An Unusual Mechanism for HOMO-LUMO Gap Narrowing in a Minimal Near-IR Dye Generated by the Deprotonation of Bis(dicyanomethylene)indan

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A minimal near-IR (NIR) dye with the lower molecular-weight than 250 is produced by the deprotonation of 1,3-bis(dicyanomethylene)indan. Despite the small π -conjugation system, the anionic dye shows light absorption and fluorescence in the red to near infra-red region. This paper reports on the unusual mechanism for HOMO-LUMO gap narrowing for the NIR dye. Density functional theory (DFT) analyses show the molecular-orbital transition from the LUMO+1 to HOMO by the deprotonation, which significantly reduces the HOMO-LUMO gap. Time-dependent DFT and group-theory analyses well explain the electronic-excitation properties. This is a new mechanism for reducing a HOMO-LUMO gap without extending π -conjugation systems.

1. INTRODUCTION

Control of light-absorption properties of molecules is a fundamental subject in chemistry.[1-17] So far, the following two strategies have been successfully employed for molecular design of near infra-red (NIR) dyes. One is based on the extension of π -conjugation systems and the other is owing to the electron-donor (*D*) and –acceptor (*A*) or push-pull concept.[1-17] Recently, a minimal NIR fluorescent dye with the lower molecular-weight (241.23) than 250 was reported by Heo *et al.*[18] This dye is characteristically generated by the self-deprotonation of colourless 1,3-bis(dicyanomethylene)indan (abbreviated as BDCI), as shown in Figure 1. Interestingly, in spite of the much smaller π -conjugation system as compared to the so-far reported NIR dyes[1-11], the deprotonated 1,3-bis(dicyanomethylene)indan anion (abbreviated as BDCIA) shows light absorption and fluorescence in the red to NIR region. This result implies a somewhat new mechanism to generate absorption bands at longer wavelengths. This paper reports on the mechanism to generate the absorption band in the red region by the deprotonation.

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2. COMPUTATIONAL DETAILS

In this work, the structures, electronic properties, and electronic-excitation spectra of BDCI and BDCIA are thoroughly examined with density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations. The optimized structures of BDCI and BDCIA were calculated by DFT [19] with the BPV86 functional [20-22] and 6-31G+(d,p)[23,24] basis set. Absorption spectra of the optimized structures were calculated by TD-DFT [25] at the same level (BPV86-6-31G+(d,p)) of theory. The BPV86 functional was chosen because it well reproduces the energy of the lowest singlet (S_1) excited state in BDCIA. In the DFT and TD-DFT calculations, solvent effects of water that was used in the previous experiment [18] were taken into account with the conductor-like polarizable continuum model (CPCM)[26,27]. All the calculations were performed using a Gaussian 09 software[28]. It was confirmed that similar results are obtained with other functionals such as B3LYP[20,29] and basis sets.

3. RESULTS AND DISCUSSION

The optimized structures of BDCI and BDCIA are shown in Figure 2. BDCI and BDCIA have analogous planar aromatic structures. BDCI has two out-of-plane hydrogen atoms attaching to the C_2 atom, reflecting the sp^3 hybrid orbital. On the other hand, BDCIA has an in-plane hydrogen atom at the C_2 position, reflecting the sp^2 hybrid orbital. By comparing the bond lengths between BDCI and BDCIA, it can be seen that the structure of the five-membered ring in BDCI is remarkably varied by the deprotonation as compared to the dicyanomethylene groups and benzene ring. With the deprotonation, the C_1 - C_2 and C_2 - C_3 bond lengths are shorten by 0.1 Å and the C_1 - C_5 , C_3 - C_4 , C_1 - C_6 , and C_3 - C_7 bond lengths are elongated by 0.04 Å. This structural change indicates that two π -electrons generated by the deprotonation occupy a molecular orbital with bonding properties for the C_1 - C_2 and C_2 - C_3 bonds and weak anti-bonding properties for the C_1 - C_5 , C_3 - C_4 , C_1 - C_6 , and C_3 - C_7 bonds. It is noteworthy that both BDCI and BDCIA have the symmetry of the C_{2v} point group, because the group theory is useful for understanding the electronic and absorption properties qualitatively.

Figure 3 shows calculated absorption spectra for BDCI and BDCIA. For BDCI, electronic excitations occur at the wavelengths of 425 and 429 nm in the near-UV (NUV) region. On the other hand, in BDCIA two electronic excitations take place at 596 and 416 nm in the visible and NUV regions, respectively. As reported by Heo *et al.*, BDCI show an absorption band with a peak at ca. 340 nm in the NUV region and BDCIA show two bands with peaks at 580 and 360 nm in the visible and NUV regions, respectively.[18] Therefore, the TD-DFT calculations qualitatively well-reproduce the experimental result. The calculated energy (2.08 eV) of the absorption band in the visible region in BDCIA is close to the experimental data (ca. 1.97 eV) of the S_1 (0-0) excitation. On the other hand, the calculated energies (2.92 eV in BDCI and 2.98 eV in BDCIA) of the NUV bands are underestimated as compared to the experimental data (ca. 3.65 eV in BDCI and 3.44 eV in BDCIA) at the absorption peaks. The calculated energies should be compared to the (0-0) excitation energies rather than the peak energies. Unfortunately, the (0-0) excitation energies of the NUV bands in BDCI and BDCIA are not available.

As for the configurations of the excitations, the strong band at 425 nm in the NUV region in BDCI is attributed to the electronic transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) with a minor contribution (3%) of the transition from the second highest occupied molecular orbital (HOMO-1) to the second lowest unoccupied molecular orbital (LUMO+1). The negligible NUV band at 429 nm in BDCI is attributed to the strongly mixed excitation by configuration interaction between the HOMO-1→LUMO (65%) and HOMO→LUMO+1 (35%) transitions. On the other hand, for BDCIA, the visible band at 596 nm is contributed by the HOMO→LUMO transition with a minor contribution (10%) of the HOMO-1→LUMO transition. The NUV band at 416 nm in BDCIA is dominated by the HOMO-1→LUMO transition with a little contribution (10%) of the HOMO→LUMO transition. From the fact that both the S_1 excited states in BDCI and BDCIA are predominantly attributed to the (HOMO, LUMO) excited states, it is suggested that the appearance of the absorption band in the visible region by the deprotonation is attributed to a significant reduction of the HOMO-LUMO gap from BDCI to BDCIA.

Figure 4 shows the energy level diagram and electronic distributions of the HOMO-1, HOMO, LUMO, and LUMO+1 in BDCI and BDCIA. The electronic distributions of HOMO and LUMO in BDCI and BDCIA are in accordance with those [18] calculated by DFT with B3LYP/6-31G(d,p). The electronic distributions of the HOMO, LUMO and LUMO+1 in BDCI have similar symmetries in the moiety other than the C_2 atom to those of the HOMO-1, LUMO and HOMO in BDCIA. This result indicates that the HOMO-1, HOMO, and LUMO in BDCIA originate from the HOMO, LUMO+1, and LUMO in BDCI, respectively, as shown by the dotted lines in Figure 4. In order to support the molecular-orbital transitions, the dependence of the energies of the HOMO-1, HOMO, LUMO, and LUMO+1 in BDCI on the C-H bond length at the C_2 position is examined. As shown in Figure 5, with increasing the C-H bond length, the local structure around the C_2 atom gradually changes from a tetrahedral structure with the sp^3 hybrid orbital to a planar one with sp^2 . In addition, interestingly, the LUMO+1 is drastically stabilized with increasing the C-H bond length in contrast to the unmoving other orbitals and, then, intersect with the LUMO at ca. 1.8 Å. Since the hydrogen atom is not dissociated as a proton, but as a hydrogen atom in the calculation, we should add two π -electrons in the molecule. In consequence of the occupancy of the stabilized LUMO+1 by the two additional π -electrons, the LUMO+1 in BDCI turns out to be the HOMO in BDCIA. The HOMO in BDCIA has bonding properties for the C_1 - C_2 and C_2 - C_3 bonds and weak anti-bonding properties for the C_1 - C_5 , C_3 - C_4 , C_1 - C_6 , and C_3 - C_7 bonds, which are consistent with the above-mentioned changes in the bond lengths between BDCI and BDCIA. Therefore, this result supports the mentioned molecular-orbital transition from the LUMO+1 in BDCI to HOMO in BDCIA.

The higher energy shifts from the HOMO in BDCI to HOMO-1 in BDCIA by 0.42 eV and from LUMO in BDCI to the LUMO in BDCIA by 0.75 eV are considered to result from the negative charge produced by the deprotonation, which weakens attractive electron-nucleus interactions. On the other hand, the large lower energy shift by 1.47 eV from the LUMO+1 in BDCI to the HOMO in BDCIA is caused by the following two stabilization factors. (i) Change from the anti-bonding interaction (dashed red circle in Figure 4) with the pseudo $2p_z$ -like orbital consisting of the $1s$ orbitals of the two hydrogen atoms to the larger bonding interaction (solid red circle in Figure 4) with the $2p_z$ orbital of the deprotonated C_2 carbon. (ii) Much larger electronic distributions (solid blue circles in Figure 4) of the HOMO in BDCIA on the four nitrogen atoms with a high electronegativity significantly reducing the distribution on the benzene ring as compared to the LUMO+1 in BDCI. Because of the strong C_1 - C_2 and C_2 - C_3 bonding properties and increased electron distributions on the nitrogen atoms, the LUMO+1 in BDCI is significantly stabilized by the deprotonation.

The mentioned molecular-orbital transitions and excitations in BDCI and BDCIA are analyzed with the group theory. As mentioned above, BDCI and BDCIA have the symmetry of the C_{2v} point group. The HOMO-1 and LUMO in BDCI belong to the A_2 irreducible representation and the HOMO and LUMO+1 in BDCI to B_1 . On the other hand, the HOMO-1, HOMO and LUMO+1 in BDCIA belong to B_1 and the LUMO to A_2 . Thus, the molecular-orbital transitions between BDCI and BDCIA are consistent from the viewpoint of the conservation of the irreducible representations. In addition, the absorption spectra of BDCI and BDCIA in the NUV to visible region are governed by the four excitations between the four orbitals, HOMO→LUMO, HOMO-1→LUMO, HOMO→LUMO+1, and HOMO-1→LUMO+1. As shown in Table 1, the (HOMO, LUMO) and (HOMO-1, LUMO+1) excited states in BDCI and the (HOMO, LUMO) and (HOMO-1, LUMO) excited states in BDCIA belong to the B_2 irreducible representation. On the other hand, the (HOMO-1, LUMO) and (HOMO, LUMO+1) in BDCI and the (HOMO, LUMO+1) and (HOMO-1, LUMO+1) in BDCIA belong to A_1 . Since the ground states of BDCI and BDCIA are totally symmetric, the HOMO→LUMO and HOMO-1→LUMO+1 transitions in BDCI and the HOMO→LUMO and HOMO-1→LUMO transitions in BDCIA are dipole-allowed for the y-polarization (see Figure 2). On the other hand, the HOMO-1→LUMO and HOMO→LUMO+1 transitions in BDCI and the HOMO→LUMO+1 and HOMO-1→LUMO+1 in BDCIA are dipole-forbidden. This result is consistent with the calculation result in Figure 3. Since configuration interactions due to electronic repulsion are totally symmetric, configuration interactions occur between the excited states with same irreducible representations, as shown in Figure 3. Therefore, the molecular-orbital transitions with the deprotonation and electronic excitation spectra of BDCI and BDCIA were well understood based on the group theory.

Finally, the HOMO-LUMO gap narrowing mechanism is compared with the conventional strategies. As shown in Figure 6, the extension of π -conjugation systems and the introduction of *D* and *A* chemical groups reduce a HOMO-LUMO gap by elevating the HOMO level and lowering the LUMO level. On the other hand, the feature of the HOMO-LUMO gap narrowing mechanism in BDCIA is the level crossing between the LUMO+1(BDCI)-HOMO (BDCIA) and LUMO (BDCI and BDCIA). With this level crossing, this mechanism reduces a HOMO-LUMO gap even with small π -conjugation systems. By chemical controls of the stabilization energy of the LUMO+1 by the deprotonation and the energies of the LUMO and LUMO+1 before the deprotonation, it makes it possible to realize low-molecular-weight dyes.

4. CONCLUSION

In this paper, I clarified the mechanism of the HOMO-LUMO gap narrowing in a minimal NIR BDCIA dye generated by the deprotonation of BDCI. The level-crossing between the LUMO and LUMO+1 and molecular-orbital transition from the LUMO+1 in BDCI to HOMO in BDCIA by the deprotonation enables the HOMO-LUMO gap narrowing without extension of the π -conjugation system. The knowledge provided by this paper is useful for molecular design of small and low-molecular-weight dyes.

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FIGURES

Figure 1. Molecular structures of BDCI and BDCIA and the deprotonation reaction of BDCI at the C₂ position to generate the BDCIA dye.

Figure 2. Calculated bond lengths in BDCI and BDCIA. Gray: carbon, white: hydrogen, blue: nitrogen atoms. C_2 rotational axis is set to the z axis.

Figure 3. Calculated electronic excitation spectra of BDCI (blue lines) and BDCIA (red lines). The excitation wavelengths and energies, oscillator strengths (f), configurations, and polarizations are shown.

Figure 4. Kohn-Sham eigenvalue energy diagram and isosurface plots (isovalue=0.03) of HOMO-1, HOMO, LUMO, and LUMO+1 in BDCI and BDCIA. The irreducible representations of the molecular orbitals are shown in parentheses. Gray: carbon, white: hydrogen, blue: nitrogen atoms. Green and red isosurfaces stand for opposite phases in amplitude. Blue circles are all in the same size.

Figure 5. Dependences of the structure of BDCI and the energies of HOMO-1, HOMO, LUMO, and LUMO+1 in BDCI on the bond length between the C₂ and hydrogen atom. Gray: carbon, white: hydrogen, blue: nitrogen atoms.

Figure 6. Schematic picture of mechanisms for HOMO-LUMO gap narrowing. (a) extension of a π -conjugation system, (b) introduction of electron-donating and -accepting groups, and (c) LUMO+1 $\rightarrow$ HOMO molecular-orbital transition by the deprotonation.

Table 1. Irreducible representations, polarizations, and transition properties of electronic excitations in BDCI and BDCIA.

	Electronic excitation	Irreducible representation	Polarization	Transition property
BDCI	HOMO→LUMO	B_2	y	allowed
	HOMO-1→LUMO	A_1	-	forbidden
	HOMO→LUMO+1	A_1	-	forbidden
	HOMO-1→LUMO+1	B_2	y	allowed
BDCIA	HOMO→LUMO	B_2	y	allowed
	HOMO-1→LUMO	B_2	y	allowed
	HOMO→LUMO+1	A_1	-	forbidden
	HOMO-1→LUMO+1	A_1	-	forbidden

Graphical abstract