to
250 the two-dimensional octupolar complex).^[36c, 37]

251 **Cubic NLO properties of ruthenium alkynyl complexes**

252 Cubic NLO properties of ruthenium alkynyl complexes were first reported in the mid-to-late
253 1990s,^[36b, 38] and this area continues to attract interest.^[11e, 39] Similar to the situation with
254 quadratic NLO properties, structure-cubic NLO property correlations have been established
255 with organic molecules and propagated to the organometallic realm. In general, and in contrast
256 to quadratic NLO properties, the structure-property relationships are not clear-cut, with the
257 exception (up to a certain size) of a general dependence on the size of the π -system. As is the
258 case with quadratic NLO properties, there is a useful relationship to assist cubic NLO materials
259 design that has been derived from perturbation theory:

$$260 \quad \gamma \approx -\mu_{ge}^4/E_{ge}^3 + \mu_{ge}^2\mu_{ee}^2/E_{ge}^2E_{ge'} + \mu_{ge}^2(\mu_{ee} - \mu_{gg})^2/E_{ge}^3$$

261 where μ_{ee} and μ_{ge} are transition dipole moments, μ_{gg} is the ground-state dipole moment, μ_{ee} is
262 the excited-state dipole moment, and E_{ge} and $E_{ge'}$ are optical absorption energies. The third
263 component of this expression has μ_{ge} and $(\mu_{ee} - \mu_{gg})$ in the numerator and E_{ge} in the
264 denominator, similar to the expression for β , and indeed in some cases trends in the global
265 cubic NLO parameter γ have been found to be similar to those seen with β_{HRS} (e.g. varying the
266 nature of the arylalkynyl ligand). The dependence on the size of the π -system focused attention
267 on complexes with extended π -delocalizable alkynyl ligands such as ruthenium-functionalized
268 oligo(phenyleneethynylene)s (OPEs) and oligo(phenylenevinylene)s (OPVs), as well as OPE-
269 and OPV-based stars and dendrimers,^[38d, 40] necessitating development of efficient routes into
270 such species.^[41] Indeed, in accessing ruthenium alkynyl-based dendrimers, a facile synthesis
271 of dendrons by “steric control” was developed. This exploits the size of the *trans*-
272 [RuCl(X)(dppe)₂] unit to ensure its reaction with 1,3,5-triethynylbenzene proceeds at two of
273 the three ethynyl units only. The reaction thereby generates a “wedge” for dendrimer
274 construction in one step and without the need for classical organic protection/deprotection
275 sequences (Scheme 1). Studies of this broad range of ruthenium alkynyl-based complexes has
276 revealed that ferrocenyl- and OPE-linked diruthenium complexes exhibit some of the largest
277 cubic nonlinearities seen for organometallics thus far,^[42] while a new type of dendritic effect,
278 namely a nonlinear increase in nonlinearity with increase in dendrimer generation, has been
279 identified with ruthenium alkynyl-based dendrimers.^[40i, 43] Analysis of electroabsorption data
280 for such complexes has revealed that the important excited states responsible for NLO
281 properties are “arm-localized” rather than globally delocalized with octupolar/dendritic
282 complexes.^[36c, 37, 43] A key concern is that these NLO effects are wavelength dependent, and so
283 there is a need to obtain the spectral dependence of the cubic NLO coefficients (indeed, the
284 first examples of such studies for inorganic complexes were of ruthenium alkynyl complexes);



285 however, it is still the case that data are not routinely available as spectral dependence studies,
 286 and this has stymied the development of structure-property relationships.^[44]

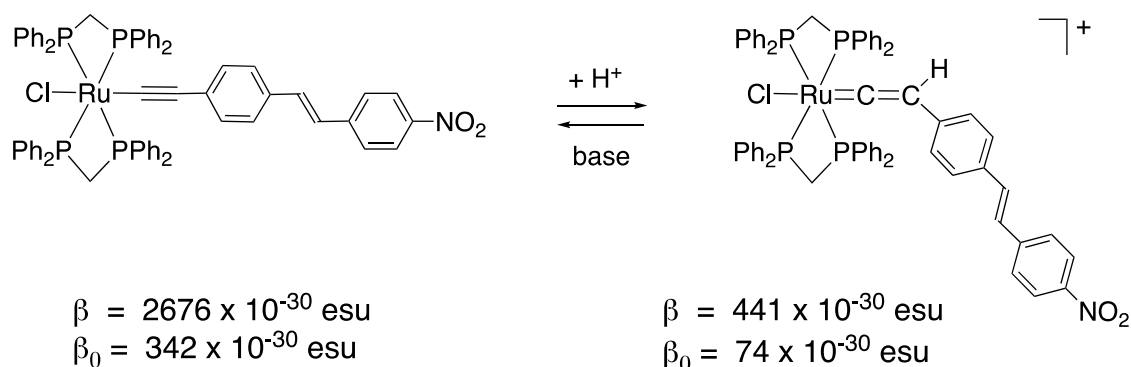
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289 **Scheme 1.** Synthesis of ruthenium alkynyl dendrimers using steric control.
 290 [Ru] = *trans*-Ru(dppe)₂.

291 Higher-order NLO properties of metal alkynyl complexes

292 Intensity-dependent absorption has attracted significant attention over the past two decades
 293 because materials exhibiting such effects have possible uses in frequency up-conversion lasing,
 294 imaging and microscopy, optical power limiting, microfabrication, data storage and
 295 processing, and various biological and medical applications, by exploiting the tight spatial
 296 control and the possibility of functioning at longer wavelengths (e.g. in the biological window
 297 or in the telecommunications windows). The molecular two-photon absorption cross-section
 298 σ_2 can be obtained from the absorptive component of the nonlinearity and this has been the
 299 figure-of-merit employed to compare the performance of disparate molecules. More recently,
 300 higher-order multi-photon absorption (three-photon absorption, 3PA, a fifth-order NLO effect,
 301 and four-photon absorption, 4PA, a seventh-order NLO effect) has attracted attention because
 302 the higher-order intensity dependence promises even greater spatial control of the excitation
 303 volume as well as access to effects at longer wavelengths.^[45] The Z-scan experiment affords
 304 both the nonlinear refractive and nonlinear absorptive components of the third-order
 305 nonlinearity, but because it samples the intensity dependence of the nonlinearity, it can also
 306 afford data corresponding to higher-order NLO effects. Such multi-photon absorption studies
 307 are still rare (for example, there have only been ca. ten reports of 4PA cross-sections). Studies
 308 of ruthenium alkynyl dendrimers have afforded record values of the molecular 3PA cross-

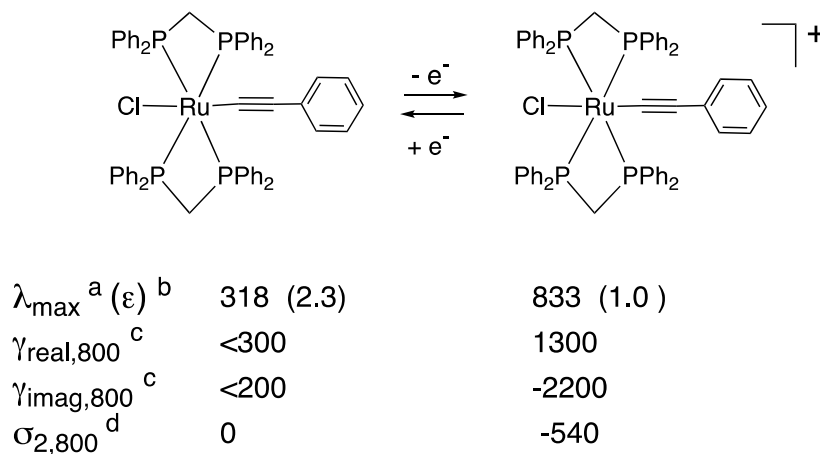
325 examined, with several examples identified where interconvertible complexes correspond to
 326 protically-switchable NLO materials. In a similar fashion, the cubic NLO performance of



327 related vinylidene and alkynyl complexes has afforded several examples of protically
 328 switchable cubic NLO materials.^[32a]

329 **Figure 7.** Switching quadratic nonlinearity in a vinylidene/alkynyl complex pair.

330 Subsequently, attention turned to electrochemical NLO switching, exploiting the reversible
 331 redox activity exhibited by many ruthenium alkynyl complexes. Small ruthenium
 332 phenylalkynyl complexes have no measurable cubic nonlinearity, but on oxidation an
 333 absorption saturation effect is observed; the cubic nonlinearity is switched on, the facile
 334 reversibility of this process affording an electrochemical cubic nonlinearity on/off switch, in
 335 the first example of in situ electrochemical switching of optical nonlinearity and the first
 336 switching of molecular nonlinear absorption (Figure 8).^[40a, 49] Studies employing the
 337 degenerate four-wave mixing technique revealed that these specific NLO effects arise from ps
 338 time-scale processes (suggesting that applications involving molecular “switching” of such
 339 properties can in principle be exceptionally fast).^[40b, 43]

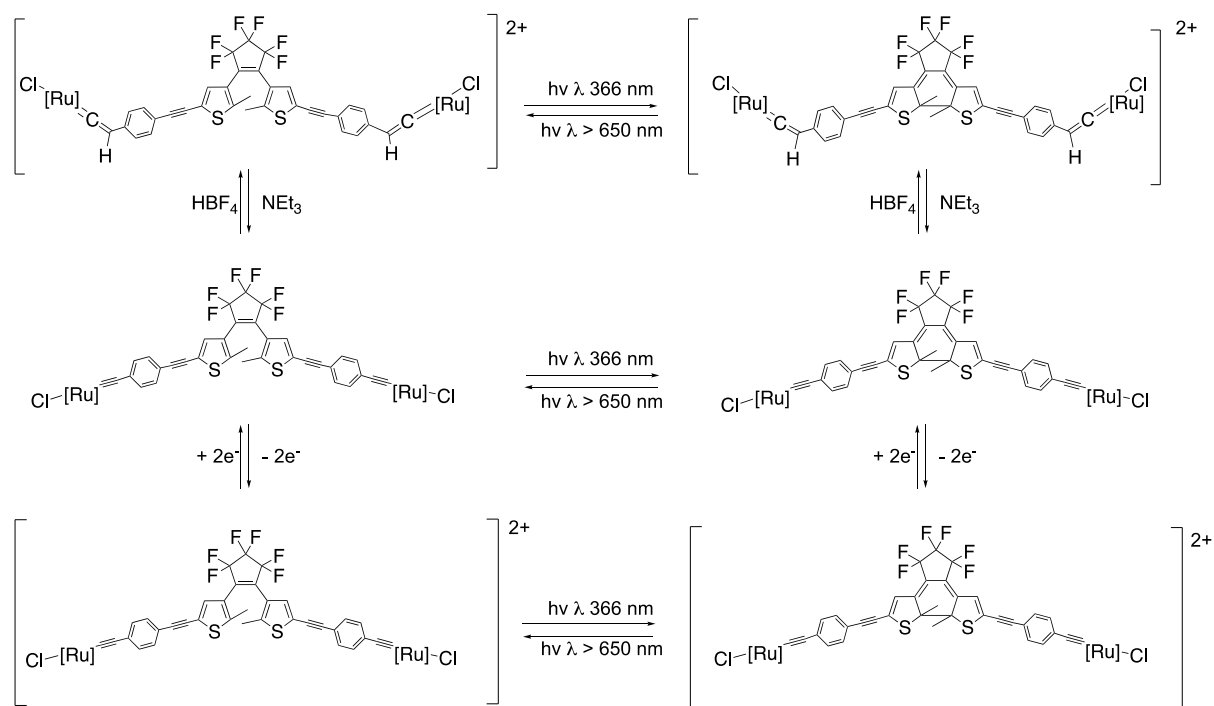


[a] nm; [b] $10^4 \text{ M}^{-1} \text{ cm}^{-1}$; [c] 10^{-36} esu at 800 nm;
 [d] σ_2 in GM ($10^{-50} \text{ cm}^4\text{s}$) at 800 nm.

340 **Figure 8.** Electrochemical switching of cubic nonlinearity in *trans*-
 341 $[\text{Ru}(\text{C}\equiv\text{CPh})\text{Cl}(\text{dppm})_2]$.^[40a]

342 Switching between three cubic NLO “states” was then demonstrated for the first time,
 343 exploiting the widely differing oxidation potentials of the metals in an iron-ruthenium

344 complex,^[50] closely followed by “orthogonal” switching of NLO properties across three states
 345 for the first time (using protic and electrochemical stimuli) in a ruthenium alkynyl cruciform
 346 complex.^[51] A specific dithienylperfluorocyclopentene-bridged diruthenium complex was then
 347 shown to be able to exist in a record six independently addressable and switchable “states”
 348 with distinct linear and NLO properties that can be interconverted by seven distinct pathways
 349 exploiting orthogonal protic, electrochemical, and photochemical switching (Figure 9). Such
 350 complexes have the potential to be used in the construction of multi-input logic gates
 351 responding to diverse stimuli across a broad spectral range.^[52] These new effects are nonlinear
 352 optical analogues of well-established phenomena (halochromism (acidochromism,
 353 protochromism), electrochromism, photochromism) in which linear optical properties are
 354 modified on application of an external stimulus, and for which materials are already in
 355 commercial use (e.g. pH indicators, smart windows, sunglasses, respectively); for the new
 356 effects, both nonlinear refractive and nonlinear absorptive “chromisms” have been
 357 demonstrated and therefore have potential application interest.



359 **Figure 9.** Interconversion of diruthenium alkynyl and vinylidene complexes.
 360 [Ru] = *trans*-Ru(dppe)₂.

361 NLO merit of metal alkynyl complexes compared to organic compounds

362 Structure-NLO property outcomes have generally been developed from studies by a specific
 363 research group using one technique under certain measurement conditions (NLO effects
 364 depend on a number of factors including laser pulse length, pulse repetition rate, laser power,
 365 wavelength, etc.) and with certain theory assumptions. However, there is a need to compare
 366 NLO measurements for disparate compounds measured in different laboratories using various
 367 techniques under different experimental conditions. There are a range of possibilities for
 368 scaling NLO data to facilitate comparisons that have been explored,^[40], 40m, 53] the most widely-
 369 accepted of which is by molecular weight (due to ease of implementation) – other scaling
 370 factors include molecular volume, number of “effective” (π -delocalizable) electrons, and cost
 371 of production. Results from these scaling studies suggest that the NLO efficiencies of

372 ruthenium alkynyl complexes are superior to comparable organics, but data comparisons are
373 still limited and further studies are needed for a definite conclusion.

374 **Conclusion**

375 Ruthenium alkynyl complexes have been shown to exhibit exceptional NLO efficiencies. In
376 several cases, these complexes exhibit world record values of the key NLO coefficients. Not
377 only can they offer superior NLO efficiencies to the best organic materials, they also possess
378 advantages due to their more facile switching between states with differing (positive/negative
379 or ON/OFF, or positive/zero/negative) NLO responses. Propagating these advantages to the
380 solid-state and thereby devices is a future challenge, but some reports are now extant, including
381 second-harmonic generation from ruthenium alkynyl complexes embedded in polymer hosts
382 and oriented in thin films by corona poling,^[54] and third-harmonic generation, all-optical
383 switching, and optical data storage applications from ruthenium alkynyl-doped polymers,^[55]
384 and with promising results thus far.

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616 Table of Contents

617 Ruthenium alkynyl complexes are highly-efficient NLO-active molecules; dipolar examples
618 exhibit record values of quadratic optical nonlinearity and specific octupolar ruthenium alkynyl
619 stars and dendrimers show record values of cubic optical nonlinearity and multi-photon
620 absorption cross-sections. Protonation/deprotonation, oxidation/reduction, and
621 photoisomerization stimuli have been employed at certain ruthenium alkynyl complexes to
622 demonstrate NLO switching across a record number of states.

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