

A molecular orbital study on a tetra-aza macrocycle containing 2,2'-bipyridines and its lithium complex



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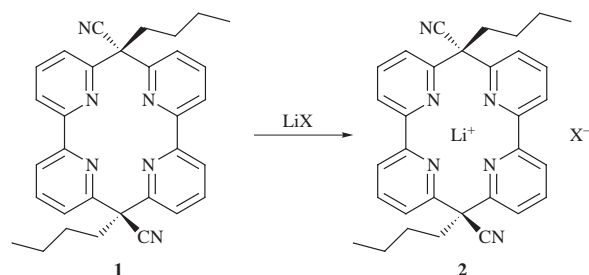
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Singlet transition energies and oscillator strengths of two configurational isomers of a dicyano dibutyl tetra-aza macrocycle containing four pyridine rings and their lithium complexes were calculated using the CNDO/S CI method at *ab initio* RHF/3-21G optimized geometries. The results were in good agreement with those derived from the UV-Visible absorption spectra. The drastic spectral changes observed upon complexation in the *trans*-isomer were found to be due to the significant conformational change in the bipyridine moiety and the resulting energy separation of the frontier π orbitals. The close proximity between the triplet states and the singlet excited state suggested that the intersystem crossing might occur in the *trans* form of the lithium free macrocycle. This is one of the possible explanations of the large discrepancy in fluorescence intensities between the *trans*-isomer of the macrocycle and its lithium complex.

Introduction

There has been much recent interest in the application of multi-dentate macrocyclic compounds to asymmetric syntheses¹ and to systems that utilize macrocycles to recognize molecules.² Most of the previous studies utilizing macrocycles have emphasized the mechanism leading to interaction with the guest.³ However, studies on the spectroscopic behavior of macrocycles themselves are also of interest for their numerous potential applications, such as that of a sensor for medical use.⁴

We have previously synthesized several new macrocycles that show chemically fascinating properties.⁵ Using lithium derivatives, we were able to observe the specific fluorescence behavior of these new macrocycles.^{5c} A great fluorescence enhancement (over 1000 fold) on the complexation with lithium ions (**2**) was observed for the *trans*-isomer of a dicyano dibutyl tetra-aza macrocycle (**1**). This property is a desirable one for use in a



sensor.⁶ However, the reason why such spectroscopic properties appear remains to be understood. Accordingly, we became interested in the possibility of explaining such properties of the new macrocycles using theoretical methods. In addition, such research might provide important information for the design of new multi-dentate macrocyclic compounds having better functionalities.

In this paper, the geometric features of the *cis/trans*-isomers of the macrocycles and the corresponding lithium complexes, the energy profile of the UV-Visible spectra, and the relationship between them were studied by *ab initio* and semi-empirical

molecular orbital (MO) calculations. In addition, the energy profiles of singlet and triplet excited states were estimated to interpret the fluorescence enhancement observed for the macrocycle lithium complex.

Computational details

Geometry optimizations by semi-empirical MNDO and *ab initio* RHF methods with STO-3G⁷ and 3-21G⁸ basis sets were carried out using the program GAMESS⁹ for Unix on IBM RS/6000, IBM SP2, and SGI Origin 2000. Force constant matrices (hessians) were calculated at stationary points in order to identify them as minima (all positive constants), transition states (one negative force constant), or higher order stationary points.

Transition energies were estimated by CIS (Configuration Interaction Singles) calculations for excited states based on the CNDO/S method at the *ab initio* RHF/3-21G optimized geometries in order to interpret the electronic spectra of the *cis/trans*-isomers of the macrocycles and their cationic lithium complexes. Active orbitals selected in the CI calculation were twelve occupied orbitals containing eight π , four σ orbitals and eight unoccupied π^* orbitals. The origins of the four σ orbitals are lone pair orbitals on nitrogen atoms. For the CNDO/S calculations, two center Coulomb integrals, γ_{AB} , were calculated using the equation proposed by Pariser and Parr.¹⁰ The program MOS-FV4 in WinMOPAC¹¹ for Windows on PC was used for these CNDO/S CI calculations.

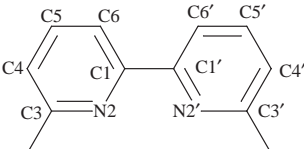
To generate the geometries of the macrocycles with various torsion angles between the two pyridine rings in the bipyridine moiety, a minimum energy path was followed based on the MNDO method using the program MOPAC97¹¹ in WinMOPAC.

Results and discussion

Geometric features of *cis/trans*-isomers of macrocycles and their lithium complexes

Geometric parameters of the metal free *trans*-isomer of a

Table 1 Selected optimized geometric parameters of the bipyridine moiety of the *trans*-isomer of dicyano dibutyl tetra-aza macrocycle in comparison with the experimental parameters from X-ray diffraction



	MNDO	RHF/STO-3G	RHF/3-21G	exptl. ^{5b}
$r(\text{C1}-\text{C1}')/\text{\AA}$	1.493	1.519	1.492	1.494(5)
$r(\text{C1}-\text{N2})/\text{\AA}$	1.355, 1.355	1.354, 1.354	1.325, 1.326	1.340(4), 1.333(4)
$r(\text{N2}-\text{C3})/\text{\AA}$	1.357, 1.357	1.352, 1.352	1.321, 1.321	1.330(4), 1.339(4)
$\theta(\text{N2}-\text{C1}-\text{C1}')^\circ$	113.5, 113.2	113.8, 114.0	115.1, 115.3	114.8(3), 113.7(3)
$\theta(\text{N2}-\text{C1}-\text{C6})^\circ$	122.0, 121.9	123.0, 123.0	121.4, 121.4	122.9(3), 121.6(3)
$\theta(\text{C1}-\text{N2}-\text{C3})^\circ$	120.6, 120.6	117.5, 117.5	121.3, 121.2	118.5(3), 118.8(3)
$\varphi(\text{N2}-\text{C1}-\text{C1}'-\text{N2}')^\circ$	78.4	57.9	60.1	58.9

dicyano dibutyl tetra-aza macrocycle were previously reported using X-ray diffraction data.^{5b} Energy minimum structures with C_i symmetry were found by both the MNDO and *ab initio* RHF calculations. Table 1 lists the optimized geometric parameters along with the experimental data. The results of the experiment on the bond lengths showed better agreement with the MNDO and the RHF/3-21G calculations than with the RHF/STO-3G calculations. The estimation of the dihedral angle $\varphi(\text{NCCN})$ by the *ab initio* RHF method (57.9 and 60.1 degrees) agreed well with the experimental value (58.9 degrees), while the MNDO method overestimated it (78.4 degrees). Results from the *ab initio* RHF/3-21G calculation, which produced the most reliable geometries, will mainly be referred to in this paper. The importance of the polarization functions had been pointed out based on geometry optimizations for the 2,2'-bipyridine itself by Howard.¹² Fig. 1 shows the optimized energy minimum structures of *trans*- and *cis*-isomers and their lithium complexes obtained by the RHF/3-21G calculation. The two pyridine rings in the bipyridine moiety twist in the *trans*-isomer, while they are coplanar in its lithium complex with C_1 symmetry (see Fig. 1a and 1b). Lone pair electrons on nitrogen atoms in the *trans*-isomer point in opposite directions in accord with the twisted conformation. On the other hand, in the lithium complex they point in the same direction due to the coordination from the lone pairs on nitrogen atoms to the lithium cation. The geometries of the *cis*-isomer¹³ (Fig. 1c) and its lithium complex (Fig. 1d) were very similar to each other, and were also similar to the geometry of the lithium complex of the *trans*-isomer (Fig. 1b), in which the two pyridine rings of the bipyridine moiety are coplanar.

Transition energies compared with UV-Visible absorption spectra

Calculated transition energies represented by their corresponding wavelengths with units of nm and oscillator strength for the *cis/trans*-isomers and their lithium complexes are shown in Fig. 2. The largest peak corresponds to the electronic transitions from S_0 to S_2 states for all four cases (Fig. 2a–d). This peak has the longest wavelength among the peaks with non-zero oscillator strength. For the metal free *cis*-isomer, the S_2 peak was estimated at around 265 nm (Fig. 2c), which corresponds to the peak at around 281 nm determined using UV-Visible spectral data in previous work by one of the present authors (S.O.).^{5b} On complexation of Li^+ , the absorption peak moves to a 10 nm-longer wavelength (red-shift), as shown in Fig. 2d. This tendency is consistent with the experimental behavior. The metal free *trans*-isomer has a peak with a shorter wavelength at 257 nm (Fig. 2a), which corresponds to the peak at around 266 nm in the spectral data.^{5b} Upon complexation of Li^+ , the peak shifts to a 15 nm-longer wavelength, and its oscillator strength

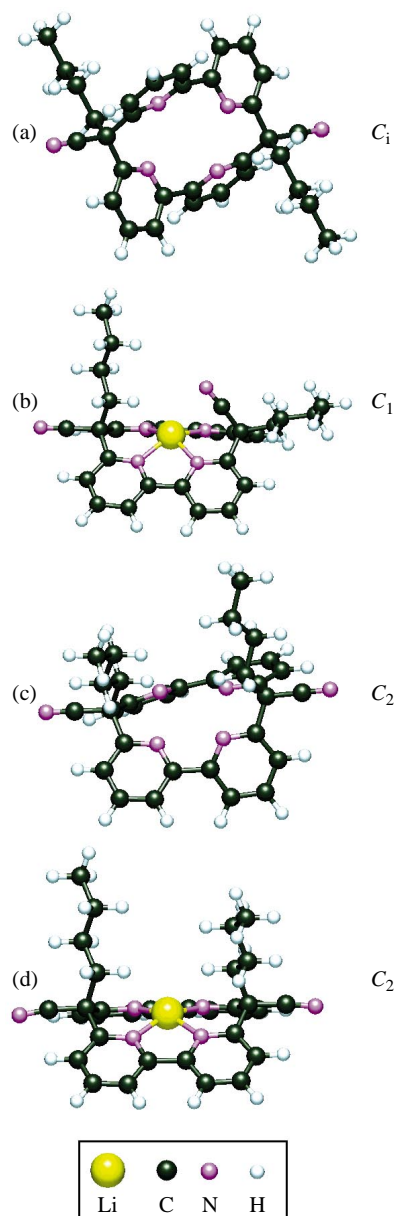


Fig. 1 Energy minimum structures of two configurational isomers of a dicyano dibutyl tetra-aza macrocycle containing 2,2'-bipyridine and its lithium complexes obtained by geometry optimization at the RHF/3-21G level of theory: *trans*-isomer (C_i) (a), lithium complex of the *trans*-isomer (C_1) (b), *cis*-isomer (C_2) (c), and lithium complex of the *cis*-isomer (C_2) (d).

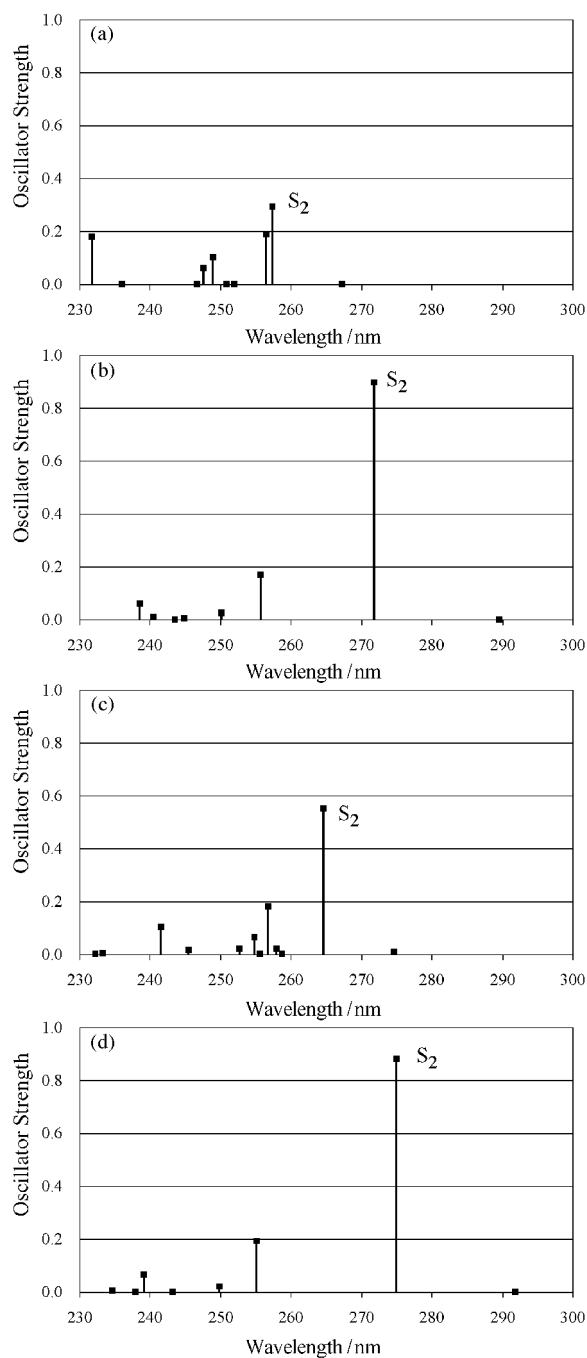


Fig. 2 Transition energies represented by their corresponding wavelengths with units of nm and oscillator strength for *trans/cis*-isomers (a, c) and their lithium complexes (b, d) estimated by CIS calculations for excited states with the CNDO/S method at the RHF/3-21G optimized geometries.

increases greatly (0.3→0.9), as seen in Fig. 2b. It is noteworthy that there is little difference in the calculated spectroscopic features between the lithium complexes of the *trans*- and *cis*-isomers (Fig. 2b and 2d). The similarity among the calculated spectral patterns of the metal free *cis*-isomer and both the lithium complexes would seem to be closely related to the similarity of the geometries. The relationship between the coplanarity or torsion angles of the two pyridines in the bipyridine moiety and the UV-Visible absorption spectra will be discussed below, along with the analysis of molecular orbitals.

Molecular orbitals and orbital energies

The tetra-aza macrocycle studied in this work has four pyridine rings, whose conformation greatly affects the characters of molecular orbitals and spectroscopic features such as UV-

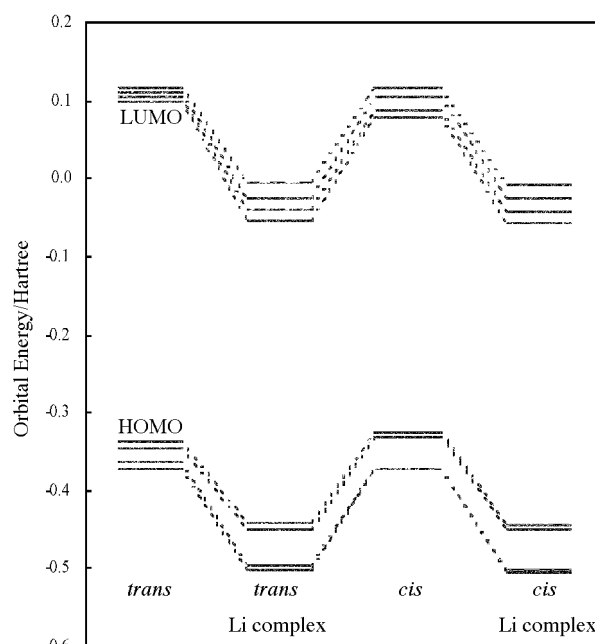


Fig. 3 Energy levels of the frontier molecular orbitals in metal free *trans*-isomer, the lithium complex of *trans*-isomer, metal free *cis*-isomer, and the lithium complex of *cis*-isomer by *ab initio* RHF/3-21G calculations.

Visible absorption spectra. The origin of the frontier molecular orbitals in this system is the π and lone pair orbitals of the constituent pyridine ring. The electronic feature greatly depends on the conformation of the four pyridine rings, especially on the coplanarity of the two pyridines in the bipyridine moiety because of the MO interaction between the pyridines connected through an inter-ring C–C bond. In the pyridine molecule itself, the HOMO and the 2nd-HOMO are π orbitals and the 3rd-HOMO is a σ orbital containing lone pair electrons on a nitrogen atom. If the four pyridine rings are not coplanar to one another, the π electron systems cannot interact with each other, and thus the HOMO should be degenerated nearly four-fold. In other words, the degeneracy depends on the coplanarity which can be measured by the torsion angles of the pyridines. In the *trans*-isomer, the four pyridine rings are not coplanar. Thus the four frontier π orbitals, which originally came from the HOMO of each pyridine ring, will be nearly degenerate. Upon complexation of Li^+ to the *trans*-isomer, the two pyridines in the bipyridine moiety become coplanar. Then the orbitals interact with one another, and this causes an energy separation between the degenerate frontier molecular orbitals. Orbital energies of the *trans*- and *cis*-isomers decrease upon complexation. As was expected, the energy separation between the 2nd-HOMO and 3rd-HOMO became large upon complexation to the *trans*-isomer. The *cis*-isomer and its lithium complex have similar energy profiles for the frontier π orbitals, except in regard to the absolute values of the orbital energies. Between the lithium complexes of the two isomers, the orbital energies are fairly similar. This is consistent with the similarity of estimated transition energies shown in Fig. 2b and 2d.

Molecular orbitals of the *cis*- and *trans*-isomers were inspected to interpret the differences of the orbital energy profile shown in Fig. 3. Fig. 4 depicts the 2nd- and 3rd-HOMOs of the two isomers. The *cis*-isomer has a more coplanar bipyridine moiety than the *trans*-isomer. Due to the coplanarity of the two pyridine rings, the 2nd-HOMO of the former has more anti-bonding character than that of the latter, as shown in Fig. 4. Furthermore, the 3rd-HOMO has more bonding character. The larger orbital energy separation between the 2nd- and 3rd-

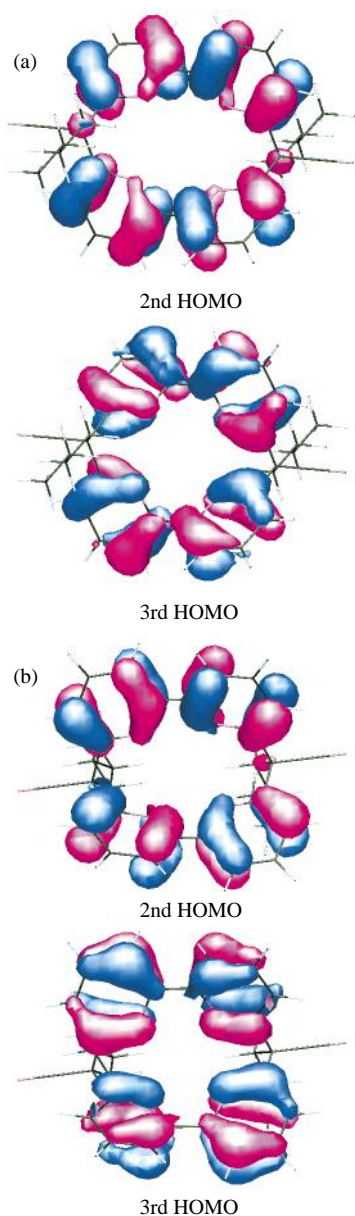


Fig. 4 The 2nd-HOMO and 3rd-HOMO of the *trans*-isomer (a) and the 2nd-HOMO and 3rd-HOMO of the *cis*-isomer (b) by *ab initio* RHF/3-21G calculations.

HOMOs in the *cis*-isomer is consistent with the MO character mentioned above.

In the *cis*-isomer, the occupied lone pair orbital, which is the most important for the reaction that generates coordinate bonds with Li^+ , is the 4th-HOMO, while in the *trans*-isomer it is the 5th-HOMO with the lower orbital energy. This is consistent with the experimental result that the complexation reaction of Li^+ occurred more easily in the *cis*-isomer than in the *trans*-isomer.

The CI vectors calculated by the CNDO/S CI method reveal that π - π^* transitions make a large contribution to low excited states. It is noteworthy that lone pair electrons are more concerned with the occupied orbitals of low energy levels than π -electrons and make little contribution to the electronic transition discussed in this paper. Only in the *trans*-isomer do the lone pairs make a small contribution to the electronic transition. The weight of CI expansion of the MOs relating to the lone pairs on N atoms in pyridine rings was 13%. Thus the electronic transition, which dominates the spectral pattern of the UV-Visible absorption, has a close relationship to the fact that the frontier molecular orbitals have π character localized mostly on the pyridine rings. Delocalization through the inter-ring C-C bond

in the bipyridine moiety depends on the coplanarity of the pyridine rings — in other words, on the torsion angles between them.

Torsion angle dependency of UV-Visible absorption spectra

There was a drastic change of geometries between the metal free *trans*-isomer and its lithium complex. As mentioned above, the coplanarity among the pyridine rings seemed to affect the spectroscopic feature of the UV-Visible absorption spectra. In order to examine the torsion angle dependency of the spectroscopic features, transition energies were estimated for various conformations. To generate the geometries of the macrocycle with various torsion angles of the two pyridine rings in the bipyridine moiety, a minimum energy path was followed against the distance of Li^+ from the center of gravity of the four nitrogens in a molecule using an eigenvector following scheme based on the MNDO method with the limitation of C_s symmetry. This limitation is only because for simplicity in the definition of the position of Li^+ . The obtained geometries on the minimum energy path are shown in Fig. 5. Figs. 5a and 5f show the optimized structures of the stationary points with a σ plane for the metal free *trans*-isomer with C_{2h} symmetry and its lithium complex with C_s symmetry, respectively, for comparison. At the first step of the geometry optimization the fixed distance between the lithium and the center of the macrocycle was 6.9 Å (Fig. 5b). Fig. 5b shows the structure very close to that of the metal free *trans*-isomer shown in Fig. 5a, in which two of the four nitrogens are up and the other two are down. The distance of the lithium from the center of the macrocycle lessens by a half of the macrocycle, namely, the two pyridines at the right side become coplanar as shown in Fig. 5c and 5d. Finally, the four nitrogens are directed in the same direction and the two pyridine rings of the bipyridine moiety become coplanar as well as in the lithium complexes (see Fig. 5e and 5f). To avoid the influence of lithium upon the estimation of transition energies, CNDO/S CI calculations were carried out for the structures on the minimum energy path shown in Fig. 5b–f without a lithium cation. Changes of the total energies along the minimum energy path were not discussed here, since the purpose of this calculation was to obtain the geometric parameters with various torsion angles around the inter-ring C-C bond in the bipyridine moiety.

Fig. 6 shows transition energies from the ground state S_0 to the electronically excited states S_2 and S_3 and their oscillator strengths against the dihedral angle of $\varphi(\text{NCCN})$ in the bipyridine moiety instead of the torsion angles of the two pyridine rings, each of which is considered to be almost planar. Alphabetical notations from a to f correspond to the structures depicted in Fig. 5. As the bipyridine moiety becomes more coplanar, transition energies to the S_2 state become smaller (red-shift) (Fig. 6a) and their oscillator strengths get much larger (Fig. 6b). Filled squares at the notation f in Fig. 6a and 6b show the values for the lithium complex itself in the structure drawn in Fig. 5f. Complexation leads the $S_0 \rightarrow S_2$ transition to red-shift and increases its oscillator strength. On the other hand, Li^+ complexation has little effect on the $S_0 \rightarrow S_3$ transition energy and makes its oscillator strength slightly larger. As a result of Li^+ complexation with the *trans*-isomer, the difference in transition energies between $S_0 \rightarrow S_2$ and $S_0 \rightarrow S_3$ transitions becomes large. These computational results coincide well with the previously reported experimental results.^{5b}

For comparison, results of the RHF/3-21G energy minimum structure for the *trans*-isomer with C_1 symmetry and its lithium complex with C_1 symmetry¹⁴ are shown as the notations g and h, respectively. Dihedral angle dependency is consistent with the model calculations described above, though there is a discrepancy in the absolute values. These model calculations suggest that a drastic change of geometry upon complexation of the lithium cation to the *trans*-isomer can enhance the oscil-

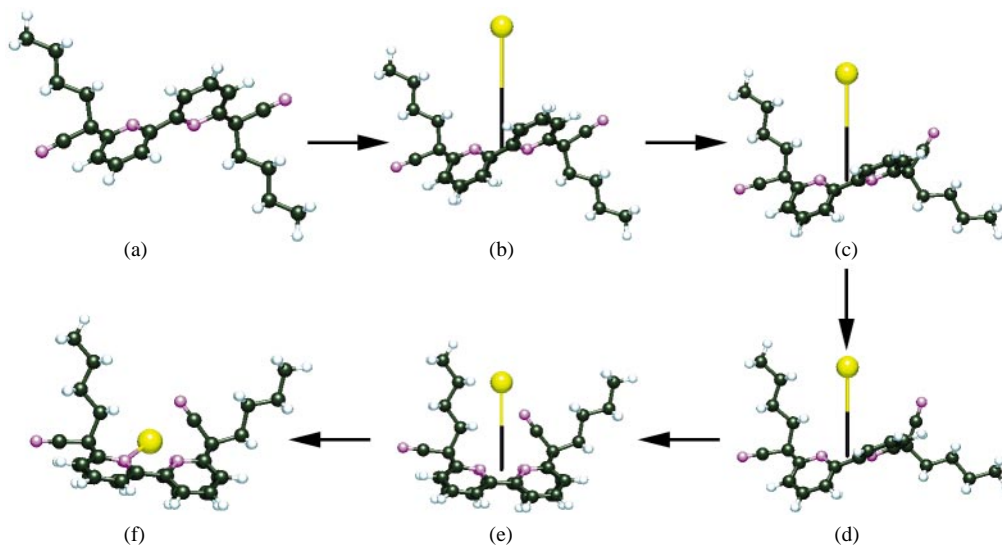


Fig. 5 Change of geometries from the dissociation limit of a lithium cation to the formation of the lithium complex: optimized structure at the stationary point with C_{2h} symmetry for the metal free *trans*-isomer as a starting point (a), minimum energy structures for fixed distances of 6.9 Å (b), 6.0 Å (c), 5.1 Å (d), 5.0 Å (e) between lithium and the center of gravity of the four nitrogens, which are shown as vertical bars, and the optimized structure at the stationary point with C_s symmetry for the lithium complex of *trans*-isomer (f).

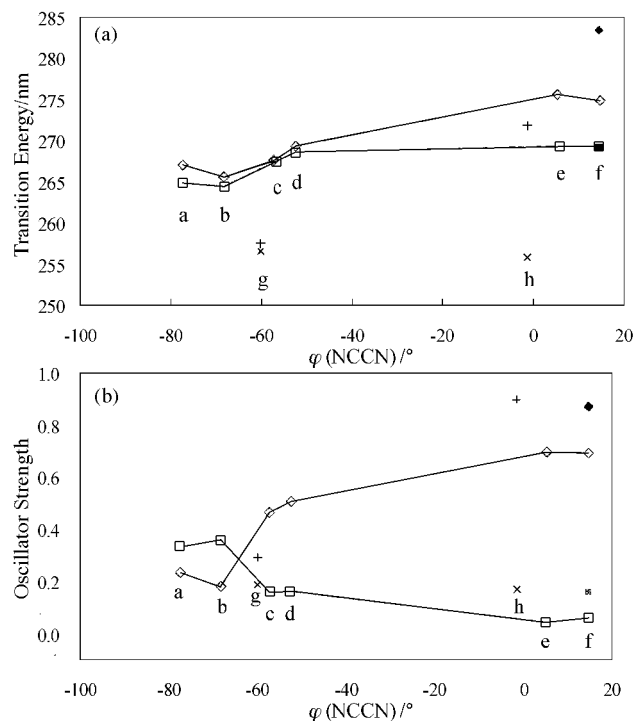


Fig. 6 Transition energies in nm units from the ground state S_0 to the electronically excited states S_2 (\diamond) and S_3 (\square) (a) and their oscillator strength (b) against the dihedral angles of N1–C2–C2'–N1' in the bipyridine moiety for the macrocycle without a lithium cation. The alphabetical characters from a to f listed below the square marks show the correspondence to the structures in Fig. 5. Calculated values for the lithium complex with the same structure as in Fig. 5f are shown as filled squares. Notations g and h denote the values at the RHF/3-21G minimum energy structures, respectively, for the *trans*-isomer (C_s symmetry) and its lithium complex (C_1 symmetry).

lator strength of electronic transitions and may have a close relationship to the specific behavior of fluorescence intensity.

Comparison with triplet transition energies in the *trans*-isomer

In order to discuss the difference of fluorescence intensities in the *trans*-isomer and its lithium complex, the possibility of intersystem crossing from the singlet to triplet states was examined. CNDO/S CI calculations were carried out to estimate the

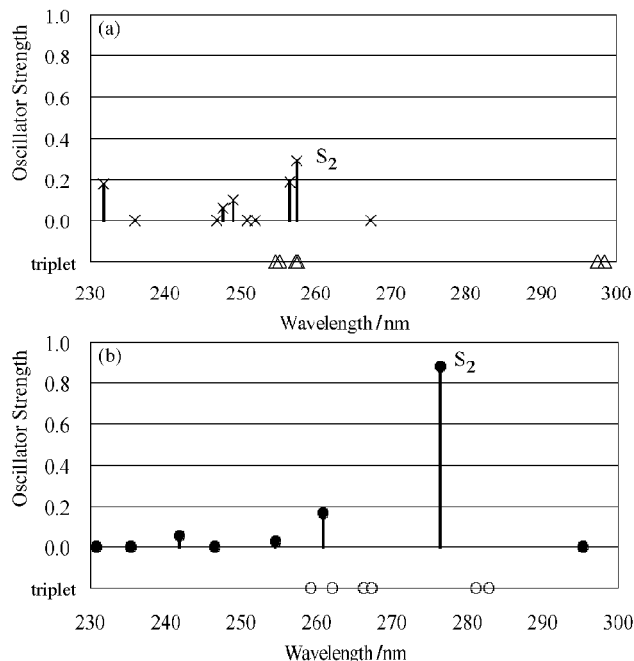


Fig. 7 Comparison of transition energies in nm units among the singlet and triplet for the metal free *trans*-isomer (a) and its lithium complex (b): singlet (\times) and triplet (Δ) for the metal free *trans*-isomer, singlet (\bullet) and triplet (\circ) for the lithium complex. Oscillator strengths are also shown for singlets. Since transition from the S_0 to triplet states is spin forbidden, oscillator strengths for triplets are zero. The marks for triplet states are shown in the lower part of the figure for comparison with the singlet states.

transition energies from S_0 to triplet excited states of the *trans*-isomer and its lithium complex. Transition from the S_0 to triplet states is spin forbidden, and therefore the oscillator strength is zero. Fig. 7 shows a comparison of the transition energies represented by their corresponding wavelengths in units of nm between the singlet and triplet states for the metal free *trans*-isomer and its lithium complex. In contrast with the lithium complex, the metal free *trans*-isomer has triplet states very close to the $S_0 \rightarrow S_2$ transition. It is possible that intersystem crossing occurs in the latter, and this may be the reason for the weak fluorescence in the metal free *trans*-isomer.^{5c} On the other hand, the lithium complex can have strong fluorescence. Another possibility is that the fluorescence intensities are weakened by

the flexibility of the molecules, which could cause energy loss due to the molecular vibration. Studies on this matter are in progress.

Concluding remarks

The geometric features of *cis/trans*-isomers of a dicyano dibutyl tetra-aza macrocycle containing 2,2'-bipyridines and their lithium complexes were examined by semi-empirical MNDO and *ab initio* RHF molecular orbital calculations. The RHF/3-21G calculations reproduced the experimental values for the bond lengths, bond angles, and torsion angles of the pyridine rings. The estimated transition energies and oscillator strengths of the two configurational isomers and their lithium complexes by CNDO/S CI calculations agreed well with the UV-Visible absorption spectra. The drastic spectral change occurring in the *trans*-isomer upon Li^+ complexation was found to be closely related to the significant conformational change in the bipyridine moiety. This spectral change was attributed to specific features of the energy levels of the characteristic frontier molecular orbitals.

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- 13 Another *cis*-isomer with the cyano groups inside instead of outside (Fig. 1c) was successful in geometry optimization and was estimated to be less stable in energy. Therefore only the latter will be discussed in this paper. The geometric features of the bipyridine moiety and the spectroscopic features were very similar between the two *cis*-isomers.
- 14 The lithium complex with C_1 symmetry has two non-equivalent positions of the bipyridine moiety with dihedral angles of -1.4 and 5.4 degrees. In Fig. 6 only the values for the former one are shown.

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