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A charge-transfer host system composed of a chiral 1,1′-bi-2-naphthol cluster and benzylviologen

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Abstract—Chiral charge-transfer (CT) complexes composed of a chiral 1,1′-bi-2-naphthol cluster as the electron donor and 1,1′-dibenzyl-4,4′-bipyridinium dichloride as the electron acceptor serve as a host system for molecular recognition. CT complexes that include guest alcohols show different diffuse reflectance spectra (DRS) depending on the included guest.

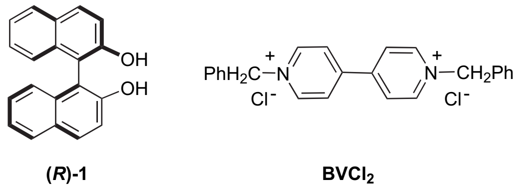
1. Introduction

The properties of organic compounds in the solid state are different from that in the solution state because molecules are densely packed and under the strong influence of neighboring molecules in the solid state. In the field of analytical chemistry, the development of a solid-state molecular recognition system has tremendous potential for the development of novel molecular recognition properties, which would be impossible in the solution state. Until now, although solid-state molecular recognition systems using organic host molecules have been reported, they are mostly composed of a single organic molecule.[1] If a solid-state molecular recognition system is composed of two or more organic molecules, molecular recognition may be easily controlled by changing the component molecules without additional synthesis.[2] Recently, we have developed strongly colored charge-transfer (CT) host systems composed of racemic (*rac*-) 1,1′-bi-2-naphthol derivatives as electron donors and *p*-benzoquinone or 1,1′-dimethyl-4,4′-bipyridinium dichloride (methylviologen) as electron acceptors.[3] These CT complexes can include aromatic molecules as guests. Interestingly, the colors of these CT complexes depend on the included guest and can be used as a visible molecular recognition system in the solid state. However, these CT host systems have no chirality and therefore can have no chiral molecular recognition properties.

In this paper, we report the formation of a chiral CT complex, which aims to control chiral molecular recognition and guest inclusion behavior by using achiral *n*-alkyl alcohols with different chain lengths. For the component molecules of this chiral CT complex, chiral (*R*)-1,1′-bi-2-naphthol [(*R*)-**1**] and 1,1′-dibenzyl-4,4′-bipyridinium dichloride ($BVCl_2$ or benzylviologen) were used as the electron donor and acceptor, respectively (Caption 1).

2. Results and discussion

Four *n*-alkyl alcohols, methanol (MeOH), ethanol (EtOH), *n*-propanol (*n*-PrOH), and *n*-butanol (*n*-BuOH), were used



(*R*)-1

$BVCl_2$

Caption 1.

Keywords: 1,1′-Bi-2-naphthol cluster; Chiral CT complex; Molecular recognition; Solid-state host system; Viologen.

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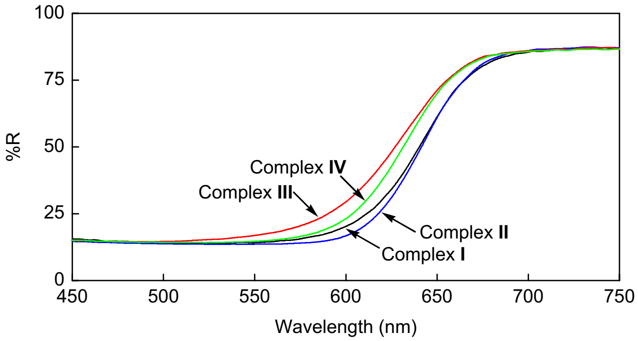


Figure 1. Diffuse reflectance spectra of crystals **I** (black line), **II** (blue line), **III** (red line), and **IV** (green line).

as guests. (R)-**1** and $BVCl_2$ were dissolved in each guest alcohol solution with heating, then left to stand at room temperature. After few days, many colored crystals, **I–IV**, were obtained, composed of (R)-**1** and $BVCl_2$ and included alcohol molecules. The diffuse reflectance spectra (DRS) of these crystals were measured and are shown in Figure 1.

Although the colors of these crystals are similarly deep red, they are quite different from those of the component solids. As expected, the DRS of these CT complexes changed depending on the included guest alcohol.

X-ray analyses of these complexes were performed to investigate the inclusion mechanisms for the guest alcohol. The crystal structures of complex **II**, which include EtOH, are shown in Figure 2.[4]

The stoichiometry of complex **II** is $BVCl_2$:(R)-**1**:EtOH=1:2:2, and the space group is $P2_12_12_1$. Characteristically, this crystal has two similar types of chiral clusters, **II-c1** and **II-c2**, composed of two (R)-**1** molecules (blue and purple molecules in Fig. 2a) connected by a hydrogen bond between a hydroxyl group and two chloride ions (green balls in Fig. 2a). Although the distances between the hydroxyl group and chloride ion in these two chiral clusters are similar, the torsion angles of the two (R)-**1** molecules in chiral cluster **II-c1** are smaller than those in chiral cluster **II-c2**. The chiral cavity (red circle in Fig. 2) is formed by self-assembly of these clusters by CT interactions with benzylviologen ion (BV^{2+}, green molecule in Fig. 2). Four types of EtOH molecules are trapped in the cavity (Fig. 2c). Two of the four types of EtOH molecules (red spacefilling molecule in Fig. 2c) are trapped with chloride ions via a hydrogen bond. The others (orange spacefilling molecules in Fig. 2c) interact with (R)-**1** and BV^{2+} by CH-π interactions (2.89 and 2.99 Å, respectively).

The crystal structures of complex **IV**, which include n-BuOH, are shown in Figure 3.

The stoichiometry of complex **IV** is $BVCl_2$:(R)-**1**:n-BuOH=1:2:1.5, and the space group is $P2_12_12_1$. This crystal also has two similar types of chiral clusters, **IV-c1** and **IV-c2**, composed of two (R)-**1** molecules (blue and purple

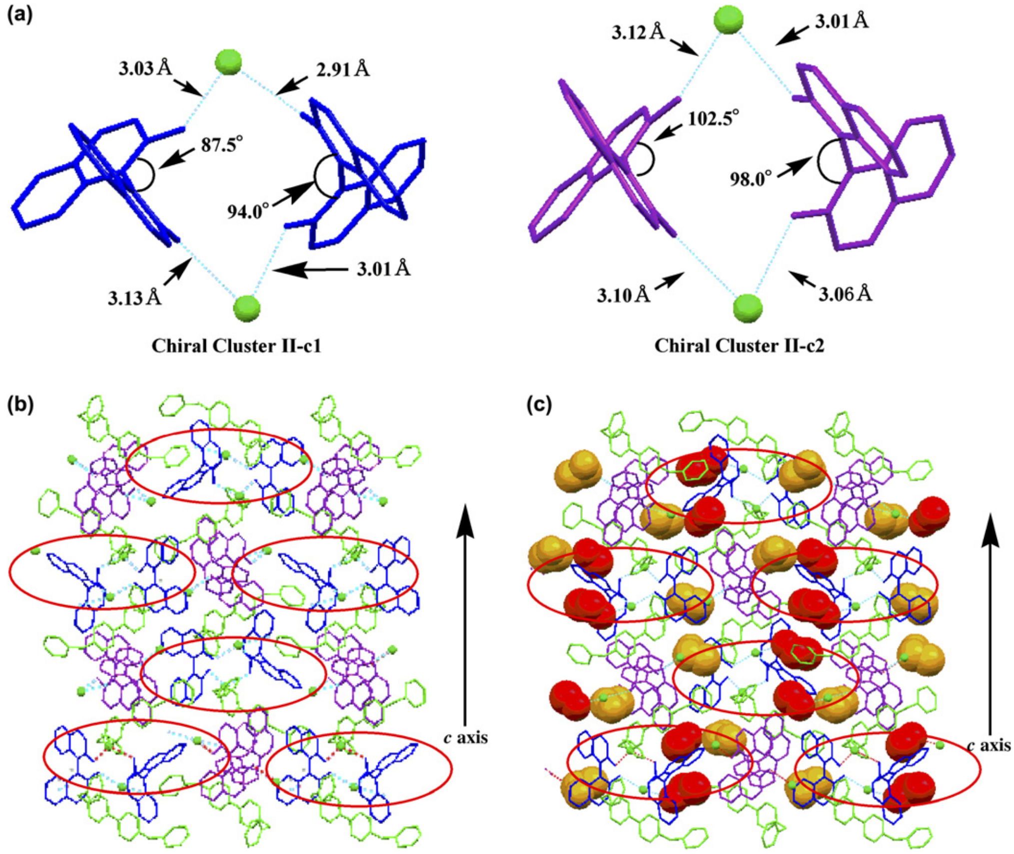


Figure 2. Crystal structures of complex **II**. (a) Structures of extracted chiral clusters **II-c1** and **II-c2**. (b) Packing structure of chiral clusters observed along the a axis. (c) Packing structure of guest alcohols observed along the a axis. Red circles show chiral cavities.

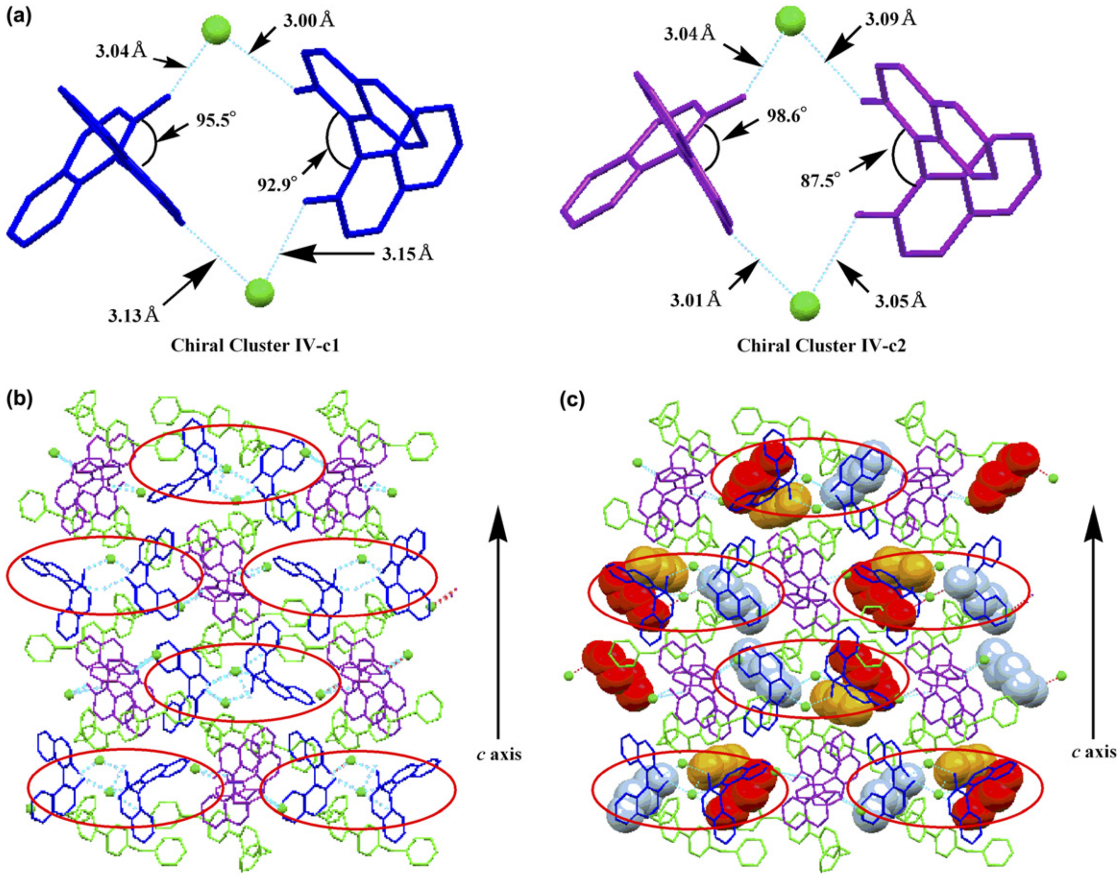


Figure 3. Crystal structures of complex **IV**. (a) Structures of extracted chiral clusters **IV-c1** and **IV-c2**. (b) Packing structure of chiral clusters observed along the *a* axis. (c) Packing structure of guest alcohols observed along the *a* axis. Red circles show chiral cavities.

molecules in Fig. 3a) and two chloride ions (green balls in Fig. 3a), same as in crystal **II**. Although the distances between the hydroxyl group and chloride ion are similar in these two chiral clusters, the torsion angles of the two (*R*)-**1** molecules are different between **IV-c1** and **IV-c2**. The chiral cavity (red circle in Fig. 3) is formed by self-assembly of these clusters by CT interactions with the BV^{2+} ion (green molecule in Fig. 3). The packing of the chiral cluster and the BV^{2+} ion are almost the same in complexes **II** and **IV**. However, in contrast to complex **II**, three types of *n*-BuOH molecules (red, orange, and light blue spacefilling molecules in Fig. 3c) are included in the chiral cavity. All *n*-BuOH molecules are trapped with chloride ions via hydrogen bonds.

Since complexes **I** including MeOH and **III** including *n*-PrOH are needle-like crystals, structural information on these crystals could not be obtained from X-ray analysis. Therefore, X-ray powder diffraction patterns of these crystals were measured and compared to those of crystals **II** and **IV** (Fig. 4).

Although complexes **I** are partly changed to amorphous by preparing the sample for measurement, the main peaks are clearly assigned. As a result, these four X-ray powder diffraction patterns, especially at low angle, are very similar. These patterns show that crystals **I** and **III** share a similar chiral cluster, which is formed from two (*R*)-**1** molecules and chloride ions, as in crystals **II** and **IV**. Moreover,

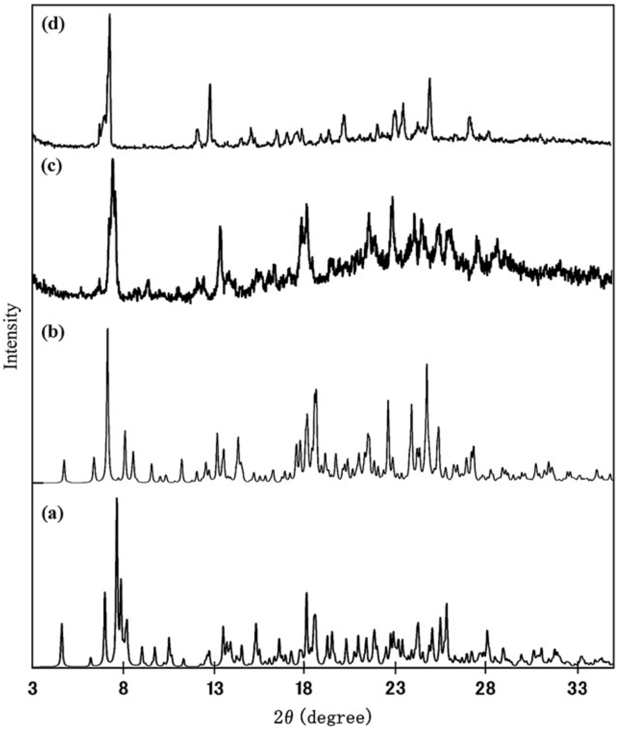


Figure 4. X-ray powder diffraction patterns of complexes (a) **II**, (b) **IV**, (c) **I**, and (d) **III**.

^{1}H NMR analysis reveals that the stoichiometries of complexes **I** and **III** are $BVCl_2$:(*R*)-**1**:MeOH=1:2:3 and $BVCl_2$:(*R*)-**1**:*n*-PrOH=1:2:1.5. That is, although the stoichiometries of $BVCl_2$ and (*R*)-**1** are the same [$BVCl_2$:(*R*)-**1**=1:2] in all complexes, as the alkyl chain of the included alcohol increases in length, its stoichiometry decreases in the crystal. These results suggest that this CT host system includes guest molecules by slightly changing the packing of this shared chiral cluster and by changing the amount of the included guest molecule.

It is expected that the guest dependence of the low-energy absorptions of these crystals (see Fig. 1) results from the guest-dependent packing of **1** (electron donor) and $BVCl_2$ (electron acceptor). To understand the compositions of the low-energy absorptions, the excited states of the CT chromophores in crystals **II** and **IV** (Fig. 5) have been examined theoretically. The calculated least energy excited states of the CT chromophores are listed in Table 1.

All these excited states are of a charge-transfer type, where an electron transfers from **1** to BV^{2+}, relative to the ground electronic state $BV^{2+}(Cl^-)_2(\mathbf{1})_4$. For this electron transition, molecule **1** loses an electron from the HOMO of a naphthol plane in many of these excited states, while an electron is lost from the second HOMO of a naphthol plane in the excited states S3 and S5 of **IIa**, S3 of **IIb**, S6 and S7 of **IVa**, and S5 and S6 of **IVb**. The excited states originating from the second HOMO have relatively large oscillator strengths, suggesting that they contribute significantly to the low-energy absorptions of crystals **II** and **IV**. The calculated oscillator strengths and the excitation energies (wavelengths) are plotted in Figure 6.

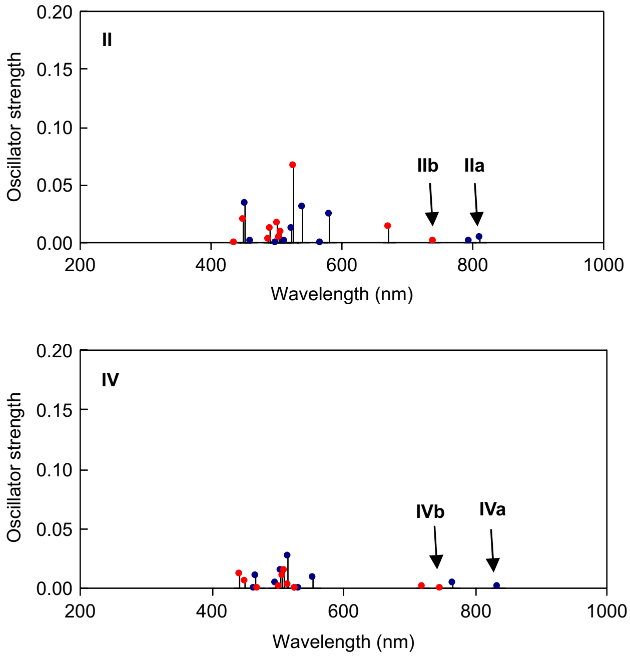
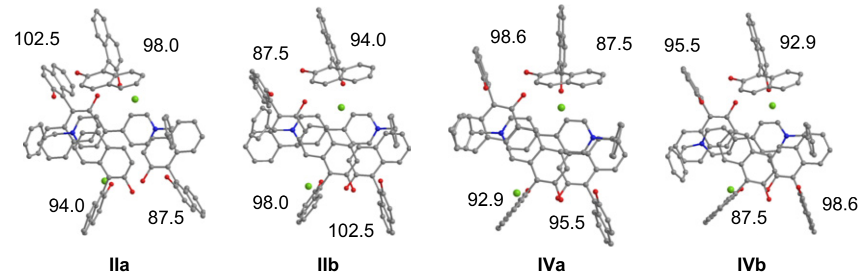


Figure 6. Plots of the calculated excitation wavelengths and oscillator strengths of the molecular clusters.

Although the experimentally observed DRS spectra implied that crystal **II** has lower excitation energies than those of **IV**, the overall distributions of the calculated excitation energies are not so different between the two crystals. The figure suggests that the different absorption edges of the two crystals result rather from the intensities of electronic transitions of these low-energy excited states.



IIa **IIb** **IVa** **IVb**

Figure 5. The molecular clusters picked out of the X-ray structures of crystals **II** and **IV**, each consisting of a viologen ion (BV^{2+}), two counter anions, and four binaphthol molecules (**1**). The chloride ions in the original X-ray structures are replaced by fluoride ions for excited state calculations by the ZINDO method. Clusters **a** and **b** correspond to the two symmetrically independent BV^{2+} centers. The BV^{2+} have N···N distances of 7.004 (**IIa**), 6.995 (**IIb**), 6.998 (**IVa**), and 6.977 Å (**IVb**). Numbers indicate the dihedral angles of **1**.

Table 1. Calculated singlet excitation energies and oscillator strengths of the molecular clusters[a,b]

	IIa			**IIb**			**IVa**			**IVb**		
	E/eV	*λ*/nm	*f*	*E*/eV	*λ*/nm	*f*	*E*/eV	*λ*/nm	*f*	*E*/eV	*λ*/nm	*f*
S1	1.53	812	0.0044	1.68	739	0.0013	1.49	833	0.0011	1.66	748	0.0005
S2	1.56	795	0.0017	1.85	670	0.0142	1.62	766	0.0047	1.72	720	0.0017
S3	2.14	580	0.0251	2.36	526	0.0663	2.24	553	0.0087	2.36	526	0.0000
S4	2.19	567	0.0003	2.45	507	0.0088	2.33	533	0.0001	2.40	517	0.0032
S5	2.29	541	0.0309	2.46	504	0.0045	2.35	528	0.0003	2.43	511	0.0156
S6	2.37	522	0.0122	2.47	502	0.0175	2.40	517	0.0275	2.44	508	0.0100
S7	2.42	513	0.0008	2.53	490	0.0125	2.46	505	0.0148	2.48	501	0.0017
S8	2.48	500	0.0005	2.54	487	0.0024	2.49	498	0.0041	2.64	469	0.0000
S9	2.70	460	0.0023	2.76	449	0.0203	2.66	467	0.0110	2.75	451	0.0067
S10	2.74	453	0.0342	2.84	436	0.0002	2.67	464	0.0002	2.81	442	0.0116

[a] Calculated by the ZINDO method. See Figure 5 for the calculated molecular clusters.

[b] Excitation energies (*E*) and wavelengths (*λ*) and oscillator strengths (*f*).

3. Conclusion

A novel CT host system composed of chiral (*R*)-**1** and $BVCl_2$ molecules was successfully created. This CT host system has a chiral cavity and can include *n*-alkyl alcohols as guest molecules by changing both the packing of the shared chiral cluster composed of (*R*)-**1** and chloride ion and the amount of the included guest molecule. Expectedly, the DRS spectra of these inclusion crystals change according to the included guest alcohols. This further enriches the ability of the chiral CT host system and may be useful for the design of novel host systems and visual indicator systems for molecular recognition.

4. Experimental

4.1. General methods

Diffuse reflectance spectra of crystals were measured with a *HITACHI U-4000 Spectrometer*. X-ray powder patterns of crystals were corrected on a *Rigaku RINT2500*. ^1H NMR spectra were recorded on a *Varian Mercury M300 Spectrometer*.

4.2. Formation of CT complexes including guest alcohol molecules

(*R*)-**1** (10 mg, 3.49×10^{-2} mmol) and $BVCl_2$ (14 mg, 3.49×10^{-2} mmol) were dissolved in each *n*-alkyl alcohol solutions (2 mL) with heating. After a few days, colored crystals [crystal **I** (8 mg), crystal **II** (11 mg), crystal **III** (9 mg), and crystal **IV** (10 mg)][5] were deposited and collected, respectively.

4.3. X-ray crystallographic study of crystal IV

X-ray diffraction data for single crystals was collected using *BRUKER APEX*. The crystal structure were solved by the direct method and refined by full-matrix least-squares using *SHELX97*. The diagrams were prepared using *PLATON*. Crystallographic data of **IV**: $2C_{24}H_{22}N_2Cl_2\cdot4C_{20}H_{14}O_2\cdot3C_4H_{10}O$, M=2185.27, orthorhombic, space group $P2_12_12_1$, a=14.9511(9), b=21.7207(13), c=35.049(2) Å, V=11,382.1(12) Å^3, Z=4, Dc=1.275 g cm^{-3}, μ(Mo Kα)=0.170 mm^{-1}, 71,424 reflections measured, 6006 unique, final $R(F^2)$=0.0977 using 19,049 reflections with $I>2.0\sigma(I)$, R(all data)=0.0655, T=100(2) K. CCDC 654089. Crystallographic data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: +44 1223 336 033; deposit@ccdc.cam.ac.uk).

4.4. Calculation method

The excited states of the CT chromophores in their X-ray structures of crystals **II** and **IV** have been calculated by the ZINDO method.[6] The GAUSSIAN 03 program[7] has been used for this quantum chemical calculation. The calculated chromophores are molecular clusters consisting of a viologen ion (BV^{2+}), four binaphthol molecules (**1**), and two counter anions (Fig. 5), where the chloride ions in the original X-ray structures have been replaced with fluoride ions to calculate the excited states by the ZINDO method. The four binapthol molecules correspond to those in **II-c1** and **II-c2** for crystal **II** (see Fig. 2), and those in **IV-c1** and **IV-c2** for crystal **IV** (see Fig. 3). Two clusters (‘**a**’ and ‘**b**’) have been created for each crystal, corresponding to the two symmetrically independent viologen-centers. It has been confirmed that the solvent molecules have little effect on the excited states. By including two ethanol molecules to cluster **IIa**, the excitation energies and oscillator strengths change only slightly to 1.55 eV(0.0002), 1.55 eV(0.0020), 2.16 eV(0.0177), 2.212 eV(0.0001) from the values in Table 1.

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