Theoretical quest for photoconversion molecules having opposite directions of the electric dipole moment in S_0 and S_1 states

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Ab initio calculations at the level of CASPT2 with Dunning's correlation consistent cc-pV*X*Z (*X*=D, T, Q) basis sets have been carried out for pyrimidine, quinoxaline, phthalazine, and their substituted compounds to find candidates that show a change in the direction of the electric dipole moment for the $S_0 \rightarrow S_1$ transition. The present calculations reveal that 6,7-difluorophthalazine and 6,7-dichlorophthalazine are strong candidates having a large and clear change in the direction of the electric dipole moment on the $S_0 \rightarrow S_1$ transition. © *2009 American Institute of Physics*.
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I. INTRODUCTION

Molecules or molecular assemblies that show a change in molecular structure, electronic structure, or level structure after photoexcitation can be powerful tools for the design and development of novel photofunctional material. "Photochromic compounds" show a change in molecular structure after photoexcitation. This leads to various changes in physicochemical properties such as refractive index, dielectric constant, oxidation/reduction potential, or absorption spectrum (color), which can be applied to various photonic devices (e.g., optical memory switch, photo-optical switch).[1]

Even if the molecular structure does not change significantly, molecules that show drastic change in electric dipole moment or molecular polarizability after excitation may have similar powerful potential application as a novel photofunctional material (e.g., as a molecule having remarkable nonlinear optical properties). Molecules whose direction of electric dipole moment in the excited state is different from that in the ground state could be used to control molecular motion by combining photoirradiation with application of external electric fields.

For molecules having a dipole moment, the dipole moment is aligned along the direction of an applied electric field because of orientational polarizability,[2,3] the fundamental mechanism of liquid crystal display. If the direction of the electric dipole moments is changed by photoirradiation during application of an electric field, molecular orientation along the field direction may change. This behavior may be applicable to a molecular switching device, which can be controlled by photons and an electric field. The simplest example is molecules whose direction of dipole moment in the excited state is opposite to that in the ground state. This is because molecular orientation may be completely opposite due to photoexcitation into the excited state during application of an electric field. It has been reported that pyrimidine,[4,5] quinoxaline,[6] or azulene,[7–9] show an electric dipole moment whose direction in the electronically excited state is opposite to that in the ground state (S_0). This is mainly based on the Stark effect on absorption spectra.

Molecular relaxation usually occurs in the subpicosecond timescale. If the decay rate of the excited state is much faster than relaxation rate, the change in orientation cannot follow the change in direction of the electric dipole moment. In condensed phases, internal conversion or intersystem crossing from higher electronic states to the lowest excited singlet or triplet state usually occurs much faster than the orientation change induced by the applied electric field. Attention should therefore be paid to the electric dipole moment in the first electronically excited state (S_1) in comparison with the dipole moment in the ground state [though azulene and some azulene derivatives show strong fluorescence emitted from the second excited state (S_2)].[10–12] Knowing the molecules in which the direction of the electric dipole moment in the first electronically excited state is opposite to the one in the ground state is important. It may then be possible not only to control the orientation and motion of molecules but also to design a molecular rotor by combining photoexcitation and application of an external electric field. The solvent-solute interaction may be also examined by measuring the time-dependent behavior of the field-induced change in the orientation of such molecules.

We searched for molecules that show a change in direction of the electric dipole moment for the $S_0 \rightarrow S_1$ transition using a systematic and highly correlated level of *ab initio* CASPT2 calculation[13] using pyrimidine, quinoxaline, phthalazine, and their substituted compounds. Phthalazine, which is also azaaromatic compound with the C_{2v} symmetry,

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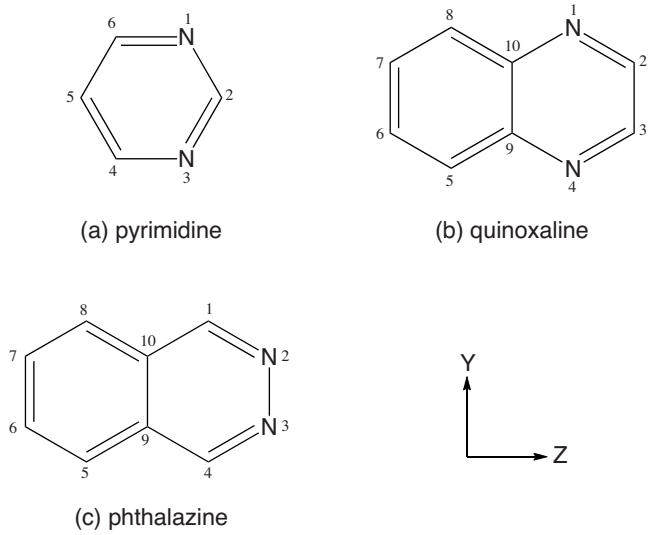


FIG. 1. The definition of molecular axis and atom numbering of (a) pyrimidine, (b) quinoxaline, (c) phthalazine, and their derivatives. In this coordinate, x, y, z, and xy belong to B_1, B_2, A_1, and A_2 irreducible representations, respectively.

has been taken as the object for comparison with pyrimidine or quinozaline, though the change in direction of the electric dipole moment of this molecule after the optical transition has not been reported. We did not focus on azulene and its derivatives because azulene has a special electronic structure and photochemical nature.

Computational details are explained in Sec. II. In Sec. III calculated excitation energies and dipole moments for the ground state and low-lying electronic states are summarized and the change in direction of the electric dipole moment in the $S_0 \rightarrow S_1$ transition is discussed using calculated results. Concluding remarks are given in Sec. IV.

II. COMPUTATIONAL DETAILS

Geometries and dipole moments in the electronic ground state and excited states have been calculated for pyrimidine, quinoxaline, phthalazine, and their substituted compounds, which are candidates for optical switching. Substituted compounds employed in the present calculation were 2 or 5 monosubstituted pyrimidine, 6,7 disubstituted quinoxaline, and 6,7 disubstituted phthalazine. We considered simple substitutions with the fluorine or chlorine atom. The definition of molecular axis and atom numbering is given in Fig. 1. Calculations were done in C_{2v} symmetry.

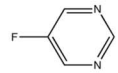
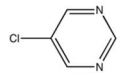
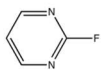
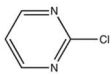
All calculations including geometry optimizations were done at the level of *ab initio* CASPT2 theory,[13] which can include static and dynamic electronic correlation effects required for accurate description of molecular electronic states. The geometry optimizations at the level of CASPT2 were carried out by using numerical gradients. In CASPT2 calculations, full π orbitals and nonbonding (n) orbitals that correspond to lone pair on nitrogen atoms were included in active space in each molecule. The size of the active space in each system is shown in Tables I–III. Core electrons of nonhydrogen atoms were kept frozen in the second-order perturbation calculations. Dunning's cc-pVDZ basis set[14] was utilized for geometry optimization, whereas larger cc-pVTZ and cc-pVQZ sets were used for single-point energy calculations at the CASPT2/cc-pVDZ optimized points. The larger basis sets were applied to check convergence of predicted excitation energies and dipole moments. To assign symmetry of the S_1 state, we considered low-lying $^1A_2$, $^1B_1$, and $^1B_2$ excited states and the second $^1A_1$ state. The excitation energies and electric dipole moments in each electronic state were calculated for the vertical and adiabatic transitions. Calculations were carried out using the MOLCAS 7.2 software package.[15] Molecular orbitals were depicted using the MOLDEN 4.7 package.[16]

III. RESULTS AND DISCUSSION

We initially assigned the symmetry of the S_1 state of pyrimidine, quinoxaline, phthalazine, and their substituted compounds. Calculated results for each molecule at the level of CASPT2/cc-pVXZ//CASPT2/cc-pVDZ (X=D, T, Q) theories for each molecule are shown in Tables I–III. They indicate that the S_1 state of each molecule was: the $^1B_1$ state for pyrimidine and its substituted compounds, the $^1B_1$ state for quinoxaline and its substituted compounds, and the $^1A_2$ state for phthalazine and its substitutions. These assignments were not affected by increasing basis size. The differences of predicted vertical and adiabatic excitation energies between cc-pVTZ and cc-pVQZ results were within 0.1 eV in all cases. This indicates that our calculation was of sufficiently high accuracy to assign the character of the excited state. To confirm the assignments for the S_1 states, it is necessary to examine whether the second $^1A_1$ state is the S_1 state or not. We performed numerical optimizations at the level of CASPT2 after two-roots state-average CASSCF/cc-pVDZ calculations with equal weight for the 2 $^1A_1$ states of pyrimidine, quinoxaline, and phthalazine. The calculations revealed that the above assignments for the S_1 state are correct: the 2 $^1A_1$ states are adiabatically higher than the above S_1 states by 3.01, 0.65, and 1.42 eV for pyrimidine, quinoxaline, and phthalazine, respectively.

We then looked for candidates that show a change in direction of the electric dipole moment for the transition $S_0 \rightarrow S_1$. Electric dipole moments of the S_0, S_1, and the other low-lying excited states obtained with CASPT2 calculations are given in Tables I–III. The dipole moments were approximately estimated at the CASPT2 level by using approximate active-active density matrices.[15] Exact CASPT2 dipole moments were calculated only for pyrimidine, quinoxaline, and phthalazine with cc-pVDZ and are listed in parentheses in Tables I–III. Differences between the approximate and exact CASPT2 dipole moments are within ca. 0.1 D. Thus it is safe to discuss using the approximate data. These dipole moments indicate that the following compounds show a change in sign of the electric dipole moment for the $S_0 \rightarrow S_1$ transition: 5-fluoropyrimidine, 5-chloropyrimidine, quinoxaline, 6,7-difluorophthalazine, and 6,7-dichlorophthalazine. Changes in the dipole moment were not greatly affected by improving the basis sets and were well converged. The differences in calculated dipole moments given by CASPT2/cc-pVTZ and

TABLE I. Excitation energy and dipole moment of pyrimidine derivatives obtained by (n,π)-CASPT2/cc-pV*XZ* (X=D, T, Q) [for the axis definition, see Fig. 1(a)].

Molecule	Active Space	Basis set		Excitation energy / eV				Dipole moment / Debye [a]			
				Electronic states				Electronic states			
				1^1A_1 (S_0)	1^1A_2	1^1B_1 (S_1)	1^1B_2	1^1A_1 (S_0)	1^1A_2	1^1B_1 (S_1)	1^1B_2
 pyrimidine	(10e, 8o)	cc-pVDZ	vertical	0.00	4.81	4.50	5.32	-2.23 (-2.21)	-1.17 (-1.15)	-0.84 (-0.77)	-2.05 (-2.05)
			adiabatic	-	4.06	4.03	5.11	-	-0.62 (-0.60)	-0.79 (-0.73)	-2.16 (-2.15)
		cc-pVTZ	vertical	0.00	4.72	4.40	5.24	-2.30	-1.21	-0.81	-2.08
			adiabatic	-	3.99	3.95	5.15	-	-0.67	-0.78	-2.18
		cc-pVQZ	vertical	0.00	4.70	4.37	5.21	-2.32	-1.23	-0.80	-2.07
			adiabatic	-	3.97	3.92	5.15	-	-0.70	-0.78	-2.17
 5-fluoropyrimidine	(12e, 9o)	cc-pVDZ	vertical	0.00	5.05	4.37	5.18	-0.48	0.29	0.89	-0.32
			adiabatic	-	4.31	3.91	4.97	-	0.87	0.94	-0.53
		cc-pVTZ	vertical	0.00	4.95	4.28	5.09	-0.56	0.19	0.89	-0.36
			adiabatic	-	4.26	3.82	4.97	-	0.75	0.93	-0.57
		cc-pVQZ	vertical	0.00	4.93	4.25	5.06	-0.56	0.17	0.91	-0.33
			adiabatic	-	4.24	3.80	4.97	-	0.72	0.94	-0.53
 5-chloropyrimidine	(12e, 9o)	cc-pVDZ	vertical	0.00	4.80	4.42	5.13	-0.39	0.76	1.00	-0.53
			adiabatic	-	4.08	3.95	4.92	-	1.30	1.05	-0.66
		cc-pVTZ	vertical	0.00	4.88	4.48	5.19	-0.46	0.75	0.96	-0.44
			adiabatic	-	4.18	4.03	5.08	-	1.27	1.09	-0.64
		cc-pVQZ	vertical	0.00	4.88	4.47	5.19	-0.46	0.73	0.97	-0.42
			adiabatic	-	4.19	4.02	5.10	-	1.24	1.09	-0.61
 2fluoropyrimidine	(12e, 9o)	cc-pVDZ	vertical	0.00	5.41	4.60	5.25	-4.20	-2.81	-2.63	-3.94
			adiabatic	-	4.73	4.12	5.04	-	-2.24	-2.66	-4.02
		cc-pVTZ	vertical	0.00	5.31	4.50	5.16	-4.16	-2.75	-2.57	-3.90
			adiabatic	-	4.68	4.04	5.05	-	-2.18	-2.60	-3.97
		cc-pVQZ	vertical	0.00	5.27	4.48	5.13	-4.19	-2.76	-2.58	-3.89
			adiabatic	-	4.66	4.03	5.05	-	-2.27	-2.62	-3.97
 2-chloropyrimidine	(12e, 9o)	cc-pVDZ	vertical	0.00	4.97	4.52	5.18	-3.71	-3.18	-2.63	-3.72
			adiabatic	-	4.28	4.04	4.97	-	-2.27	-2.51	-3.77
		cc-pVTZ	vertical	0.00	5.02	4.57	5.25	-3.75	-3.24	-2.58	-3.75
			adiabatic	-	4.36	4.11	5.13	-	-2.33	-2.47	-3.78
		cc-pVQZ	vertical	0.00	5.00	4.56	5.24	-3.76	-3.26	-2.57	-3.73
			adiabatic	-	4.36	4.10	5.15	-	-2.35	-2.59	-3.77

[a]Dipole moments were calculated with approximate CASPT2 density. Those calculated with exact CASPT2 density are given in parentheses.

CASPT2/cc-pVQZ were within 0.04 D for all the molecules in Tables I–III except for the dipole moment of the adiabatic $^1B_1$ state of 2-chloropyrimidine.

All the S_1 states are arisen from n-π^* transitions. Such a one-electron excitation of each nonsubstituted compound is as follows:

pyrimidine: $7b_2 \rightarrow 2a_2$,

quinoxaline: $16a_1 \rightarrow 4b_1$,

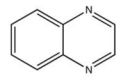
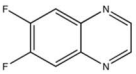
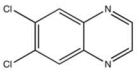
phthalizine: $13b_2 \rightarrow 4b_1$.

These CASPT2 natural molecular orbitals (NMOs) relevant to n-π^* transitions are shown in Figs. 2–4, which are very informative and clearly indicate charge transfer in a molecular plane as a consequence of an n-π^* transition for each compound. The main features of the NMOs relevant to $S_0 \rightarrow S_1$ transitions maintain even in substituted compounds.

Two experimental studies for dipole moments in the S_0 and S_1 states in pyrimidine have been reported. Ohta and Tanaka reported that the electric dipole moment in the S_1 state of pyrimidine was 0.58 D.[5] This value is much smaller than the value in the ground S_0 state, i.e., 2.334 D, which was determined by Blackman *et al.*[17] using microwave spectroscopy. Directions of the dipole moments in the S_0 and S_1 states could not be determined in these experiments. The present CASPT2/cc-pV*XZ* (X=D, T, Q) calculations gave −2.23, −2.30, and −2.32 D, respectively, for the dipole moment of the S_0 state (see Fig. 1 for polarity). Our best value of 2.32 D agreed closely with the experimental value, 2.334 D. Early *ab initio* calculations at an SCF/STO-3G level by Del Bene[18] gave −2.00 D with the same polarity as ours for the S_0 state; more accurate calculations at MRDCI/TZDP (Ref. 19) provided −2.383 D, which is almost identical to our values and the experimental one.

For the dipole moment of the S_1 state, the present CASPT2/cc-pV*XZ* (X=D, T, Q) calculations provided −0.79, −0.78, and −0.78 D for the adiabatic state and −0.84, −0.81, and −0.80 D for the vertical state, respectively. An SCI/STO-3G calculation by Del Bene[18] gave +0.52 D with the reverse polarity to ours for the vertical state. Our best value for the change in dipole moment for the adiabatic $S_0 \rightarrow S_1$ transition was 1.54 D, whereas Del Bene predicted the change to be 2.52 D. The change in dipole moment estimated by Del Bene appears erroneous, mainly because of their structure partially optimized with STO-3G: SCI/STO-3G calculations at the present optimized structure provided the S_1 dipole moment to be −0.64 D for the adiabatic state and −0.32 D for the vertical state. The present

TABLE II. Excitation energy and dipole moment of quinoxaline derivatives obtained by (n,π)-CASPT2/cc-pV*XZ* (X=D, T, Q). For the axis definition, see Fig. 1(b).

Molecule	Active Space	Basis set		Excitation energy / eV				Dipole moment / Debye[a]			
				Electronic states				Electronic states			
				1^1A_1 (S_0)	1^1A_2	1^1B_1 (S_1)	1^1B_2	1^1A_1 (S_0)	1^1A_2	1^1B_1 (S_1)	1^1B_2
 quinoxaline	(14e, 12o)	cc-pVDZ	vertical	0.00	5.35	3.78	4.77	-0.20 (-0.19)	0.18 (0.22)	0.15 (0.20)	-5.51 (-5.43)
			adiabatic	-	4.75	3.46	4.39	-	0.36 (0.45)	0.68 (0.72)	-5.04 (-4.97)
		cc-pVTZ	vertical	0.00	5.23	3.68	4.54	-0.19	0.14	0.10	-5.59
			adiabatic	-	4.63	3.35	4.25	-	0.32	0.62	-5.10
		cc-pVQZ	vertical	0.00	5.20	3.65	4.46	-0.19	0.11	0.07	-5.64
			adiabatic	-	4.61	3.31	4.20	-	0.28	0.58	-5.14
 6,7-difluoroquinoxaline	(18e, 14o)	cc-pVDZ	vertical	0.00	5.39	3.83	4.89	3.04	3.31	3.40	-2.32
			adiabatic	-	4.78	3.51	4.50	-	3.62	4.01	-1.97
		cc-pVTZ	vertical	0.00	5.27	3.74	4.66	2.97	3.19	3.26	-2.53
			adiabatic	-	4.67	3.41	4.36	-	3.48	3.85	-2.14
		cc-pVQZ	vertical	0.00	5.24	3.71	4.59	3.01	3.20	3.26	-2.56
			adiabatic	-	4.65	3.38	4.32	-	3.47	3.84	-2.15
 6,7-dichloroquinoxaline	(18e, 14o)	cc-pVDZ	vertical	0.00	5.26	3.69	4.72	3.25	3.52	3.58	-2.56
			adiabatic	-	4.65	3.34	4.35	-	3.78	4.19	-2.18
		cc-pVTZ	vertical	0.00	5.14	3.59	4.45	3.27	3.53	3.58	-2.72
			adiabatic	-	4.53	3.24	4.17	-	3.78	4.17	-2.30
		cc-pVQZ	vertical	0.00	5.14	3.56	4.40	3.26	3.53	3.55	-2.79
			adiabatic	-	4.51	3.21	4.12	-	3.74	4.13	-2.36

[a]Dipole moments were calculated with approximate CASPT2 density. Those calculated with exact CASPT2 density are given in parentheses.

calculations reveal that the $S_0 \rightarrow S_1$ transition does not initiate a change in the direction of the dipole moment for pyrimidine. Hochstrasser estimated the change in the dipole moment of pyrimidine in moving from S_0 to S_1 by the Stark shift in a mixed crystal of benzene to be -0.88 D.[20] Using absorption and fluorescence spectra in non-hydrogen-bonding solvents, Baba *et al.* determined the change in dipole moment in the transition from S_0 to S_1 to be -2.72 D.[4] The difference between these experimental and the present changes in dipole moment may be attributed to solvent effects.

For 5-fluoropyrimidine and 5-chloropyrimidine, the dipole moments of -0.56 and -0.46 D of the S_0 state change to +0.94 and +1.09 D, respectively, on adiabatic $S_0 \rightarrow S_1$ transition, indicating a clear change in direction of the dipole moment. Differences (1.50 and 1.53 D) in the dipole moments between the S_0 and S_1 states for these molecules are almost identical to that (1.54 D) for pyrimidine. We could estimate the dipole moment of the S_1 state for the substituted compound if we knew the change in dipole moment in the $S_0 \rightarrow S_1$ transition of a molecule and the dipole moment of the S_0 state for its substituted compound. For 2-fluoropyrimidine and 2-chloropyrimidine, direction change of the electric dipole moment does not occur because of the very large S_0 dipole moments of 4.19 and 3.76 D, whereas differences in the dipole moments between the S_0 and S_1 states for these molecules remain nearly constant (1.6–1.3 D).

Udagawa and Hanson investigated the change in dipole moment on the $S_0 \rightarrow S_1$ transition of quinoxaline using the electronic Stark effect.[6] They found the changes in durene and naphthalene host crystals to be 0.90 and 1.55 D, respectively.[6] The changes in dipole moment on the $S_0 \rightarrow S_1$ transition of quinoxaline obtained by the present CASPT2/cc-pV*XZ* (X=D, T, Q) calculations were 0.88, 0.81, and 0.77 D, respectively, which agree well with the experimental change in the durene host crystal. The present calculations reveal that the $S_0 \rightarrow S_1$ transition in quinoxaline causes the change in the direction of the dipole moment from -0.19 to 0.58 D. Dipole moment changes remain almost constant (1.0–0.8 D) in substituted compounds of quinoxaline.

Phthalazine has a very large dipole moment in its ground S_0 state, so the change in the direction of the dipole moment on the $S_0 \rightarrow S_1$ transition does not occur, but the change in dipole moment was the largest in the molecules examined. Changes given by the present CASPT2/cc-pV*XZ* (X=D, T, Q) calculations were 3.58, 3.63, and 3.65 D, respectively. Thus 6,7-difluorophthalazine and 6,7-chlorophthalazine, which have dipole moments of -1.7 to -1.6 D [see Fig. 1(c) for polarity] in the ground states, cause the change in the direction of the dipole moment on the $S_0 \rightarrow S_1$ transition. The dipole moment change is caused by an n-π^* transition from $13b_2$ to $4b_1$ molecular orbitals shown in Fig. 4.

Judging that the present CASPT2 results maintained sufficient accuracy for discussion of dipole moments in the electronic ground state and excited states, we discussed what

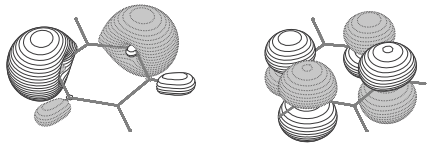
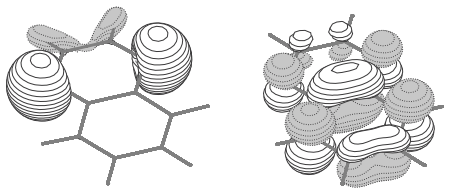
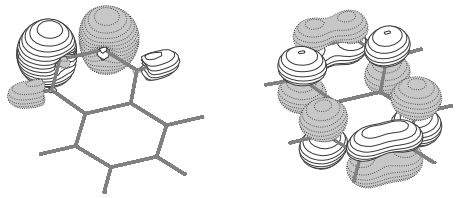


FIG. 2. (a) $7b_2$ and (b) $2a_2$ NMOs of pyrimidine. The S_1 ($1\,^1B_1$) state of pyrimidine is caused by a n-π^* transition from $7b_2$ to $2a_2$ orbitals. The MOLDEN package (Ref. 16) was utilized.



(a) 16a$_1$ natural orbital (b) 4b$_1$ natural orbital

FIG. 3. (a) $16a_1$ and (b) $4b_1$ NMOs of quinoxaline. The S_1 ($1\,^1B_1$) state of quinoxaline is caused by a n-π^* transition from $16a_1$ to $4b_1$ orbitals. The MOLDEN package (Ref. 16) was utilized.



(a) 13b$_2$ natural orbital (b) 5b$_1$ natural orbital

FIG. 4. (a) $13b_2$ and (b) $4b_1$ NMOs of phthalazine. The S_1 ($1\,^1A_2$) state of phthalazine is caused by a n-π^* transition from $13b_2$ to $4b_1$ orbitals. The MOLDEN package (Ref. 16) was utilized.

kind of molecule and chemical substitution would be the best molecular candidate for optical control of a dipole moment. As shown in Tables I–III, 5-fluoropyrimidine, 5-chloropyrimidine, quinoxaline, 6,7-difluorophthalazine, and 6,7-dichlorophthalazine show the dipole moment whose direction becomes opposite after the $S_0 \rightarrow S_1$ transition. Of these compounds, 6,7-difluorophthalazine and 6,7-dichlorophthalazine are strong candidates because of a drastic change in orientation as well as magnitude of the electric dipole moment after the $S_0 \rightarrow S_1$ transition. To confirm the present results, polarization measurements of the electroabsorption and electrofluorescence spectra (i.e., polarization measurements of the electric-field-induced change in absorption and fluorescence spectra in solution) are strongly recommended.

IV. CONCLUSIONS

We tried to find the molecules whose direction of the electric dipole moment becomes opposite after the $S_0 \rightarrow S_1$ transition using CASPT2/cc-pVXZ//CASPT2/cc-pVDZ (X=D, T, Q) calculations. Pyrimidine, quinoxaline, phthalazine, and their chlorine- or fluorine-substituted compounds were the reference molecules. The following could be candidate compounds that show photoconversion of the direction of the electric dipole moment after the $S_0 \rightarrow S_1$ (n-π^*) transition: 5-fluoropyrimidine, 5-chloropyrimidine, quinoxaline, 6,7-difluorophthalazine, and 6,7-dichlorophthalazine. The latter two compounds are the best candidates because of a large and clear change of the electric dipole moment.

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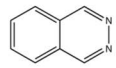
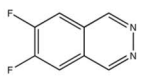
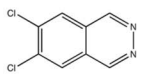
TABLE III. Excitation energy and dipole moment of phthalazine derivatives obtained by (n, π)-CAPST2/cc-pVXZ (X=D, T, Q). For the axis definition, see Fig. 1(c).

Molecule	Active Space	Basis set		Excitation energy / eV				Dipole moment / Debye[a]			
				Electronic states				Electronic states			
				1^1A_1 (S_0)	1^1A_2	1^1B_1 (S_1)	1^1B_2	1^1A_1 (S_0)	1^1A_2 (S_1)	1^1B_1	1^1B_2
 phthalazine	(14e, 12o)	cc-pVDZ	vertical	0.00	3.76	4.24	5.54	-4.79 (-4.75)	-1.61 (-1.49)	-1.20 (-1.11)	-9.29 (-9.19)
			adiabatic	-	2.83	3.82	5.24	-	-1.21 (-1.10)	-0.88 (-0.79)	-8.79 (-8.73)
		cc-pVTZ	vertical	0.00	3.69	4.15	5.33	-4.84	-1.60	-1.19	-9.48
			adiabatic	-	2.78	3.73	5.07	-	-1.21	-0.88	-8.94
		cc-pVQZ	vertical	0.00	3.68	4.12	5.27	-4.88	-1.62	-1.21	-9.57
			adiabatic	-	2.76	3.70	5.02	-	-1.23	-0.91	-9.01
 6,7-difluorophthalazine	(18e, 14o)	cc-pVDZ	vertical	0.00	3.76	4.25	5.74	-1.57	1.67	1.84	2.27
			adiabatic	-	2.83	3.82	5.26	-	2.09	2.21	1.75
		cc-pVTZ	vertical	0.00	3.69	4.15	5.55	-1.70	1.57	1.74	2.26
			adiabatic	-	2.78	3.75	5.13	-	1.99	2.10	1.73
		cc-pVQZ	vertical	0.00	3.68	4.13	5.50	-1.70	1.57	1.75	2.31
			adiabatic	-	2.76	3.72	5.10	-	2.00	2.11	1.76
 6,7-dichlorophthalazine	(18e, 14o)	cc-pVDZ	vertical	0.00	3.58	4.08	5.51	-1.59	1.88	2.40	2.39
			adiabatic	-	2.68	3.65	5.08	-	2.29	2.81	1.88
		cc-pVTZ	vertical	0.00	3.52	3.99	5.31	-1.61	1.95	2.46	2.53
			adiabatic	-	2.62	3.57	4.93	-	2.35	2.86	2.00
		cc-pVQZ	vertical	0.00	3.56	4.03	5.31	-1.58	1.93	2.45	2.54
			adiabatic	-	2.66	3.60	4.95	-	2.32	2.84	2.01

[a]Dipole moments were calculated with approximate CASPT2 density. Those calculated with exact CASPT2 density are given in parentheses.

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