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Application of Time-Dependent Density Functional Theory and Optical Spectroscopy toward the Rational Design of Novel 3,4,5-Triaryl-1-R-1,2-diphospholes

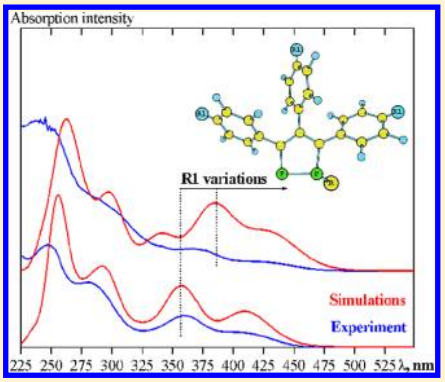
Elena E. Zvereva,*[,†,‡] Stefan Grimme,*[,‡] Sergey A. Katsyuba,[†] Timur I. Burganov,[†] Almaz A. Zagidullin,[†] Vasily A. Milyukov,[†] and Oleg G. Sinyashin[†]

[†]A.E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Centre, Russian Academy of Sciences, Arbuzov str. 8, 420088 Kazan, Russia

[‡]Mulliken Center for Theoretical Chemistry, Institut für Physikalische und Theoretische Chemie, Universität Bonn, Beringstr. 4, 53115 Bonn, Germany

Supporting Information

ABSTRACT: Twenty 3,4,5-triaryl-1-R-1,2-diphospholes were studied within the framework of density functional theory (DFT) and experimentally by UV/vis spectroscopy to check their suitability for opto-electronic applications. Time-dependent DFT (TD-DFT) calculations employing the PBE0 hybrid density functional combined with moderately sized def-TZVP basis set were shown to excellently reproduce the experimental absorption spectra of various 1,2-diphospholes. Frontier molecular orbital analysis reveals that HOMO and LUMO are mainly localized on the diphosphole ring and, to some extent, on the aryl moieties. The HOMO−LUMO energy gap can be easily tuned by variation of substituents introduced in para-positions of the aryl moieties and, to a lesser extent, by modification of the R group at phosphorus atom. As a result, both position and intensity of the absorption bands with highest wavelength are strongly influenced by the above structural changes. The UV-spectra simulations reveal that the introduction of donor groups like *para*-OMe, *para*-NMe_2, and *para*-N(H)Ph, which are in n−π conjugation with the aryl moieties, should result in absorption of visible light by the corresponding 1,2-diphospholes, thus making them promising candidates for new functional materials.

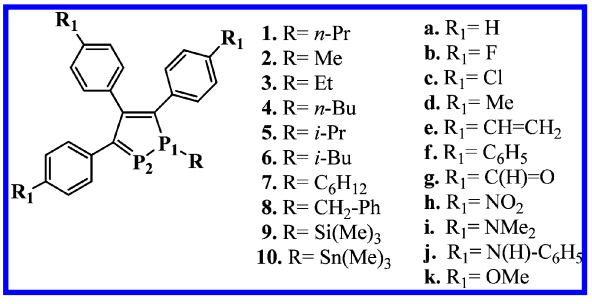


INTRODUCTION

Since the 1990s the π-conjugated materials based on organophosphorus compounds represent a valuable addition to the pool of building blocks for molecular electronics.[1−3] Phospholes (five-membered 6π-systems with one or more phosphorus atoms) as subunits for the π-conjugated systems are the most widely investigated P-heterocycles, because they display interesting electronic properties with both high electron-accepting and electron-transporting abilities.[4,5] The key property of these P-rings for molecular engineering of π-conjugated systems is based on their electronic structure[6] with a reactive phosphorus center. Low aromatic character of these P-heteroles with a low-lying LUMO, σ^*(P-R)−π^*(1,3-diene) hyperconjugation[7,8] and high electronic affinity allow tuning the photophysical properties of phosphole-based π-conjugated systems by chemical modifications of the reactive P-atoms and influencing the extent of conjugation over the diene moiety.[2,8,9] Richness and diversity of phosphorus chemistry together with mentioned specific properties of organophosphorus derivatives should be fully exploited for the engineering of a wide range of novel conjugated materials.[10]

The main objective of this work is to rationalize the structure−property relationship of some 3,4,5-triaryl-1-R-1,2-diphospholes (Chart 1). They are based on a five-membered ring with two neighboring phosphorus atoms, unlike the monophospholes with only one phosphorus atom in the cycle, which are the most studied and described in literature. These 1,2-diphospholes combine the structural elements of both 1H- and 2H-phospholes in one molecule, which increases its

Chart 1. 3,4,5-Triaryl-1-R-1,2-diphospholes Investigated in the Present Paper



1. R= *n*-Pr
2. R= Me
3. R= Et
4. R= *n*-Bu
5. R= *i*-Pr
6. R= *i*-Bu
7. R= C_6H_{12}
8. R= CH_2-Ph
9. R= $Si(Me)_3$
10. R= $Sn(Me)_3$

a. R_1= H
b. R_1= F
c. R_1= Cl
d. R_1= Me
e. R_1= $CH{=}CH_2$
f. R_1= C_6H_5
g. R_1= C(H)=O
h. R_1= NO_2
i. R_1= NMe_2
j. R_1= N(H)-C_6H_5
k. R_1= OMe

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aromaticity[11−13] and, hence, most probably can change dramatically their optical properties. In present paper we study the UV/vis spectra of the title compounds and use quantum chemical calculations to better understand the origin of the absorption bands and to find their relationship with the electronic and geometrical structure of the molecules. We demonstrate that the computations can be used as a practical tool for prediction of the spectra of yet nonsynthesized molecules, thus allowing the design of new compounds performing light-absorption/emission properties necessary for promising candidates for new materials.[1,5]

COMPUTATIONAL DETAILS

All calculations were performed with the Turbomole 6.4 program package.[14] In the ground state SCF calculations with hybrid density functionals, the RI-JK approach for the two-electron integrals[15−18] was employed. In general the def-TZVP[19] AO basis set with accompanying auxiliary basis sets[20−22] was used, but the def-SVP[19] and the def-QZVP[19] AO basis sets were tested as well. All structures were optimized with the PBE functional.[23,24] Time-dependent density functional response theory (TD-DFT)[25,26,16,27] has been employed to compute the vertical excitation energy (i.e., absorption wavelength) and oscillator strength for the ground state optimized geometries in the gas phase. The influence of surrounding media was neglected, as inclusion of weakly interacting solvent molecules within PCM or COSMO continuum solvation models just induces a small (4−10 nm) bathochromic shift of the entire spectrum.[28,29] Various functionals have been used in the literature for the computation of absorption spectra of organic molecules.[28−33] The semilocal PBE[23] functional and two hybrid functionals PBE0[34] and BHLYP[35,36] have been tested by comparing results of the computations with available experimental results. PBE0 and BHLYP importantly differ by the amount of nonlocal Fock-exchange included in the functional (25% vs 50%) which is known to influence excitation energies and excited state properties rather strongly.[30] In most cases, the spectra were broadened by Gaussian functions with a half-width at 1/e height of 0.4 eV. No energy shift has been applied. The dipole length representation is used to calculate oscillator strengths discussed in the present paper. Molecular orbitals based on PBE/def-TZVP optimized structures recalculated within Gaussian 03[37] (PBE0/def-TZVP) were visualized in the ChemCraft 1.6 program[38] with a 0.03 contour value. The diagrams were created with using Xmgrace.[39]

EXPERIMENTAL SECTION

1,2-Diphospholes **1a**, **1b**, **1c**, **10a**, and **5k** were synthesized according to the earlier described protocol.[40]

UV/vis spectra were recorded at room temperature on a Perkin-Elmer Lambda 35 spectrometer, using 10 mm quartz cells. Spectra were registered with a scan speed of 480 nm/min, using a spectral width of 1 nm. All samples were prepared as solutions in hexane with the concentrations of ca. ~10^{-4} mol/L.

RESULTS AND DISCUSSION

Electronic Absorption Spectra in the Gas Phase from TD-DFT Calculations. Several publications were devoted to TD-DFT computations of UV/vis spectra of some monophosphole derivatives with various functional and basis sets.[4,8,41] No simulations of UV/vis spectra of the polyphospholes were reported, though DFT and MP2 quantum chemical methods have been applied for the analysis of structure, IR spectra and magnetic properties of polyphospholes.[13,42]

Therefore, it was first necessary to find an acceptable level for the computations yielding within reasonable CPU times reliable results. For this purpose the UV/vis spectrum of **1a** was recorded and used as a benchmark (Figure 1) for the simulations. The experimental spectrum comprises an intensive band at 211 nm and a weaker band at 244 nm due to absorptions of aromatic units[43,44] and three even weaker bands at 281, 359, and 408 nm, which preliminary can be attributed with absorptions of 1,2-diphosphole moiety. It should be noted

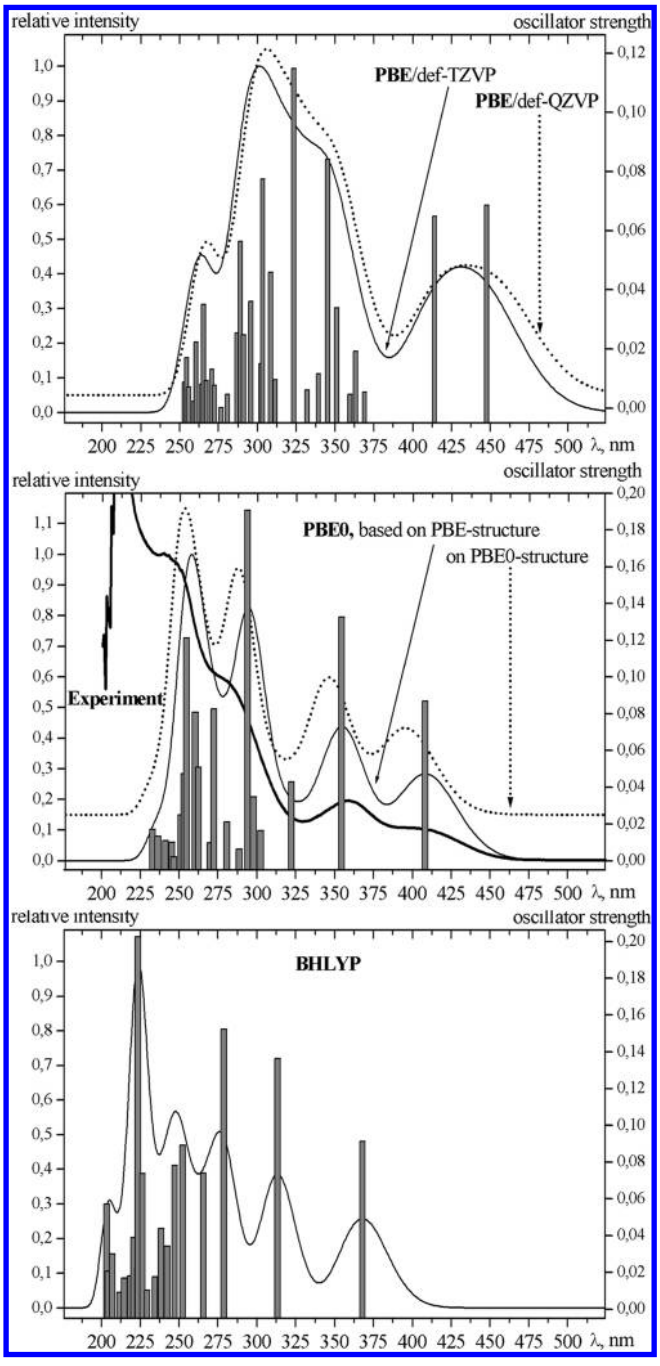

Figure 1. Experimental (bold) and simulated UV/vis absorption spectra of **1a** (calculated with different functionals and basis sets).

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that the lowest excitation at 408 nm is bathochromicaly shifted relative to the positions of the HOMO → LUMO transitions in 1,2,5-triphenyl- and pentaphenyl-phospholes.[1,45]

To interpret the observed absorption bands, quantum chemical calculations were conducted. First, the structure of **1a** was optimized at the PBE/def-TZVP level. The spectrum from the 30 lowest singlet states calculated for the optimized ground state structure is in reasonable agreement with the experimental spectrum (Figure 1). Test calculations with the extended def-QZVP AO basis set took considerably more CPU-time but did not lead to any noticeable changes in the simulated spectrum.

As hybrid functionals are expected to produce better quality simulations,[28,30] the spectrum was recalculated (Figure 1) with the hybrid functionals PBE0[23] (25% of Fock exchange) and BHLYP[35] (50% of Fock exchange) for structure **1a** optimized at the same levels of theory. In these cases only 20 singlet states were computed because the use of hybrid functionals substantially increased the computational time in comparison to the case of PBE. Moreover, hybrid functional produces less artificial so-called "ghost" states due to the self-interaction error[46−48] in the semilocal part of the functional, and hence, for the same spectral energy range a smaller number of states is required.

The PBE0 functional was reported to yield accurate simulations of absorption spectra of benzosiloles,[29] while the BHLYP functional was successfully applied earlier for UV/vis and CD spectra simulation of some monophosphole derivatives.[49] Nevertheless, the UV/vis spectrum of **1a** obtained with the BHLYP functional (Figure 1) agrees less well with the experimental spectrum than for PBE0. In fact the PBE0 functional with a smaller contribution of Fock exchange yields an excellent agreement with the experimental spectrum in the region 475−225 nm, both in band positions as well as their relative intensities (absolute intensities were computed but are experimentally not available for comparison). Thus, only the PBE0 functional was further considered for the spectra simulations.

As the calculations with the use of hybrid functionals are rather CPU-time-consuming, some simplifications are highly desirable. We reduced the necessary computational time considerably using the resolution-of-identity (RI) approximation.[15] The spectra simulated with and without RI-approximation completely coincided with each other. Further minimization of the computational expense was achieved by a PBE0 simulation performed for the structure of **1a** optimized with the computationally more efficient PBE functional. The spectrum obtained in this way is practically identical to that from the structure directly optimized within the same hybrid functional, except for a small bathochromic shift of all bands by ∼13 nm (Figure 1). This effect can be traced back to systematically smaller bond lengths (by about 1−2 pm) in the PBE0 compared to the PBE treatment. Thus, for the studied 1,2-diphospholes it is acceptable to calculate the spectra at the PBE0/def-TZVP level of theory (for 20 singlet states) on PBE/def-TZVP optimized structures. In the case of limited computational resources the smaller def-SVP AO basis set can be used as well, because together with the PBE0 functional it also provides UV spectra in good agreement with the experimental ones (see Figure S1, ESI). Finally, it was established that variation of conformation of the alkyl substituent at the P1 atom does not introduce pronounced changes to the calculated spectra; therefore, there is no necessity for time-consuming searches of the dominant conformers (Figure S2, ESI). In the following only data obtained within the above simplified approach are discussed.

The excitation energies and oscillator strengths of all 20 calculated transitions are listed in Table 1. According to the TD-DFT calculations the band at 408 nm in the simulated spectrum is assigned to the transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). Several frontier molecular orbitals (FMOs) of diphosphole **1a** are given in Figure 2. As can be seen, the HOMO is predominantly localized in the P═C and C═C bonds of the diphosphole-ring and partly in the aromatic substituents. The LUMO involves mainly a remaining part of the ring, including the lone pair of phosphorus atom P1. The second calculated singlet state at 354 nm is due to the HOMO-

Table 1. Experimental UV/vis Absorption Bands and TD-DFT (PBE0/def-TZVP) Calculated Excitation Energies (nm), Oscillator Strengths (f), and Assignments of the Electronic Transitions (N) of Molecule 1a[a]

N	energy/f	assignment	λ_{abs}
1	408/0.087	98 → 99 (94.6%)	409
2	354/0.133	97 → 99 (92.8%)	358
3	322/0.043	96 → 99 (93.6%)	
4	302/0.017	94 → 99 (57.2%)	
		93 → 99 (20.2%)	
		98 → 100 (11.9%)	
5	298/0.035	95 → 99 (61.1%)	
		98 → 100 (24.9%)	
6	294/0.191	98 → 100 (52.6%)	279
		95 → 99 (29.6%)	
7	289/0.006	93 → 99 (48.8%)	
		94 → 99 (29.6%)	
8	281/0.021	92 → 99 (54.1%)	
		98 → 101 (23.1%)	
		93 → 99 (13.2%)	
9	272/0.083	98 → 102 (83.4%)	
10	270/0.009	98 → 101 (66.0%)	
		92 → 99 (19.1%)	
11	262/0.051	97 → 100 (43.5%)	
		91 → 99 (35.8%)	
12	260/0.081	97 → 100 (47.8%)	
		91 → 99 (24.9%)	
		98 → 103 (9.9%)	
13	255/0.121	98 → 103 (61.8%)	242
		90 → 99 (16.3%)	
14	253/0.047	90 → 99 (58.9%)	
		91 → 99 (10.1%)	
15	251/0.025	98 → 104 (48.7%)	
		98 → 105 (12.7%)	
16	247/0.002	98 → 105 (43.0%)	
		98 → 104 (22.6%)	
17	245/0.010	97 → 101 (38.3%)	
		98 → 105 (22.4%)	
18	241/0.011	97 → 102 (72.5%)	
		97 → 101 (18.4%)	
19	236/0.013	96 → 100 (79.8%)	
20	233/0.017	97 → 103 (17.7%)	
		97 → 101 (15.1%)	
		96 → 100 (10.6%)	

[a]Only single excitation contributions of more than 10% are given.

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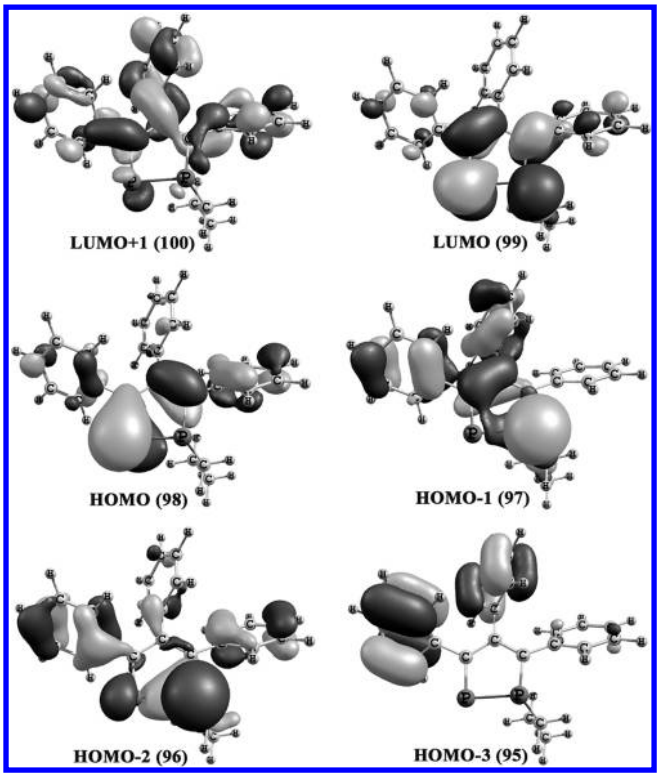

Figure 2. Some frontier molecular orbitals of **1a** and their numbers (in parentheses).

1 → LUMO transition (92.8%). The HOMO-1 is localized in the π-system of dienic moiety and exocyclic P−C σ-bond, forming hyperconjugation and involves also the lone pair of the phosphorus atom P1 and two phenyl rings. The third relatively broad band with a maximum at 294 nm in the spectrum of **1a** is composed of four transitions, the main contributions coming from HOMO → LUMO+1 (52.6%) and HOMO-3 → LUMO (29.6%) excitations. Finally, the fourth band in the spectrum with a maximum at 257 nm is composed of many transitions and is difficult for straightforward interpretation.

The above assignments and composition of FMOs suggest that chemical modification of substituents both at the P1 atom and at carbon atoms of the ring should change the optical properties of the 1,2-diphospholes. Earlier it was reported that the HOMO−LUMO gap and observed absorptions of 1-R-2,5-diaryl-monophospholes depend strongly on the nature of both the R-group and aryl substituents of the monophosphole ring.[1,9,10] A comparison of the simulated absorption spectra of model molecules **2a**−**10a** (Chart 1) demonstrates that variation of the alkyl moiety at P1 (**2a**−**7a**) does not change the HOMO → LUMO and HOMO-1 → LUMO energy gaps significantly (Table 2). Introduction of a benzyl substituent (**8a**) leads only to a small bathochromic shift of the first two excitations.

Introduction of $-Si(CH_3)_3$ (**9a**) or $-Sn(CH_3)_3$ (**10a**) moieties at P1 of the 1,2-diphosphole cycle increases the energy gaps between the HOMO → LUMO and HOMO-1 → LUMO by 0.21 and 0.12 eV, respectively, compared to **1a** (Table 2). In full agreement with the computations, the band attributed to the mentioned excitations in an experimental spectrum of **10a** (Figure 3) exhibits a hypsochromic shift relative to the position of the corresponding band in the UV spectrum of **1a**. The excellent overall agreement of the simulated spectrum of **10a** with the experimental one demonstrates the reliability of our computational approach for the current purpose.

Table 2. TD-DFT (PBE0/def-TZVP) Calculated Lowest Singlet Excitation Energies in the Investigated Molecules

	energies, eV (nm)	
	HOMO → LUMO	HOMO-1 → LUMO
1a	3.04 (408)	3.49 (354)
2a	3.03 (409)	3.51 (353)
3a	3.03 (409)	3.49 (354)
4a	3.03 (410)	3.49 (355)
5a	3.02 (411)	3.47 (357)
6a	3.09 (401)	3.51 (353)
7a	3.06 (405)	3.49 (354)
8a	2.96 (418)	3.35 (370)
9a	3.26 (380)	3.61 (343)
10a	3.25 (381)	3.61 (343)
1b	3.02 (410)	3.47 (358)
1c	3.00 (413)	3.42 (362)
1d	2.98 (415)	3.42 (363)
1e	2.90 (427)	3.24 (381)
1f	2.85 (435)	3.16 (392)
1i	2.88 (430)	3.23 (384)
1j	2.66 (465)	2.86 (433)
1k	2.66 (466)	2.80 (442)

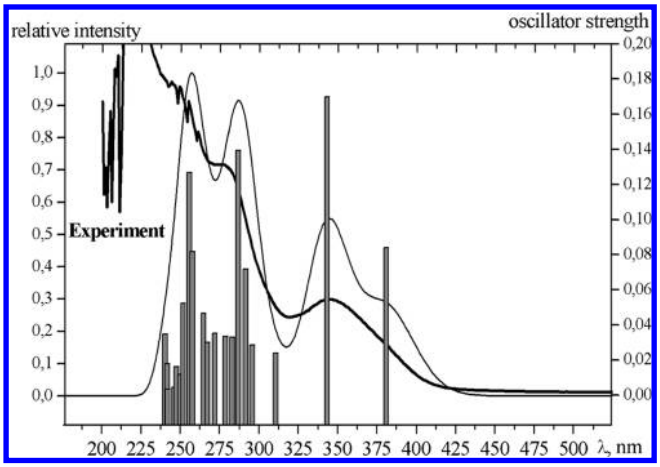

Figure 3. Experimental (bold) and simulated absorption spectra of **10a**.

According to the simulations presented in the Table 2, introduction of F, Cl, or Me substituents in the para-positions of the phenyl groups causes almost negligible bathochromic shifts of the HOMO → LUMO and HOMO-1 → LUMO transitions of molecules **1b**−**1d** compared to **1a**. Probably, the influence of these substituents is restricted to the π-systems of the phenyl groups, but not to the diphosphole ring. These observations are supported by experimental UV/vis spectra of the *para*-F and *para*-Cl derivatives (**1b, 1c**), which are very similar to the spectrum of **1a** and agree well with the corresponding simulated spectra (Figure S3 and S4, ESI).

Insertion of substituents $-CH{=}CH_2$ (**1e**) or $-C_6H_5$ (**1f**) which are able to be in conjugation with aromatic rings leads to the appearance of additional strong absorptions near 330−340 nm due to substantial shift of bands belonging to the aromatic moieties (Figure 4), similar to the earlier reported case of the para-substituted phenols.[50] Moreover, only a moderate bathochromic shift of two lowest transitions attributed to 1,2-

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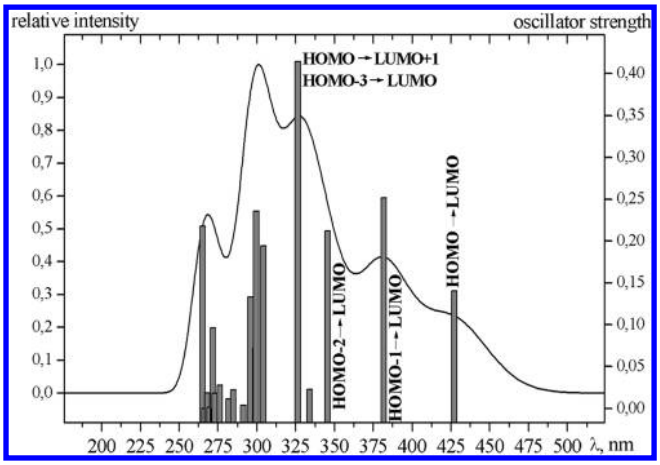

Figure 4. Simulated UV/vis absorption spectrum of **1f**.

diphosphole unit (HOMO → LUMO and HOMO-1 → LUMO) is calculated (Table 2).

More pronounced changes in the simulated spectra are caused by introduction of *para*-C(H)O (**1g**) and *para*-NO_2 groups (**1h**) (see Figure 5, assignments are listed in the Table S2 and S3, ESI). According to the calculations in the Vis-region (>400 nm) a band at ~420 nm appears due to the HOMO → LUMO transition, whereas the HOMO-1 → LUMO excitation is bathochromic shifted, and mixes with HOMO → LUMO+1 and HOMO → LUMO+2 transitions. As a result, the calculations yield two strong overlapping absorption bands in the UV region 300−370 nm. As in the case of **1a** the HOMO of these derivatives (Figure 6) is predominantly localized in the

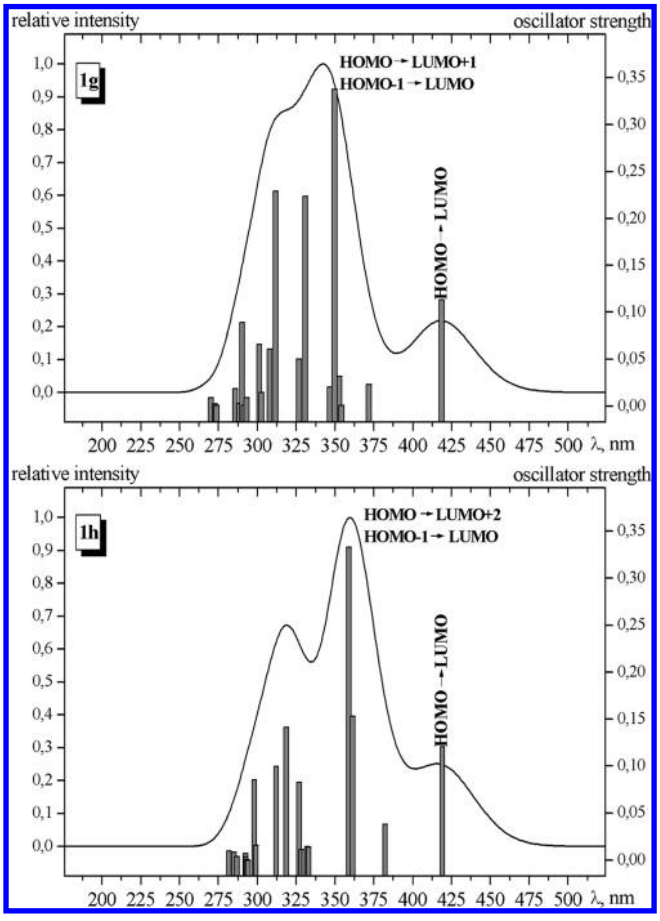

Figure 5. Simulated UV/vis absorption spectra of **1g** and **1h**.

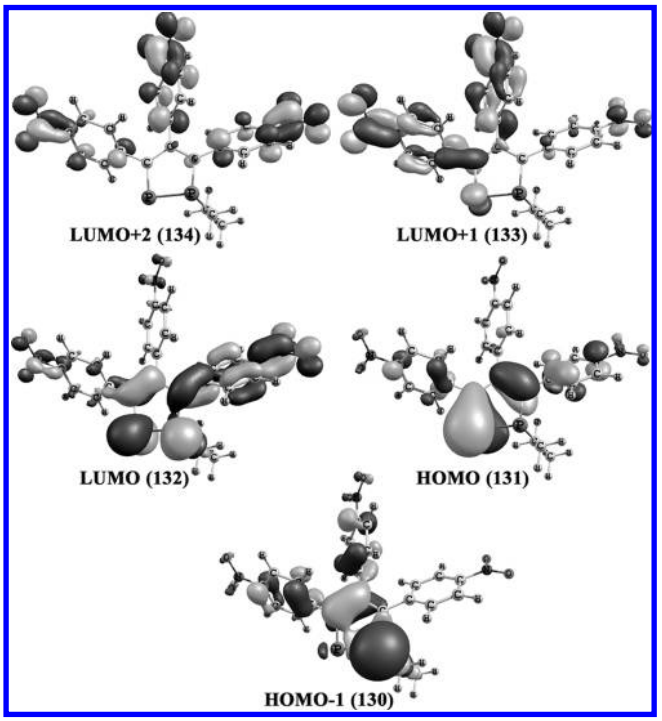

Figure 6. Some frontier molecular orbitals of **1h** (the number of the orbital is shown in the parentheses).

P═C and C═C bonds of the diphosphole-ring and partly in the aromatic substituents with small additions from the NO_2 group. The LUMO involves the diphosphole ring and the lone pair of phosphorus atom P1 as in the case of **1a**, but a substantial contribution from phenyl and NO_2 moieties results in moderately diminished energy gap. The main contributions to these transitions are from frontier unoccupied MOs in the aryl-substituents conjugated with electron acceptor groups (see Figure 6).

In the case of *para*-substitutions with electron-donor groups like -NMe_2 (**1i**), -N(H)Ph (**1j**), and −OMe (**1k**), the calculations show substantial changes of the energy gaps between FMOs. A similar reduction of the HOMO−LUMO energy gap due to insertion of −OMe and −N(H)Me groups was reported earlier for phosphole-based oligomers.[51] As a result, three overlapped bands in the near UV/vis region appear due to transitions between HOMO → LUMO, HOMO-1 → LUMO, and HOMO-2 → LUMO orbitals, which are placed separately from another short-wavelength absorption bands (Figure 7, Table 3). The presence of electron-donor groups influences the π-systems of the phenyl moieties, but it also changes the composition of the FMOs. For these derivatives the HOMO is localized in the aromatic substituents with contribution from lone pairs of O or N atoms (Figure 8) and to a less extent at the P═C and C═C bonds of the diphosphole ring contrary to the HOMO of **1a** (Figure 2). The HOMO-1 is mainly spread on the two phenyl rings and lone pairs of O or N atoms, but contributions from the π-system of diene moiety, exocyclic P−C σ-bond and the lone pair of phosphorus atom P1 are diminished relative to **1a**. Also as can be seen from Figure 8 for these derivatives hyperconjugation between the π-system of dienic moiety and the exocyclic P−C σ-bond is

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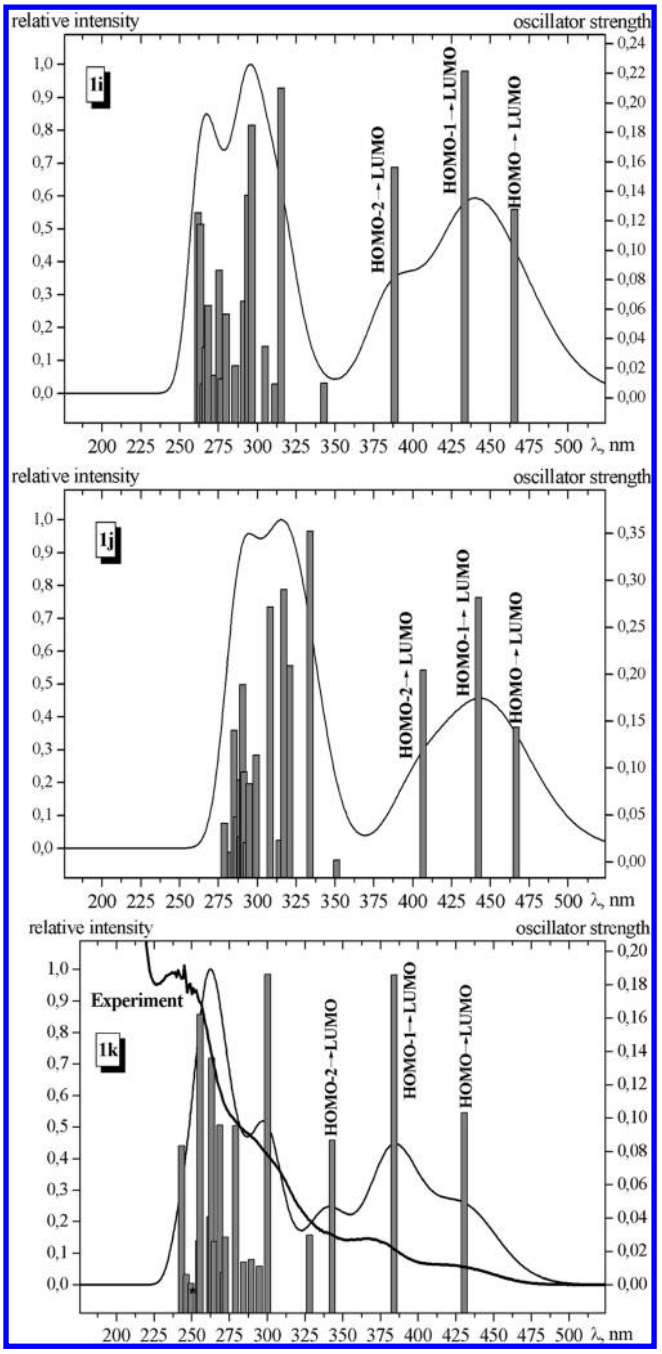

Figure 7. Simulated UV/vis absorption spectra of **1i**, **1j**, and **1k** and experimental (bold) UV/vis absorption spectrum of **5k**.

decreased dramatically and that changes the HOMO-1 composition. The HOMO-2 is formed by equal fractions from the phenyl rings, cyclic bonds and lone pairs of P1 and O and N atoms.

To validate the above predictions a derivative containing *para*-OMe substituents at the phenyl groups (**5k**) was synthesized after the TD-DFT computations had been performed according to the previously described protocol.[40] The experimental UV/vis absorption spectrum of this derivative corresponds well to the simulated spectrum of **1k** (Figure 7) and demonstrates a bathochromic shift of the first transitions in full agreement with the computational predictions (Table 3). These results clearly indicate that the −OMe, $-N(Me)_2$, and −N(H)Ph groups, bringing extended π-

Table 3. Experimental UV/vis Absorption Bands of Molecule 5k and TD-DFT Calculated Excitation Energies (nm), Oscillator Strengths (f), and Assignments of the Electronic Transitions (N) of Molecule 1k[a]

N	energy/f	assignment	λ_{abs}
1	431/0.103	122 → 123 (95.1%)	427
2	384/0.186	121 → 123 (95.7%)	368
3	343/0.087	120 → 123 (95.1%)	341
4	328/0.030	119 → 123 (88.8%)	
5	300/0.186	122 → 124 (87.4%)	292
6	295/0.011	122 → 125 (83.9%)	
7	289/0.015	118 → 123 (46.8%)	
		122 → 126 (25.6%)	
		117 → 126 (14.4%)	
8	284/0.013	117 → 123 (65.9%)	
		118 → 123 (18.4%)	
9	279/0.095	122 → 126 (58.6%)	
		118 → 123 (23.1%)	
10	273/0.028	122 → 127 (35.4%)	
		121 → 124 (16.5%)	
		115 → 123 (12.9%)	
		114 → 123 (11.7%)	
11	271/0.007	116 → 123 (65.4%)	
		121 → 125 (10.4%)	
12	269/0.096	121 → 124 (70.6%)	
13	265/0.026	114 → 123 (60.1%)	
		121 → 125 (16.8%)	
14	263/0.136	121 → 125 (42.2%)	
		115 → 123 (27.0%)	
15	262/0.041	122 → 127 (44.5%)	
		115 → 123 (44.0%)	
16	256/0.162	122 → 128 (80.6%)	238
17	255/0.026	121 → 126 (75.5%)	
18	250/0.001	122 → 129 (62.7%)	
		121 → 127 (10.5%)	
19	246/0.006	121 → 127 (61.5%)	
		122 → 129 (13.6%)	
20	243/0.083	120 → 124 (78.9%)	

[a]Only single excitation contributions of more than 10% are given.

delocalization into the systems, leads to a lower optical gap and absorptions in the visible region of the spectra as a result. The calculated absorptions in the range of 350−500 nm imply that the corresponding compounds could produce emission at still higher wavelengths, which would make them candidates for new materials.

■ CONCLUSIONS

Twenty 1,2-diphospholes have been investigated for the first time within the framework of (time-dependent) density functional theory ([TD]-DFT) and experimentally by UV/vis spectroscopy. It is shown that the PBE0 hybrid density functional combined with the moderate-size def-TZVP AO basis set can be used for the calculation of UV/vis absorption spectra of the title compounds yielding overall excellent agreement between theory and experiment. The simulations allowed a detailed interpretation of the experimental spectra of the title compounds and revealed relationships between chemical modification of the 1,2-diphospholes and their light-absorption properties. In particular, it is shown that variation of substituent at phosphorus atom P1 does not change a HOMO−LUMO gap significantly while the studied 1,2-

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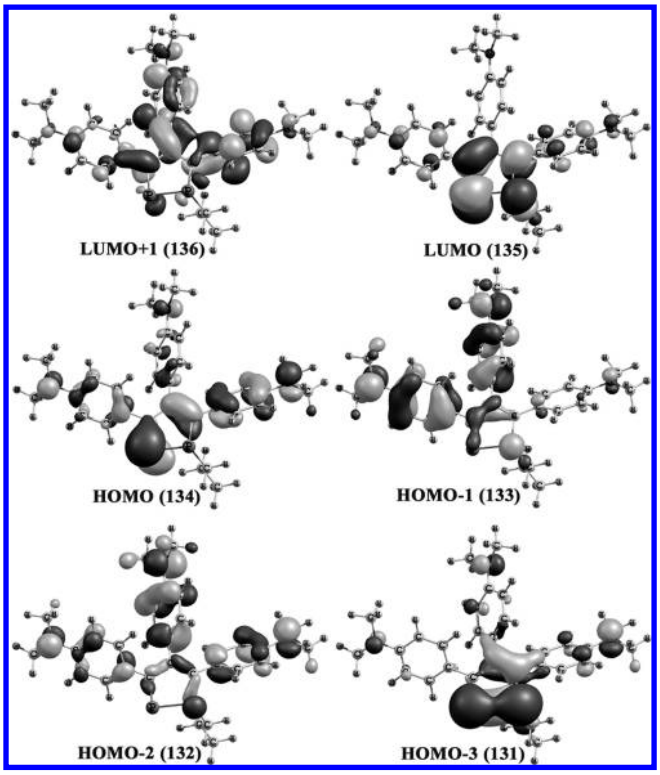

Figure 8. Some frontier molecular orbitals of **1i** (the number of the orbital is shown in the parentheses).

diphospholes are more sensitive to para-substitution in phenyl moieties, which essentially changes the gaps between frontier molecular orbitals. Introduction of electron-donor substituents, containing heteroatoms with lone pairs able to be in conjugation with the phenyl groups, not only shift frontier molecular orbitals but also change their compositions. In particular, *para*-OMe, *para*-NMe_2, and *para* -N(H)Ph derivatives are found to have the smallest HOMO−LUMO gap among all studied molecules. They should absorb in the visible and near UV range and, thus, can be recommended for further practical testing as novel compounds for application in electronic devices.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figure S1. Experimental and simulated UV/vis absorption spectra of **1a** for different basis sets (with the PBE0 functional). Figure S2. Simulated absorption spectra of **3a** for different conformations of the P1-ethyl-substituent. Figure S3. Experimental and simulated absorption spectra of **1b**. Figure S4. Experimental and simulated absorption spectra of **1c**. Table S1. TD-DFT calculated excitation energies, oscillator strengths, and assignments of the electronic transitions of molecule **1g**. Table S2. TD-DFT calculated excitation energies, oscillator strengths, and assignments of the electronic transitions of molecule **1h**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: zverevaelena@ymail.com.

Notes

The authors declare no competing financial interest.

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