

Computational and experimental studies of the electronic excitation spectra of EDTA and DTPA substituted tetraphenylporphyrins and their Lu complexes

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Abstract Ethylenediaminetetraacetic acid (EDTA) substituted and diethylenetriaminopentaacetic acid (DTPA) substituted aminated free-base tetraphenylporphyrins (H_2ATPP) and the corresponding lutetium(III) complexes have been studied computationally at the density functional theory (DFT) and second-order algebraic diagrammatic construction (ADC(2)) levels using triple- ξ basis sets augmented with polarization functions. The molecular structures were optimized using Becke's three-parameter hybrid functional (B3LYP). The electronic excitation spectra in the range of 400–700 nm were calculated using the ADC(2) and the linear-response time-dependent DFT methods. The calculated spectra are compared to those measured in ethanol solution. The calculated excitation energies agree well with those deduced from the experimental spectra. The excitation energies for the Q_x band calculated at the B3LYP and ADC(2) level are 0.20–0.25 eV larger than the experimental values. The excitation energies for the Q_y band calculated at the B3LYP level are 0.10–0.20 eV smaller than the ADC(2) ones and are thus in good agreement with experiment. The calculated excitation energies corresponding to the B_x and B_y bands are 0.10–0.30 eV larger than the experimental values. The excitation energies of the B_x and B_y bands calculated at the B3LYP

level are in somewhat better agreement with experiment than the ADC(2) ones. The calculated and measured band strengths largely agree.

Keywords Ethylenediaminetetraacetic acid · Tetraphenylporphyrins · The approximate second-order coupled-cluster

Introduction

Porphyrins and their complexes with metals are successfully used for charge transport layers in electroluminescent devices, nonlinear switches and as colorants, pigments, and drugs. The lanthanide-porphyrin complexes can be utilized in medicinal applications, because they have useful luminescent and magnetic properties [1]. The relatively low chemical stability in comparison with many other metaloporphyrins and the very small energy loss due to infrared (IR) luminescence are some important properties for applications of lanthanide-porphyrin complexes as luminescent probes. The design of new stable lanthanide-porphyrin complexes is therefore one of the active research fields of modern porphyrin chemistry. A deeper knowledge of relations between optical properties and their molecular structures is of central importance when aiming at the design of lanthanide-porphyrin based optical devices and functional molecules.

The approximate second-order coupled-cluster (CC2) method has proven to be useful in studies of excited states of large molecules [2–6]. A closely related Hermitian method is the algebraic diagrammatic construction model through second-order ADC(2), which was originally proposed by Schirmer [7, 8]. It has more recently been implemented by Hättig in Turbomole employing the resolution of the identity

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(RI) approximation [9]. The ADC(2) method is roughly a factor of three faster than CC2 when excitation energies and oscillator strengths are calculated. CC2 and ADC(2) are though computationally more expensive than the time dependent density functional theory (TDDFT) method [10, 11]. However, all virtual orbitals are not needed for describing the differential correlation effects between the ground and the lowest excited states [12–19]. The feasibility of using a reduced-virtual-space (RVS) approach in the calculation of excitation energies of large molecules at the CC2 level has recently been demonstrated [19]. In the RVS calculations, all virtual orbitals above a given orbital energy threshold are omitted in the correlation calculation of the excitation energies. The accuracy of the RVS approach has been investigated by performing CC2 calculations with different energy thresholds on a rhodopsin model and other biochromophores [19]. Omitting all virtual orbitals above 50 eV introduces errors in the excitation energies that are smaller than 0.1 eV, which can be compared to the generally expected accuracy of ± 0.1 – 0.3 eV for excitation energies obtained using the ADC(2) method [19]. A very extensive study of triplet states of organic semiconductors showed that the relative splitting between

higher excited states is even less affected by the omission of virtual orbitals due to cancellation of errors [20].

The use of the RVS approach significantly reduces the computational time of ADC(2) and CC2 calculations rendering application on large molecules at the ADC(2) and CC2 levels feasible. The RVS approach can also be used in combination with other ab initio correlation methods as well as for speeding up TDDFT calculations.

New interesting mezasubstituted porphyrins have recently been synthesized [21]. They consist of aminated free-base tetraphenylporphyrin (H_2ATPP) with ethylenediaminetetraacetic acid (EDTA) or diethylenetriaminopentaacetic acid (DTPA) substituted to one of the phenyls attached to the porphyrin ring in the meta position. The EDTA and DTPA groups can complex a lutetium(III) cation forming a chelate. The substituted tetraphenylporphyrins and their rare earth complexes can be used as probes in medicine or for capturing solar energy in solar-cell devices [22–24]. In the work of Ermolina et al., the energies of the obtained peak positions of the absorption bands of H_2ATPP -EDTA, H_2ATPP -DTPA, H_2ATPP -LuEDTA, and H_2ATPP -LuDTPA in ethanol solution were reported [25]. In the recent studies of Valiev et al., the experimental extinction

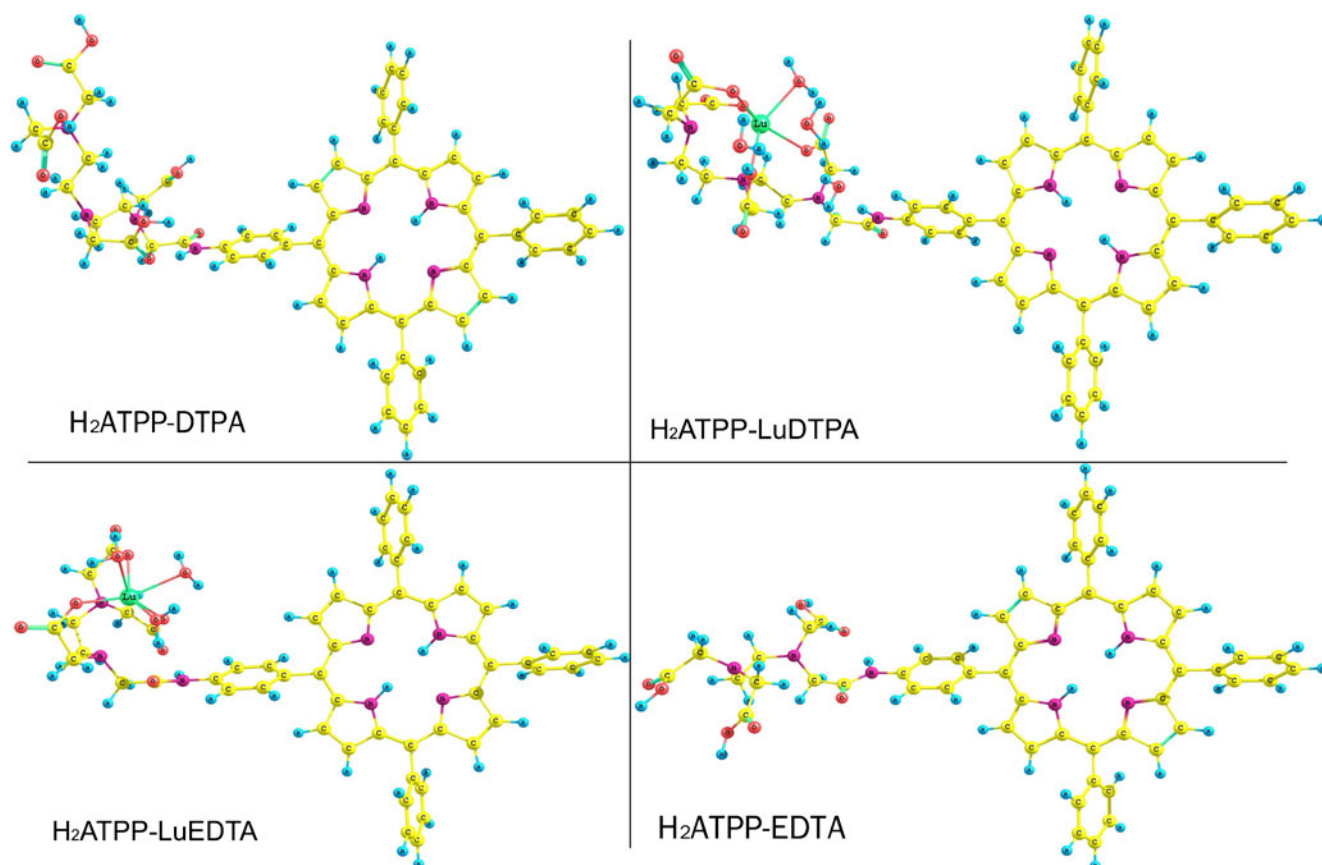


Fig. 1 The ground-state molecular structures of H_2ATPP -EDTA, H_2ATPP -DTPA, H_2ATPP -LuEDTA and H_2ATPP -LuDTPA optimized at the B3LYP/TZVP level of theory

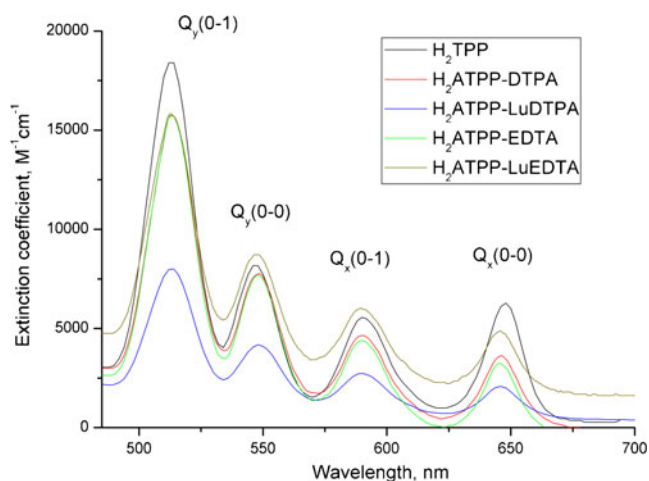


Fig. 2 The electronic absorption spectra of H_2TPP -EDTA, H_2ATPP -DTPA, H_2ATPP -LuEDTA and H_2ATPP -LuDTPA recorded for a porphyrin concentration of $C=2 \cdot 10^{-5}$ M in C_2H_5OH

coefficients were reported for H_2ATPP -EDTA and H_2ATPP -DTPA. The theoretical analysis of the absorption spectra of H_2ATPP -EDTA and H_2ATPP -DTPA were carried out at the TDDFT/6-31G(d,p) level [26, 27].

In this work, the absorption spectra in the range of 400–700 nm have been recorded for H_2ATPP -LuEDTA and H_2ATPP -LuDTPA dissolved in ethanol. The experimental absorption spectra of H_2ATPP -EDTA, H_2ATPP -DTPA, H_2ATPP -LuEDTA and H_2ATPP -LuDTPA have been analyzed by performing quantum chemical calculations. The electronic excitation energies and the corresponding oscillator strengths have been calculated using the second-order algebraic diagrammatic construction and the linear-response time-dependent density functional theory methods. H_2ATPP -EDTA and H_2ATPP -DTPA were studied at the B3LYP and

ADC(2) levels, whereas the H_2ATPP -LuEDTA and H_2ATPP -LuDTPA spectra were studied computationally using merely B3LYP calculations.

Experimental and calculation details

The title compounds were synthesized according to the procedures described in Ref. 25. Their purity and identity were assessed using elemental analysis, thin-layer chromatography, mass spectrometry, and 1H NMR spectroscopy. Chemically pure ethanol (96 %) was used as solvent. The ultraviolet–visible (UV–vis) absorption spectra were recorded at 298 K using an Evolution 600 (Thermo Scientific) spectrophotometer. The concentration of the free-base tetraphenylporphyrin (H_2TPP) and the substituted aminated free-base tetraphenylporphyrins (H_2ATPP -EDTA and H_2ATPP -DTPA), and their Lu complexes (H_2ATPP -LuEDTA and H_2ATPP -LuDTPA) in the ethanol solution was $C=2 \cdot 10^{-5}$ M. The line positions were recorded with accuracy of about 0.5 nm and the extinction coefficients were determined with errors smaller than 10 %.

The molecular structures were optimized at the density functional theory (DFT) level using Becke's three-parameter functional (B3LYP) [28, 29] as implemented in Turbomole [30]. The Karlsruhe triple- ξ basis sets (def2-TZVP) [31, 32] were employed in the calculations. We omit def2 in the following.

The vertical excitation energies were calculated at the linear-response time-dependent DFT (TDDFT) level using the B3LYP functional [10, 11]. The electronic excitation energies were also calculated at the second-order algebraic diagrammatic construction ADC(2) level using the resolution of the identity (RI) approximation to speed up the calculations

Table 1 Comparison of vertical excitation energies (E in eV) and oscillator strengths (f) for H_2TPP calculated at the B3LYP and ADC(2) levels with values deduced from spectroscopic measurements in

C_2H_5OH . The experimental extinction coefficients (ϵ in $M^{-1} cm^{-1}$) and the half-widths of the peaks (in cm^{-1}) are also reported

State	B3LYP		ADC(2)		Experiment ^a				
	E	f	E	f	Band	E	ϵ	$\Delta\nu_{1/2}$ (cm^{-1})	f
Qx	2.15	0.018	2.16	0.063	$Q_x(0-0)$	1.91	6183	453	0.012
	2.13	(0.03) ^b			$Q_x(0-1)$	2.10	5567	744	0.018
Qy	2.29	0.027	2.48	0.13	$Q_y(0-0)$	2.26	8169	773	0.027
	2.27	(0.05) ^b			$Q_y(0-1)$	2.42	18402	877	0.070
Bx	3.15	0.85	3.25	1.46	B_x and B_y	3.01	400000	1000	1.73
	3.14	(0.85) ^b							
By	3.25	1.33	3.29	1.65					
	3.25	(1.35) ^b							

^a The experimental values are taken from Ref. [26]

^b Calculated at the PCM/TDDFT/B3LYP/6-31G(d,p) level in Ref. [26]

Table 2 Comparison of vertical excitation energies (E in eV) and oscillator strengths (f) for H₂TPP-EDTA calculated at the B3LYP and ADC(2) levels with values deduced from spectroscopic measurements in C₂H₅OH. The experimental extinction coefficients (ϵ in M⁻¹ cm⁻¹) and the half-widths of the peaks (in cm⁻¹) are also reported

State	B3LYP		ADC(2)		Experiment ^a				
	E	f	E	f	Band	E	ϵ	$\Delta\nu_{1/2}$ (cm ⁻¹)	f
Q _x	2.14	0.024	2.10	0.076	Q _x (0–0)	1.91	3238	470	0.007
	2.1	(0.03) ^b			Q _x (0–1)	2.11	4391	600	0.011
Q _y	2.29	0.037	2.44	0.18	Q _y (0–0)	2.25	7684	780	0.027
	2.25	(0.06) ^b			Q _y (0–1)	2.42	15752	900	0.060
B _x	3.12	1.03	3.22	1.58	B _x and B _y	3.00	309500	1010	1.34
	3.14	(0.9) ^b							
B _y	3.2	1.28	3.27	1.69					
	3.19	(1.09) ^b							

^a The experimental values are taken from Ref. [26]

^b Calculated at the PCM/TDDFT/B3LYP/6-31G(d,p) level in Ref. [26]

[7, 9, 33, 34]. The reduced-virtual-space (RVS) approach with an energy threshold of 50 eV [19] was used at the ADC(2) level making the ab initio correlation calculations on the large substituted porphyrins feasible. All calculations have been done with TURBOMOLE [30].

Results and discussion

The molecular structures

The molecular structures were optimized at the B3LYP/TZVP level. The obtained structures agree well with experimental data such as X-ray structures for EDTA [35], DTPA [36], LuEDTA, LuDTPA [37] and H₂TPP [38, 39], whereas

the X-ray structures have not been determined for the studied molecules. The available X-ray data were used as initial structures for the optimization of the ground-state structures of H₂ATPP-EDTA, H₂ATPP-DTPA, H₂ATPP-LuEDTA, and H₂ATPP-LuDTPA. The optimized molecular structures are depicted in Fig. 1. The Cartesian coordinates are given as [Supplementary material](#).

Electronic excitation spectra

The experimental absorption spectra in the visible range measured for considered molecule in ethanol are shown in Fig. 2. The corresponding excitation energies obtained in the TDDFT and ADC(2) calculations are compared to experimental data in Table 1, 2, 3, 4 and 5. The experimental oscillator strengths

Table 3 Comparison of vertical excitation energies (E in eV) and oscillator strengths (f) for H₂TPP-DTPA calculated at the B3LYP and ADC(2) levels with values deduced from spectroscopic measurements

State	B3LYP		ADC(2)		Experiment ^a				
	E	f	E	f	Band	E	ϵ	$\Delta\nu_{1/2}$ (cm ⁻¹)	f
Q _x	2.10	0.032	2.09	0.074	Q _x (0–0)	1.91	3619	430	0.007
	2.11	(0.06) ^b			Q _x (0–1)	2.10	4643	714	0.014
Q _y	2.20	0.063	2.44	0.19	Q _y (0–0)	2.25	7763	866	0.029
	2.25	(0.10) ^b			Q _y (0–1)	2.42	15732	877	0.060
B _x	3.07	0.9	3.21	1.57	B _x and B _y	3.00	285000	1030	1.23
	2.98	(1.35) ^b							
B _y	3.08	1.2	3.27	1.69					
	3.04	(1.18) ^b							

^a The experimental values are taken from Ref. [27]

^b Calculated at the PCM/TDDFT/B3LYP/6-31G(d,p) level in Ref. [27]

Table 4 Comparison of vertical excitation energies (E in eV) and oscillator strengths (f) for H₂TPP-LuDTPA calculated at the B3LYP level with values deduced from spectroscopic measurements inC₂H₅OH. The experimental extinction coefficients (ε in M⁻¹ cm⁻¹) and the half-widths of the peaks (in cm⁻¹) are also reported

State	B3LYP			Experiment			
	E	f	Band	E	ε	Δν _{1/2} (cm ⁻¹)	f
Q _x	2.10	0.024	Q _x (0–0)	1.92	2077	552	0.005
			Q _x (0–1)	2.10	2745	954	0.011
Q _y	2.30	0.038	Q _y (0–0)	2.25	4179	866	0.016
			Q _y (0–1)	2.42	8000	1000	0.035
B _x	3.10	1.03	B _x and B _y	3.00	150000	1050	0.6
B _y	3.2	1.3					

were deduced from the recorded spectra using $f = 4.32 \cdot 10^{-9} \int \epsilon d\nu$ [40]. The integral was estimated as $\int \epsilon d\nu = \epsilon_{\max} \Delta\nu_{1/2}$, where ϵ_{\max} (in M⁻¹ cm⁻¹) is the extinction coefficient at the peak maximum and $\Delta\nu_{1/2}$ (in cm⁻¹) is the half-width of the spectral line. This expression for the experimental oscillator strengths results in uncertainties that are less than 6 % [40].

The electronic absorption spectra of porphyrins and their derivatives depend very weakly on the solvent [41]. The excitation energies and oscillator strengths deduced from spectra recorded for molecules in solvents can therefore be readily compared with excitation energies and oscillator strengths obtained in calculations on isolated molecules. According to the Frank-Condon principle, the calculated excitation energy of the Q_x band must be compared to the peak maximum of the vibrational band (Q_x(0–0) or Q_x(0–1)) with the largest extinction coefficient. The same holds for the vibrational bands of the Q_y transition. As no vibrational effects are considered in the present calculations, the calculations cannot provide any separate values for the individual vibrational bands. As the Q_x(0–1) and Q_y(0–1) bands have larger oscillator strengths than Q_x(0–0) and Q_y(0–0), respectively, the calculated excitation energies must be compared to the energies of the Q_x(0–1) and Q_y(0–1) bands. The

excitation energies of the Q_x and Q_y bands of H₂ATPP-EDTA and H₂ATPP-DTPA calculated at the ADC(2) level are generally in better agreement with experiment than the corresponding values calculated at the B3LYP level. The differences between the ADC(2) and B3LYP excitation energies are at most 0.2 eV. The oscillator strengths of Q_x, Q_y, B_x, B_y and the excitation energies of the B_x and B_y bands calculated at the B3LYP level are in rather good agreement with experiment. The present calculations confirm that the bonding of EDTA or DTPA to H₂TPP decreases the intensities of the Q_x and Q_y bands. The calculated oscillator strengths of the Soret (B) bands are generally much larger than the ones deduced from the experimental spectra. Similar results have previously been obtained in other computational studies on porphyrins [42]. The calculated excitation energies and oscillator strengths of H₂TPP, H₂ATPP-EDTA and H₂ATPP-DTPA are compared to experimental values in Tables 1, 2 and 3, respectively.

The experimental absorption spectra in the visible range (400–700 nm) recorded for H₂ATPP-LuEDTA and H₂ATPP-LuDTPA in ethanol are shown in Fig. 2. The EDTA and DTPA molecules do not absorb light in the visible nor in the near UV regions. Lutetium has closed shells in LuEDTA and LuDTPA

Table 5 Comparison of vertical excitation energies (E in eV) and oscillator strengths (f) for H₂TPP-LuEDTA calculated at the B3LYP level with values deduced from spectroscopic measurements inC₂H₅OH. The experimental extinction coefficients (ε in M⁻¹ cm⁻¹) and the half-widths of the peaks (in cm⁻¹) are also reported

State	B3LYP			Experiment			
	E	f	Band	E	ε	Δν _{1/2} (cm ⁻¹)	f
Q _x	2.15	0.023	Q _x (0–0)	1.92	4874	450	0.009
			Q _x (0–1)	2.10	6017	750	0.019
Q _y	2.29	0.036	Q _y (0–0)	2.25	8724	866	0.033
			Q _y (0–1)	2.42	15824	1000	0.07
B _x	3.13	0.97	B _x and B _y	3.00	444400	1060	1.92
B _y	3.22	1.47					

complexes implying that it does not directly influence the electronic absorption spectra of the H₂ATPP-LuEDTA and H₂ATPP-LuDTPA complexes in the visible range. The differences in the electronic absorption spectra relative to H₂TPP are due to structural distortions of the tetraphenylporphyrin moiety caused by the EDTA and DTPA substitutions, which are also affect the electronic structure of the porphyrin. The absorption spectra and the excitation energies for H₂ATPP-LuDTPA given in Table 4 show that the Q_x(0–0) peak of the experimental spectrum of H₂ATPP-LuEDTA is blue shifted by 4 nm as compared to unsubstituted H₂TPP.

The calculated excitation energies for H₂ATPP-LuEDTA are compared in Table 5. The differences between the experimental absorption spectra of the studied molecules are mainly due to differences in the absorption intensities. The Soret band (B) as well as the Q_x(0–1) and Q_y(0–0) bands have the largest intensity in the absorption spectrum of H₂ATPP-LuEDTA. The weakest absorption intensities were obtained for H₂ATPP-LuDTPA.

ADC(2) calculations could not be employed in the studies of the excited states of the H₂ATPP-LuEDTA and H₂ATPP-LuDTPA lutetium complexes, because no auxiliary basis sets have been optimized for that element. Calculations on the corresponding free-base porphyrins showed that the excitation spectra obtained at the ADC(2) and B3LYP levels are very similar. The electronic excitation spectra obtained in the B3LYP calculations are in somewhat better agreement with experiment than the ADC(2) ones. For H₂ATPP-LuEDTA and H₂ATPP-LuDTPA, the calculated excitation energies of the Q_x band agree well with values deduced from the experimental spectra. For the Q_y, B_x, and B_y bands the discrepancies between the calculated and measured excitation energies are in the range of 0.10–0.20 eV. The calculated oscillator strengths for the Q_y band is somewhat smaller than the ones obtained experimentally, whereas the calculated and experimental band strengths of the Q_x transitions agree well.

Conclusions

In the present work, the equilibrium molecular structures of the electronic ground state of the recently synthesized H₂ATPP-EDTA, H₂ATPP-DTPA, H₂ATPP-LuEDTA, and H₂ATPP-LuDTPA compounds were calculated at the DFT level using the B3LYP functional and TZVP basis sets. The experimental UV–vis spectra show that the peak positions of the absorption band of H₂TPP, H₂ATPP-EDTA, H₂ATPP-DTPA, H₂ATPP-LuEDTA, and H₂ATPP-LuDTPA molecules almost coincide with wavelength shifts that do not exceeded 4 nm. The main differences in the absorption spectra of the investigated molecules are due to the absorption intensities of bands. Calculations of the few lowest excitation energies using the second-order algebraic

diagrammatic construction method (ADC(2)), which is a modern ab initio correlated quantum chemistry approach, yield for the Q bands a somewhat better agreement with experiment than time-dependent DFT (TDDFT) calculations. For the Soret band the TDDFT methods seems to perform better than ADC(2). The oscillator strengths calculated at the TDDFT level are in better agreement with experimental data than the ones obtained using ADC(2) calculations.

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References

1. Winpenny REP (1998) The structures and magnetic properties of complexes containing 3d- and 4f-metals. *Chem Soc Rev* 27:447–452
2. Send R, Sundholm D (2007) Coupled-cluster studies of the lowest excited states of the 11-cis-retinal chromophore. *Phys Chem Chem Phys* 9:2862–2867
3. Köhn A, Hättig C (2004) On the nature of the low-lying singlet states of 4-(dimethyl)aminobenzonitrile. *J Am Chem Soc* 126:7399–7410
4. Lehtonen O, Sundholm D (2006) Coupled-cluster studies of the electronic excitation spectra of silanes. *J Chem Phys* 125:144314
5. Sobolewski AL, Domcke W, Hättig C (2006) Photophysics of organic photostabilizers. Ab initio study of the excited-state deactivation mechanisms of 2-(2'-hydroxyphenyl)benzotriazole. *J Phys Chem A* 110:6301–6306
6. Hellweg A, Hättig C, Merke I, Stahl W (2006) Microwave and theoretical investigation of the internal rotation in m-cresol. *J Chem Phys* 124:204305
7. Schirmer J (1982) Beyond the random-phase approximation: a new approximation scheme for the polarization propagator. *Phys Rev A* 26:2395–2416
8. Trofimov AB, Schirmer (1995) An efficient polarization propagator approach to valence electron excitation spectra. *J J Phys B* 28:2299–2325
9. Hättig C (2005) Structure optimizations for excited states with correlated second-order methods: CC2 and ADC(2). *Adv Quantum Chem* 50:37–60
10. Bauernschmitt R, Ahlrichs R (1996) Treatment of electronic excitations within the adiabatic approximation of time dependent density functional theory. *Chem Phys Lett* 256:454–464
11. Furche F, Ahlrichs R (2002) Adiabatic time-dependent density functional methods for excited state properties. *J Chem Phys* 117:7433–7447
12. Hada M, Yokono H, Nakatsuji H (1987) Frozen core and virtual orbitals in the MCSCF theory. *Chem Phys Lett* 141:339–345
13. Adamowicz L, Bartlett RJ (1987) Optimized virtual orbital space for high-level correlated calculations. *J Chem Phys* 86:6314–6324
14. Sosa C, Geertsen J, Trucks GW, Bartlett RJ (1989) Selection of the reduced virtual space for correlated calculations. An application to the energy and dipole moment of Water. *Chem Phys Lett* 159:148–154
15. Taube AG, Bartlett RJ (2005) Frozen Natural orbitals: systematic basis set truncation for coupled cluster theory. *Collect Czech Chem Commun* 70:837–850

16. Neogrady P, Pitonak M, Urban M (2005) Optimized virtual orbitals for correlated calculations: an alternative approach. *Mol Phys* 103:2141–2157
17. Köhn A, Olsen J (2006) Coupled-cluster with active space selected higher amplitudes: performance of seminatural orbitals for ground and excited state calculations. *J Chem Phys* 125:174110
18. Piacenza M, Della Sala F, Fabiano E, Maiolo T, Gigli (2007) Torsional effects on excitation energies of thiophene derivatives induced by -substituents: comparison between time-dependent density functional theory and approximated coupled cluster approaches. *G J Comput Chem* 29:451–457
19. Send R, Kaila VRI, Sundholm D (2011) Reduction of the virtual space for coupled-cluster excitation energies of large molecules and embedded systems. *J Chem Phys* 134:214114
20. Pabst M, Sundholm D, Köhn A (2012) Ab initio studies of triplet-state properties for organic semiconductor molecules. *J Phys Chem C* (submitted)
21. Semenishin N, Rusakova N, Mazepa A, Korovin Y (2009) Synthesis of ditopic porphyrins and lanthanide complexes on their basis: luminescent features. *Macrocyclics* 2(1):57–59
22. Gunes S, Neugebauer H, Sariciftci NS (2007) Conjugated polymer-based organic solar cells. *Chem Rev* 107:1324–1338
23. Evans R, Douglas P (2009) Design and color response of colorimetric multilumophore oxygen sensors. *Appl Mater Interfaces* 1:1023–1030
24. Evans R, Douglas P, Winscom C (2006) Coordination complexes exhibiting room-temperature phosphorescence: evaluation of their suitability as triplet emitters in organic light emitting diodes. *Coord Chem Rev* 250:2093–2126
25. Ermolina EG, Kuznetsova RT, Gadirov RM, Maier GV, Semenishin NN, Rusakova NV, Korovin YV (2010) Luminescence of the free bases of chelate substituted tetraphenylporphyrin derivatives and their complexes with lutetium. *High Energy Chem* 44:387–424
26. Valiev RR, Ermolina EG, Kalugina YN KRT, Cherepanov VN (2012) Electronic absorption spectrum of monoamine tetraphenylporphyrin with the complexon of ethylenediaminetetraacetic acid as substitute. *Spectrochim Acta A*. doi:10.1016/j.saa.2011.10.075
27. Valiev RR, Ermolina EG, Kuznetsova, RT, Cherepanov VN (2012) Electronic absorption spectrum of monoamine tetraphenylporphyrin with the complexon of diethylenetriaminediacetic acid as substitute. *Russian J Phys* 54:1160–1165
28. Lee C, Yang W, Parr RG (1988) Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys Rev B* 37:785–789
29. Becke AD (1993) Density-functional thermochemistry. III. The role of exact exchange. *J Chem Phys* 98:5648–5652
30. Ahlrichs R, Bär M, Häser M, Horn H, Kölmel C (1989) Electronic structure calculations on workstation computers: the program system TURBOMOLE. *Chem Phys Lett* 162:165–169, current version: see <http://www.turbomole.com>.
31. Schäfer A, Huber C, Ahlrichs R (1994) Fully optimized contracted gaussian-basis sets of triple zeta valence quality for atoms Li to Kr. *J Chem Phys* 100:5829–5835
32. Weigend F, Ahlrichs R (2005) Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. *Phys Chem Chem Phys* 7:3297–3305
33. Hättig C, Köhn A (2002) Transition moments and excited-state first-order properties in the coupled-cluster model CC2 using the resolution-of-the-identity approximation. *J Chem Phys* 117:6939–6952
34. Hättig C, Weigend FJ (2000) CC2 excitation energy calculations on large molecules using the resolution of the identity approximation. *Chem Phys* 113:5154–5161
35. Ladd MFC, Povey DC (1973) Crystallographic and spectroscopic studies on ethylenediaminetetraacetic acid (edta). *J Chem Cryst* 3:15–23
36. Shkolnikova LM, Polyanchuk GV, Dyatlova NM, Polyakova IA (1984) An X-ray study of organic ligands of complexon type. *J Struct Chem* 25:445–448
37. Aime S, Benetollo F, Bombieri G, Colla S, Fasano M, Paoletti S (1997) Non-ionic Ln(III) chelates as MRI contrast agents: synthesis, characterisation and ¹H NMR relaxometric investigations of bis(benzylamide)diethylenetriaminopentaacetic acid Lu(III) and Gd(III) complexes. *Inorg Chim Acta* 254:63–70
38. Silvers SJ, Tulinsky A (1967) The crystal and molecular structure of trichloro tetraphenylporphyrin. *J Am Chem Soc* 89:3331–3337
39. Gassman PG, Ghosh A, Almlöf J (1992) Electronic effects of peripheral substituents in porphyrins: x-ray photoelectron spectroscopy and ab initio self-consistent field calculations. *J Am Chem Soc* 114:9990–10000
40. McGlynn SP, Azumi T, Kinoshita M (1969) Molecular spectroscopy of the triplet state. Prentice-Hall Englewood Cliffs, NJ
41. Solov'ev KN, Gurinovich GP, Sevchenko AN (1963) The spectroscopy of the porphyrins. *Sov Phys Usp* 6:67–105
42. Baerends EJ, Ricciardi G, Rosa A, van Gisbergen SJA (2002) A DFT/TDDFT interpretation of the ground and excited states of porphyrin and porphyrazine complexes. *Coord Chem Rev* 2002:230