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Spectroscopic and Second-order Nonlinear Optical Properties of Ruthenium(II) Complexes: A DFT/MRCI and ADC(2) Study.

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In this communication we use the density functional theory-based multi-reference configuration interaction (DFT/MRCI) and the second-order algebraic diagrammatic construction (ADC(2)) methods to compute the spectroscopic and second-order nonlinear optical (NLO) properties of Ru(II)-based NLO-phores. For some of the complexes, an appropriate treatment of doubly excited states is essential to correctly describe their spectroscopic and photochemical properties. Geometrical and solvent relaxation effects are also assessed. An adequate treatment of solvent effects seems critical for an accurate description of the NLO properties of these complexes.

Molecular materials with sizable nonlinear optical (NLO) properties are of increasing interest due to their applicability in optoelectronic and photonic technologies.[1] Organometallic complexes are good candidates as NLO materials since they combine large second-order NLO properties with other desired characteristics (i.e. low dielectric constants, strong UV/Vis absorption bands, and ultrafast response times).[2] Ruthenium complexes bearing ammonia and (pyridyl)pyridinium ligands fulfill these requirements. Coe and coworkers have synthesized and experimentally characterized a series of these Ru(II)-based electron donor-acceptor (D-A) compounds, with one-,[3] two-,[4] or three-dimensional[5] structures. Their NLO properties were studied using Stark spectroscopy and hyper-Rayleigh scattering measurements. Additionally, their spectroscopic and NLO properties were examined with density-functional theory (DFT) and time-dependent DFT (TD-DFT) calculations.[3c,6] Multiconfigurational methods, such as, e.g., the restricted-active-space second-order perturbation theory (RASPT2), were also applied and proved to yield values with spectroscopic accuracy for excitation energies, oscillator strengths, and first hyperpolarisabilities (β) of Ru(II) complexes.[7] Unfortunately, these methods are still restricted to small and medium-size systems, thus making their use for larger Ru(II)-complexes unrealistic.[8] Conversely, TD-DFT results are strongly functional dependent. For these NLO-phores, hybrid functionals with intermediate amounts of exact exchange (ca. 20-30%), such as, e.g. B3LYP, M06 or B3P86, were found to be superior to the other tested functionals, including long-range corrected functionals.[9] Still, not all the experimental trends are recovered by the TD-DFT calculations. To compute and analyze β (using either DFT-based or wavefunction-based data), two types of methods have been employed up to date: i) the summation-over-states (SOS) scheme, which can identify the essential states contributing,[10] and hence is directly comparable to Stark spectroscopy data; and ii) the quadratic response schemes,[11] which are usually employed to estimate the whole second harmonic generation response of the compounds, and can be compared with the values derived from hyper-Rayleigh scattering measurements.

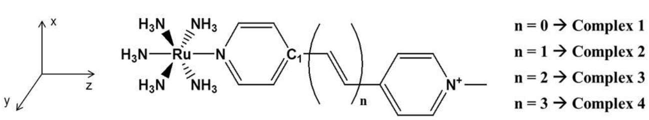

Chart 1. Chemical structure of complexes **1**-**4**.

In this communication, we revisit the spectroscopic and NLO properties of a series of Ru(II) complexes having one increasingly large ligand (see Chart 1) using the DFT-based multi-reference configuration interaction (DFT/MRCI) method. The results are then compared to those obtained from the second-order algebraic diagrammatic construction (ADC(2)) method.[12] In DFT/MRCI,[13] dynamic correlation effects are captured by the Kohn-Sham (KS)-DFT treatment while non-dynamic correlation effects are included at the MRCI level. The DFT/MRCI method has proven successful for organic chromophores[14] and transition metal (TM) complexes.[9,15] It is capable of yielding accurate excitation energies and oscillator strengths of excited states of very different character and permits the calculation of electronic spectra of large molecules. The ADC(2) method has been shown to give accurate excitation energies and associated excited-state properties of organic chromophores, provided that the excited states are dominated by single excitations.[16] Chart 1 presents the chemical structure of the Ru(II) complexes **1-4** studied in this work. The study of their excited states faces all the inherent complexities encountered in the excited states of TM complexes. Among them we highlight the presence of: i) multi-reference character; ii) relativistic effects (especially spin-orbit couplings); iii) environmental effects; and iv) multiply excited states of different character.[17] The presence of a polyene spacer unit on the (pyridyl)pyridinium moiety introduces further difficulties: it is well documented that single-reference methods fail for linear polyenes, since some of their excited states have strong contributions from double excitations.[18] Systematic studies have been carried out for linear polyenes using a range of correlated ab initio wave function methods[19] and TD-DFT methods.[20] The TD-DFT shortcomings were attributed to an inadequate treatment of long-range charge-transfer (CT) states and the failure to properly deal with doubly or multiply excited states.

The optimized geometries for complexes **1**-**4** were taken from Ref. 6. Single-point DFT/MRCI and ADC(2) calculations were performed at these geometries using the def2-SVP and def2-TZVP basis sets (together with a Stuttgart/Dresden pseudopotential for Ru). In the DFT/MRCI case, the initial KS-BHLYP calculations were carried out with the TURBOMOLE program[21] to generate the molecular orbitals (MOs); BHLYP is the standard functional for DFT/MRCI. The subsequent MRCI calculations were done with the DFT/MRCI code.[13] Initial reference configurations were generated by promoting up to two electrons in an active space of ten electrons in ten orbitals. Single and double excitations from the chosen reference configurations were included in the MRCI treatment provided that they satisfied the standard energy-based selection criterion (threshold value of 1.0 hartree). Standard DFT/MRCI parameters for singlet states were employed (see Table II of Ref. 13 for the specific parameter values). Single-point ADC(2) calculations were performed with the TURBOMOLE program.[21] Solvent effects were included in the ADC(2) calculations using the recent implementation of the conductor-like screening model (COSMO),[22] which accounts for state-specific and linear-response terms.[23] The longitudinal β values (β_{zzz}, with z the CT axis) were evaluated using the SOS scheme truncated to the dominant first dipole-allowed excited state (FDAES), giving rise to the so-called two-state approximation.[24] The spectroscopic quantities (excitation energies, transition dipoles) and the ground- and excited-state dipole moments were obtained from DFT/MRCI and ADC(2).

Table 1 summarizes the results for some of the lowest excited states, i.e. the FDAES and the lowest doubly excited state (LDES), of complexes **1**-**4** at different levels of theory. The gas phase TD-B3P86 results are only given for the FDAES, since the LDES is not accessible through linear-response (LR)-TD-DFT calculations. The experimental results in MeCN solution are taken from Table 5 of Ref. 6. In complexes **1**-**3**, the FDAES can be characterized as a metal-to-ligand charge transfer (MLCT) excitation from Ru(II) to the (pyridyl)pyridinium ligand, regardless of the level of theory. In complex **4**, however, the FDAES is described either as a $\pi\pi^*$ excitation (DFT/MRCI) or as a MLCT excitation (TD-B3P86). This difference reflects the more delocalized character of the B3P86 orbitals compared to the BHLYP orbitals.

Experimentally, the excitation energies for the FDAES state in **1**-**4** are close to each other, lying between 2.08 and 2.18 eV (in MeCN solution). They tend to increase slightly with the size of the polyene spacer unit, following the order **2** < **1** < **3** < **4**. Having in mind the mean absolute deviations of state-of-the-art correlated methods for excitation energies (between 0.1-0.2 eV),[25] attaining the correct trend of the FDAES excitation energies of complexes **1**-**4** is a difficult task regardless of the chosen level of theory. In a previous study,[6] IEFPCM-TD-B3P86 excitation energies matched the experimental band maxima within ca. 0.2 eV, but showed a reverse sequence, i.e. **4** < **3** < **2** < **1**. The present gas-phase TD-B3P86 values exhibit a partially correct trend, i.e. **4** < **2** < **1** < **3**, except for complex **4** where the computed excitation energy is too small. Aiming at a better description of the spectroscopic properties of complexes **1**-**4**, we performed DFT/MRCI and ADC(2) calculations. Table S2 of the ESI documents the results for complexes **1**-**2** obtained with the def2-SVP and def2-TZVP basis sets. The DFT/MRCI results are very similar for both basis sets (changes up to 0.06 eV), whereas the ADC(2) results are more sensitive to basis set extension (changes up to 0.31 eV). Therefore we decided to apply the DFT/MRCI/def2-SVP and ADC(2)/def2-TZVP approaches throughout this study (see Table 1). The DFT/MRCI excitation energies for the FDAES state (see Figure S1 of the ESI for the MOs involved) follow the same energetic order as the gas phase TD-B3P86 results, i.e. **4** < **2** ≤ **1** < **3**, and the oscillator strengths are very similar. The ADC(2) excitation energies for **1** and **2** are close to those obtained from DFT/MRCI and TD-B3P86. In the case of **3** and **4**, they are shifted by ca. 0.2 eV with respect to the DFT/MRCI and TD-B3P86 results. Inclusion of solvent effects through the COSMO approach leads to considerable shifts in the excitation energies of the FDAES, such that the ADC(2)/COSMO results accurately match the experimental band maxima (to within 0.05-0.1 eV). Importantly, inclusion of solvent effects may lead to a change in character of the FDAES (see the discussion below for complex **4**). The good correlation with the DFT/MRCI and ADC(2) results confirms that the hybrid B3P86 functional is suitable for describing the MLCT character of the FDAES in complexes **1**-**3**, in which the double excitation character remains low (see Table 1) so that secondary (electronic) relaxation effects are of minor importance. To be more specific, the contribution of doubly excited configurations to the FDAES increases with the length of the polyene spacer unit, but only from 11.7% in **1** to 14.4% in **4**. On the other hand, the increase in the multi-reference excited-state character with spacer length leads to the appearance of a LDES in the low-energy region of the absorption spectrum for **3**-**4**, unlike the case of **1**-**2** (see Table 1). As an example, Figure 1 shows the leading configuration of the LDES of **3** which is the doubly excited $(d_{Ru})^1(d_{Ru}\pi)^1(\pi^*)^1(\pi^*)^1$ configuration. Similarly to the 2^1A_g state in polyenes,[26] the LDES of complexes **3**-**4**, though dark in nature, are located energetically below the FDAES, and they can thus be populated in the course of photochemical events. Therefore, to explore the photochemistry of complexes **3**-**4**, methods that appropriately deal with doubly-excited states are mandatory.

We now discuss the slight differences in the description of the FDAES of complex **4** at different levels of theory. First we consider solvent effects. Table 1 lists the ADC(2) results for the FDAES of **4** in the gas phase and in MeCN. The gas-phase ADC(2) excitation energy is ca. 0.2 eV larger than the DFT/MRCI and TD-B3P86 values. However, the ADC(2) solvent-corrected value is only 0.06 eV lower than the experimental band maximum, and thus points to an underestimation by ca. 0.15-0.2 eV of the excitation energy at the DFT/MRCI and TD-B3P86 levels. Notably, the character of the FDAES is different at the ADC(2) and ADC(2)/COSMO levels. Analogously to DFT/MRCI, the ADC(2) calculations describe the FDAES mainly as a $\pi\pi^*$ excitation in the gas phase, whereas inclusion of solvent effects leads to a mixed $\pi\pi^*$/MLCT transition in ADC(2)/COSMO (see the character of the FDAES in Table S1 of the ESI).

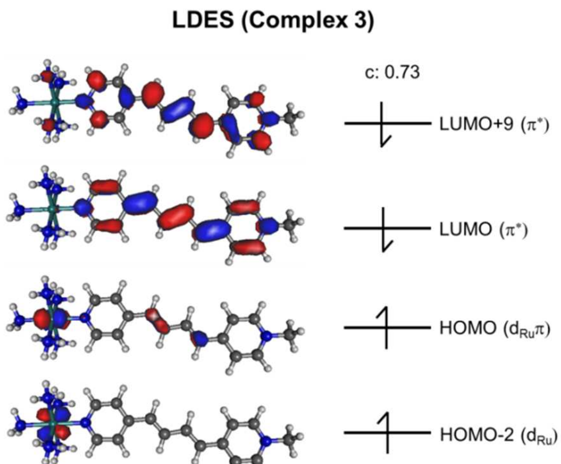

Figure 1. Main doubly excited configuration (c stands for the CI coefficient, c=0.73) of the LDES of complex **3** at the DFT/MRCI level of theory.

We next turn to the evaluation of geometric effects. It is well known for linear polyenes that geometrical relaxation has a strong indirect influence on their excitation energies.[19a] In this regard, an accurate description of the bond length alternation (BLA) is crucial.[27] A comparison of the experimental geometry of the parent *all-trans*-1,3,5,7-octatetraene molecule[28] with the optimized geometries at different levels of theory[19a,29] (Hartree-Fock (HF), different DFT functionals, MP2, CASSCF) reveals that the HF-optimized geometry yields C-C bond distances that are closer to experiment (probably due to fortuitous error cancelations). On the other hand, the metal-ligand environment in TM complexes is normally described reasonably well by DFT.[30] It is thus difficult to find a theoretical method that treats the geometries of both the polyene spacer unit and the transition metal core in complex **4** equally well. Therefore, we decided to partially reoptimize the polyene part of the DFT geometry of **4** at the HF/6-31G*(ECP-28-mwb) level, while keeping frozen the coordinates of the $(NH_3)_5$Ru(pyridyl) unit (up to the C_1 atom, see Chart 1). Single-point DFT/MRCI calculations were performed for the resulting complex **4'** (see Table 1). The FDAES shifts to the blue by 0.04 eV. Geometrical relaxation also affects the excited-state composition of the FDAES. As seen in Table 1, the doubly-excited character is smaller at this geometry (**4'**) than at the fully optimized B3P86 geometry (**4**).

Finally we address the longitudinal static first hyperpolarizabilities within the two-state approximation at different levels of theory (see Table 2). For **1**-**2**, DFT/MRCI, ADC(2), and TD-B3P86 give values in fair agreement with experiment. However, solvent effects become more important for **3**-**4** (compare e.g. the TD-B3P86 and PCM-TD-B3P86 values in Table 2). Hence, while the experimental β_{zzz} value for **3** is well reproduced by PCM-TD-B3P86, the β_{zzz} value for **4** is strongly overestimated at this level. Therefore, the latter complex deserves further exploration. As seen in Table 2, only ADC(2)/COSMO is capable of estimating both Δμ (i.e. the difference between the excited-state and ground-state dipole moments) and β_{zzz} accurately. Evidently, the change in the character of the FDAES in ADC(2) when going from the gas phase to solution leads to a substantial shift in both the Δμ and β_{zzz} values in complex **4**. Geometric relaxation effects are in this case less important than solvent effects (compare the DFT/MRCI values for **4** and **4'** in Table 2). In summary, the accurate prediction of NLO properties for such TM complexes requires both an appropriate treatment of their excited states with highly correlated electronic structure methods and an adequate inclusion of solvent effects. Overall, the ADC(2)/COSMO protocol provides the best agreement with experiment and is thus recommended for studying the NLO properties of these NLO-phores.

Table 1. Selected electronic transition energies (in eV) and oscillator strengths (in parentheses) of complexes **1**-**4** at different levels of theory.

Complex	State	TD-B3P86[a]	DFT/MRCI/ def2-SVP	ADC(2)/ def2-TZVP[b]	Exp[c]	Doubly exc. (%)
1	FDAES	2.83 (0.254)	2.80 (0.297)	2.72 (0.10) *2.13 (0.09)*	2.10	11.7
2	FDAES	2.78 (0.430)	2.80 (0.537)	2.80 (0.19) *2.00 (0.13)*	2.08	12.6
3	FDAES	2.85 (0.908)	2.91 (0.853)	3.01 (0.50) *2.08 (0.19)*	2.12	14.0
	LDES	-	2.72 (0.000)	-	-	93.2
4	FDAES	2.75 (2.069)	2.76 (2.033)	2.99 (1.68) *2.12 (0.29)*	2.18	14.4
	LDES	-	1.80 (0.000)	-	-	92.3
4'	FDAES	-	2.80 (2.125)	-	2.18	10.3
	LDES	-	1.86 (0.000)	-	-	92.9

[a] Results obtained at the TD-B3P86/6-31G*-LANL2DZ level of theory.
[b] Values in italics correspond to ADC(2)/COSMO values.
[c] Results in MeCN solvent from Refs. 3b-3c.

Table 2. Longitudinal static first hyperpolarizability, β_{zzz}, (in 100 a.u., T convention) of complexes **1**-**4** at different levels of theory within the two-state approximation. Theoretical $\Delta\mu_z$ and experimental Δμ values (in a.u.) for the FDAES are provided in parentheses.

Complex	DFT/ MRCI/ def2-SVP	ADC(2)/ def2-TZVP	ADC(2)/ COSMO/de def2-TZVP	TD-B3P86 *PCM-TD-B3P86*[a]	Exp.[b]
1	163 (6.66)	63 (6.78)	156 (8.93)	112 (8.33) *167 (6.16)*	139 (5.43)
2	326 (7.35)	117 (7.48)	306 (10.22)	112 (10.26) *359 (7.20)*	203 (6.37)
3	451 (7.20)	228 (6.84)	431 (10.96)	156 (10.99) *651 (9.54)*	558 (8.81)
4	353 (2.02)	281 (2.48)	638 (11.31)	134 (7.40) *1107 (11.62)*	550 (10.66)
4'	321 (1.84)		-	-	550 (10.66)

[a] Values from Ref. 3c. In italics: IEFPCM-TD-B3P86 values from Ref. 6.

[b] β_{zzz} values calculated from Stark spectroscopy data from Refs. 3b-3c.

Conclusions

The quantum-chemical characterization of electronically excited states and NLO responses is a fundamental ingredient towards designing the next generation of NLO-phores. The excited states of the herein reported Ru(II)-based NLO-phores present many inherent difficulties, including long-range CT and doubly excited states, which makes them especially challenging computationally. In this communication, we have revisited the spectroscopic and second-order NLO properties of Ru(II) complexes **1**-**4** bearing ammonia and (pyridyl)pyridinium ligands using correlated *ab initio* methods. ADC(2), DFT/MRCI and TD-B3P86 yield accurate excitation energies, oscillator strengths, and β values for the FDAES of **1**-**2**. However, the LDES can only be described with methods that appropriately deal with doubly excited states, such as DFT/MRCI. The effects of geometrical and solvent relaxation are found to be most relevant for the largest compound **4**. In this case, inclusion of solvent effects is indispensable to predict accurate NLO properties. The ADC(2)/COSMO protocol seems most reliable for the NLO properties of these NLO-phores

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Notes and references

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Electronic Supplementary Information (ESI) available: character of the FDAES of complex **4**, basis set dependence of the DFT/MRCI and ADC(2) results for **1** and **2**, main BHLYP orbitals involved in the FDAES of **3** and **4**. See DOI: 10.1039/c000000x/

[1] Molecular Nonlinear Optics Materials, Physics and Devices, ed. J. Zyss, Academic Press, Boston, MA, 1994.

[2] (a) D. R. Kanis, M. A. Ratner and T. J. Marks, *Chem. Rev.,* 1994, **94**, 195; (b) H. S. Nalwa, *Appl. Organomet. Chem.,* 1991, **5**, 349; (c) C. Manzur, M. Fuentealba, J. R. Hamon and D. Carrillo, *Coord. Chem. Rev.*, 2010, **254**, 765.

[3] (a) B. J. Coe, M. C. Chamberlain, J. P. Essex-Lopresti, S. Gaines, J. C. Jeffery, S. Houbrechts and A. Persoons, *Inorg. Chem*, 1997, **36**, 3284; (b) B.J. Coe, L.A. Jones, J.A. Harris, B.S. Brunschwig, I. Asselberghs, K. Clays, and A. Persoons, *J. Am. Chem. Soc.*, 2003, **125**, 862; (c) B.J. Coe, L.A. Jones, J.A. Harris, B.S. Brunschwig, I. Asselberghs, K. Clays, A. Persoons, J. Garin, and J. Orduna, *J. Am. Chem. Soc.*, 2004, **126**, 3880; (d) B. J. Coe, J. L. Harries, M. Heliwell, L. A. Jones, I. Asselberghs, K. Clays, B. S. Brunschwig, J. A. Harris, J. Garin and J. Orduna, *J. Am. Chem. Soc.*, 2006, **128**, 12192.

[4] (a) B. J. Coe, J. A. Harris, L. A. Jones, B. S. Brunschwig, K. Song, K. Clays, J. Garin, J. Orduna, S. J. Coles and M. B. Hursthouse, *J. Am. Chem. Soc.*, 2005, **127**, 4845; (b) B. J. Coe, J. Fielden, S. P. Foxon, I. Asselberghs, K. Clays and B. S. Brunschwig, *Inorg. Chem.*, 2010, **49**, 10718.

[5] B. J. Coe, J. A. Harris, B. S. Brunschwig, I. Asselberghs, K. Clays, J. Garin and J. Orduna, *J. Am. Chem. Soc.,* 2005, **127**, 13399.

[6] Y. Zhang, B. Champagne, *J. Phys. Chem. C*, 2013, **117**, 1833.

[7] (a) B. J. Coe, A. Avramopoulos, M. G. Papadopoulos, K. Pierloot, S. Vancoillie and H. Reis, *Chem. – Eur. J.,* 2013, **19**, 15955; (b) D. Escudero and L. González, *J. Chem. Theory Comput.*, 2012, **8**, 203.

[8] L. González, D. Escudero and L. Serrano-Andrés, *ChemPhysChem*, 2012, **13**, 28.

[9] D. Escudero and W. Thiel, *J. Chem. Phys.*, 2014, **140**, 194105.

[10] (a) B.J. Or rand J.F. Ward, *Mol. Phys.*, 1971, **20**, 513; (b) D.M. Bishop, *J. Chem. Phys.,* 1994, **100**, 6535.

[11] T. Helgaker, S. Coriani, P. Jørgensen, K. Kristensen, J. Olsen and K. Ruud, *Chem. Rev.*, 2012, **112**, 543.

[12] A. B. Trofimov, G. Stelter and J. Schirmer, *J. Chem. Phys.,* 1999, **111**, 9982.

[13] S. Grimme and M. Waletzke, J. Chem. Phys., 1999, **111**, 5645.

[14] (a) M. R. Silva-Junior, M. Schreiber, S. P. A. Sauer and W. Thiel, *J. Chem. Phys.,* 2008, **129**, 104103; (b) J. P. Götze and W. Thiel, *Chem. Phys.*, 2013, **415**, 247; (c) J.-M. Mewes, V. Jovanovic, C. M. Mariand and A. Dreuw, *Phys. Chem. Chem. Phys.*, 2014, **16**, 12393.

[15] F. Réal, V. Vallet, C. M. Marian, U. Wahlgren, *J. Chem. Phys.*, 2007, **127**, 214302.

[16] A. Dreuw and M. Wormit, *WIREs Comput. Mol. Sci.,* 2015, **5**, 82.

[17] D. Escudero and D. Jacquemin, *Dalton Trans.*, 2015, **44**, 8346.

[18] J. H. Starcke, M. Wormit, J. Schirmer and A. Dreuw, *Chem. Phys.*, 2006, **329**, 39.

[19] (a) C. M. Marian and N. Gilka, *J. Chem. Theory Comput.,* 2008, **4**, 1501; (b) M. Parac and S. Grimme, *Chem. Phys.,* 2003, **292**, 11; (c) L. Serrano-Andrés, R. Lindh, B. O. Roos and M. Merchán, *J. Phys. Chem.,* 1993, **97**, 9360.

[20] C.-P. Hsu, S. Hirata and M. Head-Gordon, *J. Phys. Chem. A*, 2001, **105**, 451.

[21] R. Ahlrichs, M. Bär, M. Häser, H. Horn and C. Kölmel, *Chem. Phys. Lett.* 1989, **162**, 165.

[22] A. Klamt and G. J. Schüürmann, *J. Chem. Soc. Perkin Trans.,* 1993, **2**, 799.

[23] B. Lunkenheimer and A. Köhn, *J. Chem. Theory Comput.,* 2013, **9**, 977.

[24] J. L. Oudar and D.S. Chemla, *J. Chem. Phys.*, 1977, **64**, 2664.

[25] M. Schreiber, M. R. Silva-Junior, S. P. A. Sauer and W. Thiel, *J. Chem. Phys.*, 2008, **128**, 134110.

[26] (a) B. G. Levine and T. J. Martínez, *J. Phys. Chem. A,* 2009, **113**, 12815; (b) A. Makida, H. Igarashi, T. Fujiwara, T. Sekikawa, Y. Harabuchi and T. Taketsugu, *J. Phys. Chem. Lett.,* 2014, **5**, 1760.
[27] M. Barborini and L. Guidoni, *J. Chem. Theory Comput.,* 2015, **11**, 508.
[28] R. H. Baughmann, B. E. Kohler, I. J. Levy and C. Spangler, *Synth. Met.*, 1985, **11**, 37.
[29] K. Nakayama, H. Nakano and K. Hirao, *Int. J. Quantum Chem.*, 1998, **66**, 157.
[30] C. J. Cramer and D. G. Truhlar, *Phys. Chem. Chem. Phys.,* 2009, **11**, 10757.

TOC:

We present an assessment of correlated electronic structure methods for the nonlinear optical properties of Ru(II) dyes.