coupling was that expected for a peptide nitrogen. We speculate that the unusual coordination which imparts the large quadrupole coupling to N1 is associated with a unique coordination structure which is intimately associated with the catalytic function of the H cluster.

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Unique Ultraviolet-Visible and Circular Dichroism Behavior Due to Exciton Coupling in a Biscyanine Dye

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The cyanine dyes are characterized by intense and sharp absorption bands in the UV–vis region, and this could provide a powerful new tool for CD studies of biopolymer conformations in solution. The biscyanine dye **3**, prepared during an exploratory search for such chromophores, shows two *distinct and widely separated* vis bands at 550 (ϵ 182000)/480 nm (191000). Moreover, the sign of its exciton-coupled CD curve is negative, i.e., *opposite* to that expected;[1] the bis-Schiff base **4** also exhibits similar properties. In the following we account for this unique behavior.

Reaction of (1*S*,2*S*)-(+)-*trans*-1,2-cyclohexanediamine (**1**) and 7-piperidinohepta-2,4,6-trienal (**2**, merocyanine)[2] followed by flash chromatography yielded biscation **3a**;[3] the reaction was performed in milligram scale, under argon in the dark.[4] Deprotonation of **3a** to bis-Schiff base **4**[3] was achieved in a UV cell; subsequent titration of a solution of **4** by addition of TFA led to spectral changes shown in Figure 1. Neutral **4**, UV–vis, λ_{max} 383 nm (ϵ, 80000), exhibits a bisignate CD, 412 nm ($\Delta\epsilon$ −73), 362 (+63), the Cotton effects (CE's) of which are *opposite* in sign to its dibenzamide **5**[5] and bis-*p*-methoxycinnamate **6**[6] (MeCN), 312 nm ($\Delta\epsilon$ +36), 274 (−25); λ_{max} (MeCN), 287 nm (ϵ 41000). Upon titration of Schiff base **4** with TFA, a new UV–vis peak (Figure 1A) and a negative CD band appeared at 520 nm. The data indicate the formation of the monocation species, λ_{max} 522 nm (cf., the monocyanine from cyclohexylamine, λ_{max} 515 nm, CH_2Cl_2). Under more acidic conditions, the monocation peak is displaced by *two* strong UV–vis maxima at 550/480 nm (Figure 1B) accompanied by intense bisignate CE's with signs opposite to that expected (Figure 2).

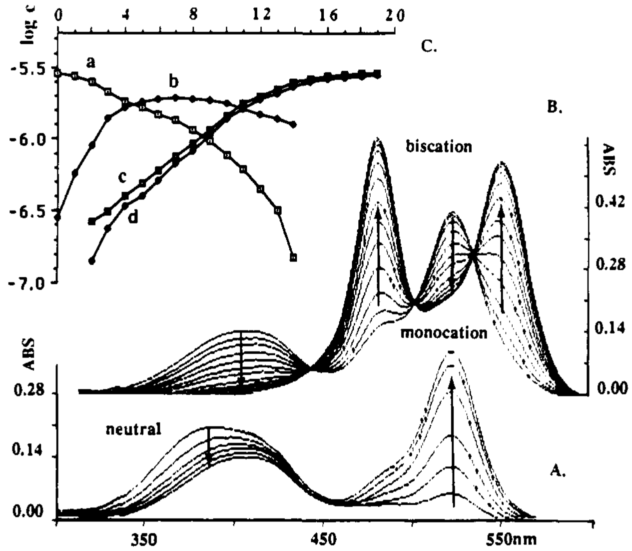
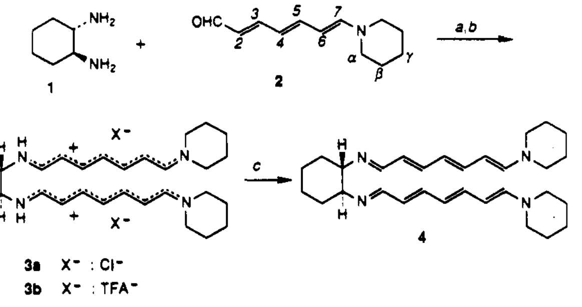


Figure 1. Changes in UV–vis spectrum accompanying stepwise addition of a 5.0 × 10^{-4} M solution of TFA to a solution of bis-Schiff base **4**, *c* = 3 × 10^{-6} M both in CH_2Cl_2. Arrows denote the direction of changes. (A) Equilibrium between neutral Schiff base **4** and monocation. (B) Equilibrium between neutral Schiff base **4**, monocation, and biscation **3b**. (C) Stepwise addition of 20 aliquots of TFA to a solution of neutral Schiff base **4**, both in CH_2Cl_2. Horizontal axis: Each aliquot represents 1.56 × 10^{-3} μmol of TFA (5.0 × 10^{-4} M solution) added to 1.3 mL of a 3.00 × 10^{-6} M solution of **4**. Vertical axis: log molar concentration of respective species, calculated from ϵ values. (a) Neutral, 383 nm (ϵ 80000); (b) monocation, 522 nm (207000); (c) biscation, 480 nm (191000); (d) biscation, 550 nm (192000).

Scheme I



[a](a) Dry MeOH, 60–65 °C, 4 h. (b) SiO_2 flash chromatography, $MeOH/CHCl_3$/1 N HCl (20/80/0.4). (c) CH_2Cl_2/NaOH.

Two mechanisms are conceivable for the appearance of two vis peaks: coexistence of two species absorbing at different wavelengths, or exciton coupling in biscation **3b**. The first possibility can be discounted because the titration curves plotted at 550 and 480 nm are very similar, indicating the presence of a single species (Figure 1C, curves c and d). The following aspects support an exciton coupling mechanism: (i) the two peaks at 550 and 480 nm are equidistant from that of the monocyanine (515 nm); and (ii) the CD shows bisignate CE's of similar intensities. Such large separations of the two UV–vis peaks arising from exciton coupling have only been encountered in anthracene crystals[7] and not in solution.[8]

The biscyanine dye **7** (structure in Figure 2) was chosen as the model to calculate the preferred conformation by MMP1 and

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(3) **3a**: FTIR ($CHCl_3$/MeOH) 2400, 1529, 1389, 1211 cm^{-1}; MS (FAB/glycerol), **3a** deprotonates in the matrix leading to the *M* + 1 peak for **4** at 461; the NMR could not be measured due to instability under our sample preparation conditions. **4**: FTIR ($CHCl_3$/MeOH) 1477, 1371, 1195 cm^{-1}.

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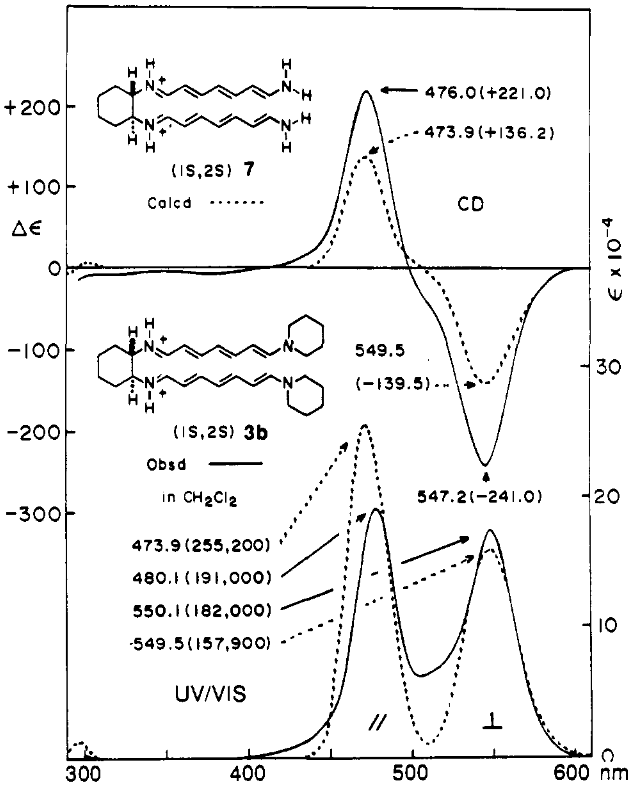
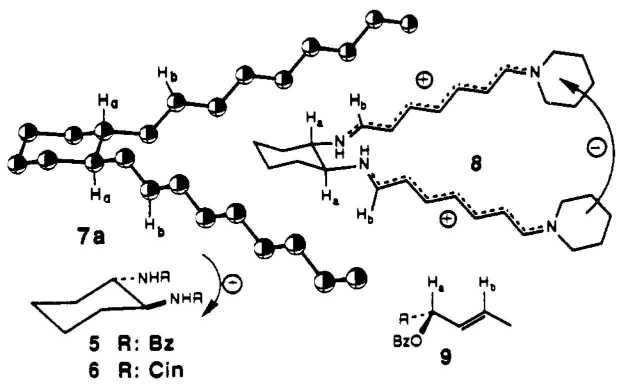


Figure 2. (—) Observed CD and vis spectra of biscation **3b** in CH_2Cl_2, $c = 3 \times 10^{-6}$ M. (⋯) Calculated CD and vis spectra of model biscation **7**.

MMP2[9] to rationalize these results. In its most stable conformation **7a**, protons H_a and H_b are almost syn; this leads to a *counterclockwise* twist for the two chromophores (**8**), and hence the negative exciton coupling. In acyclic allylic benzoates, the signs of the benzoate CE's were also governed by conformation **9** where H_a/H_b are syn.[10] The CD and UV-vis spectra of (1*S*,2*S*)-**7** were calculated by the π-electron SCF-CI-DV MO method[1,11,12] and the atomic coordinates obtained above. For evaluation of MO parameters, the four N atoms were treated as being the same, and doubly charged cores were assigned to them. Although the calculated CE's are weaker than the observed ones (Figure 2), the latter are in good agreement with conformation **7a**, where the angle between the two long-axis-polarized cyanine transitions is ca. 70°. The following points are responsible for the strong exciton splitting in the UV-vis spectrum of biscation **3** (Figure 2): (i) the energy gap between two bands is as large as 2890 cm^{-1}, and the bands are located in a long wavelength region; the energy splitting is thus emphasized on the wavelength scale; (ii) typically for cyanine dyes,[13] the UV-vis bands have very narrow 1/e band widths of $2\Delta\sigma = 1524$ cm^{-1}; this is much smaller than ordinary UV bands (ca. 5000 cm^{-1}).[1]

The CD and UV curves of the neutral compound **4** were similarly calculated: UV λ_{max} 357 nm (ε 122200); CD 377 nm (Δε -85.6) and 339 nm (+49.7); obsd UV λ_{max} 383 nm (ε 80000), CD 412 nm (Δε -73.2) and 362 nm (+63.4). The calculated bands are at shorter wavelengths, but the overall shapes of the UV and CD bands, as well as the CE signs, are well-reproduced. The fact that in both the biscation and neutral molecule the sign of the exciton split CD couplet is opposite to that expected indicates that this sign reversal is not a consequence of charge repulsion in biscation **3** but results from the unique conformations of **3** and **4**. This example demonstrates the importance in knowing the spatial dispositions of interacting electric transition moments in the exciton chirality method. The vis spectrum of **3** appears to be the first case where exciton-split peaks appear in solution as two distinct bands separated by 70 nm.



7a **8**

5 R: Bz
6 R: Cin

9

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1,2,3,4,5-Tetrathiametallolanes of Group 14 Metals, $RR'MS_4$ (M = Si, Ge, and Sn): Synthesis and Crystal Structures

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The chemistry of polychalcogenides, particularly that of metal-containing cyclic polychalcogenides, is currently enjoying great popularity.[1] Polychalcogenido complexes of metals are interesting not only because of their unique structures and reactivities but also because of their possible applications. They can, for example, be used as versatile chalcogen sources to prepare chalcogen rings of predetermined size,[2] and they are also suspected to play a role in catalysis (particularly in hydrodesulfurization).[3] For transition-metal compounds there have been several reports on the synthesis of cyclic polychalcogenides such as Cp_2TiS_5,[2a,4]

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