Donor–Acceptor Systems

Circular Dichroism of a Chiral Tethered Donor–Acceptor System: Enhanced Anisotropy Factors in Charge-Transfer Transitions by Dimer Formation and by Confinement**

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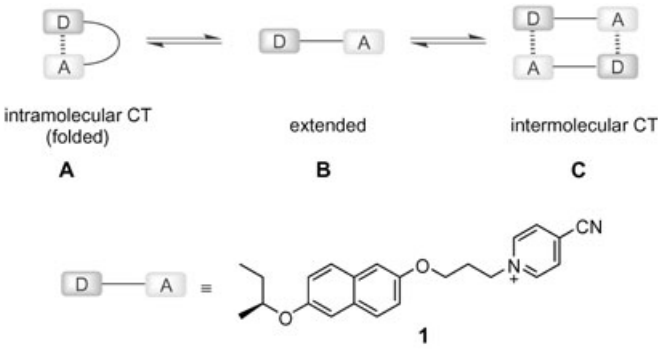
Charge-transfer (CT) interactions between a donor and an acceptor[1] are an important class of weak interactions that have been extensively exploited in molecular assemblies such as rotaxanes, catenanes, and molecular machines and devices.[2] A large number of tethered donor–acceptor pairs, or CT dyads, have been prepared[3] in the study of electron-transfer mechanisms and also in the development of molecular devices, such as nonlinear optical materials.[4] Chiral CT interaction is expected to be a useful tool not only for developing unique chiral molecular devices, but also for understanding and controlling molecular recognition phenomena, especially in solution. Therefore, optical rotatory dispersion and circular dichroism of optically active donor–acceptor complexes have already been examined for CT complexes that involve n–π* transitions.[5] Herein, we report the circular dichroism of intra- and intermolecular CT complexes with π–π* transitions, and also novel strategies for controlling the anisotropy factor by dimer formation and by confinement.

We chose 2,6-dimethoxynaphthalene and 4-cyano-*N*-methylpyridinium as a donor–acceptor pair, since these compounds possess low oxidation and reduction potentials ($E_{ox} = 1.1$–1.3 and $E_{red} = -0.64$ V versus the saturated calomel electrode (SCE), respectively)[6] and are expected to form a strong CT complex in solution. By linking these components with a trimethylene tether, we obtained CT dyad **1** as the BF_4^- salt, which was then subjected to electronic absorption (UV/Vis) and circular dichroism (CD) spectroscopy to study the CT complexation behavior and to elucidate the chiroptical properties of the representative CT complex(es) formed under a variety of conditions (Scheme 1).



Scheme 1. Modes of CT complexation of the tethered chiral donor–acceptor dyad **1**.

The UV/Vis spectrum of dyad **1**, measured in dichloromethane at 25 °C, was almost superimposable on a sum of the spectra of the component donor and acceptor units, but exhibited a very weak band at 420 nm, which is assigned to a CT transition. An independent spectral titration of the intermolecular complex formation of 4-cyano-*N*-methylpyridinium with 2,6-dimethoxynaphthalene at varying concentrations also gave a CT band at comparative wavelengths. A Benesi–Hildebrand analysis[7] of the spectral titration results indicates the formation of a 1:1 complex with an association constant ($K_{CT} = 0.48\ M^{-1}$) and spectral properties ($\lambda_{max} = 420$ nm, $\varepsilon_{CT} = 450\ M^{-1}cm^{-1}$) comparable to those reported for analogous nonchiral donor–acceptor pairs.[8] In contrast, the intensity of the CT band of **1** was linearly proportional to the concentration of **1** (at least up to 10 mM), which unequivocally indicated the intramolecular character of the CT complex observed. A face-to-face stacked complex with a

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[**] Financial support of this work by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science, and Technology of Japan (No. 16750034, to T.M.) is gratefully acknowledged.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

 © 2005 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim DOI: 10.1002/ange.200462071

folded structure (Scheme 1, folded monomer **A**) is probably formed upon the intramolecular CT interaction of **1**, as judged from the ROESY spectrum of **1** in CD_2Cl_2 at 25 °C (see the Supporting Information). A similar conformation was reported for the intermolecular CT complex of 2,6-dimethoxynaphthalene with methyl viologen in an X-ray crystallographic study.[9]

The UV/Vis spectrum of **1** showed a dramatic temperature dependence, particularly at temperatures lower than −50 °C; as the temperature decreased, a CT band at 480 nm became apparent. The dependency of the absorbance of the CT band on concentration (Figure 1), as well as the DFT calculations[10] (Figure 2), indicate that the origin of this CT band is the formation of an intermolecular 1:1 dimer in a head-to-tail orientation, in which two sets of donor–acceptor interactions are involved (Scheme 1, dimer **C**).

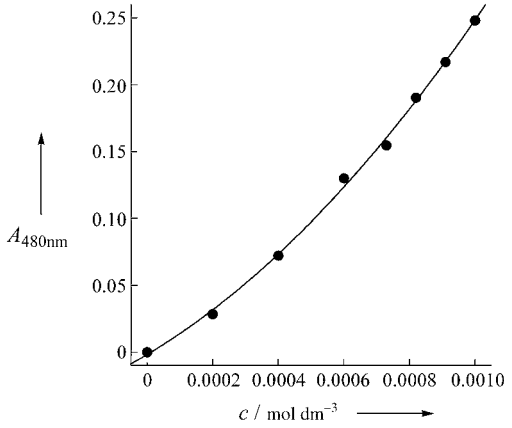

Figure 1. Experimental (●) and theoretical (——) concentration dependence of the absorbance of the CT band (at 480 nm) of dyad **1** in dichloromethane at −95 °C. The nonlinear least-squares fit revealed the dimeric nature of the CT complexation ($K = 3160\ M^{-1}$).

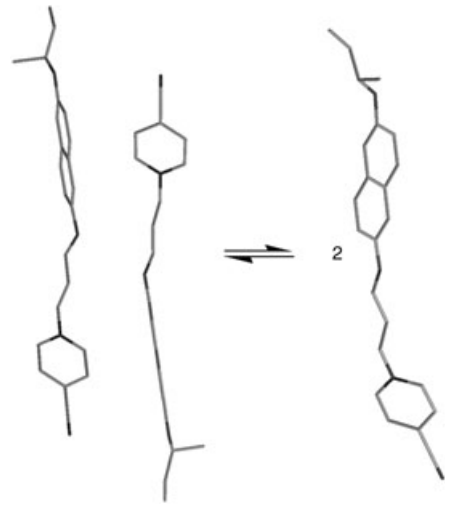

Figure 2. DFT-optimized structures of dimeric and monomeric dyad **1**. All calculations were performed with the Gaussian 98 package at the B3LYP/6-31G(d) level. Hydrogen atoms are omitted for clarity.

CD spectroscopy was also performed to elucidate the effects of the different conformation and association states **A**–**C** (Scheme 1) on the chiroptical properties of dyad **1**. A solution of **1** in dichloromethane (1 mM) showed only a weak positive CD for the ^1L_b transition of the naphthalene moiety at around 320 nm (Figure 3, trace a), which is in good agreement with the well-documented benzene sector rule.[11] The obtained *g* factor is extremely small, as low as 8×10^{-5}. However, this seems reasonable for such a chromophore that carries the smallest chiral auxiliary attached through a flexible ether linkage. Furthermore, no appreciable CT band was observed under the conditions employed. We may conclude,

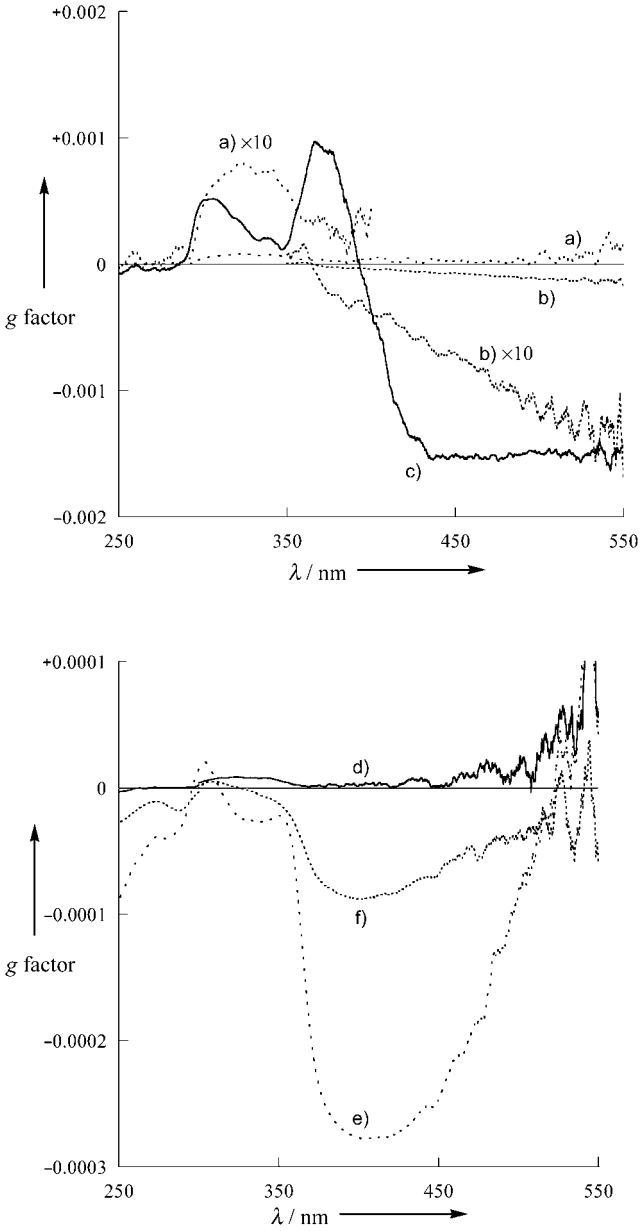

Figure 3. Anisotropy (*g*) factor profiles of **1** under different conditions: a) 1 mM in CH_2Cl_2 at 25 °C; b) 10 mM in MeCN at 25 °C; c) 1 mM in CH_2Cl_2 at −95 °C (intensities corrected for the actual concentration of dimeric species: 0.34 mM); d) 1 mM in MeOH at 25 °C, for comparison with (e) and (f); e) 1 mM in water containing 5 mM β-cyclodextrin at 25 °C; f) 1 mM in water containing 5 mM γ-cyclodextrin at 25 °C.

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therefore, that extended monomer **B** is the dominant species at a concentration of 1 mM at 25 °C.

At a higher concentration (10 mM in acetonitrile), the CD spectral behavior of **1** changed significantly; a very weak CD was observed in the ^1L_b region (300–350 nm) and an apparent negative CD in the CT transition region (Figure 3, trace b). Although we employed acetonitrile as the solvent of choice because of the lower solubility of **1** in less polar solvents, we have not observed so far a notable solvent dependence on the CD spectra of **1**. The contribution of the intramolecular CT complex **A** is probably enhanced to some extent under these conditions. The formation of the dimeric CT complex **C** was greatly promoted by reducing the temperature. Thus, a solution of **1** in dichloromethane (1 mM) exhibited a strong CD at 400–500 nm at −95 °C, along with a moderate CD in the ^1L_b region. As can be seen from Figure 3, trace c, the *g* factor reaches −0.0016 for the CT band (dimer **B**) and 0.0005–0.001 even at the shorter wavelengths. These values are at least one order of magnitude larger than the representative values reported for typical allowed transitions.[11] The anomalous *g* factors may be attributed to the conformational fixation caused by stronger interactions in the dimeric CT complex (see below).

The effects of conformational fixation caused by confinement on the chiroptical properties of the CT complex were further investigated by supramolecular interaction with cyclodextrin hosts. The host–guest interactions of **1** with cyclodextrins were first assessed by fluorescence spectroscopy. As can be seen from Figure 4, a solution of **1** in methanol (0.1 mM) showed fairly weak fluorescence at 330 nm (trace a) because of efficient intramolecular electron-transfer quenching, whereas much more intense fluorescence was observed upon the addition of β- or γ-cyclodextrin (0.5 mM) to an aqueous solution of **1** (0.1 mM; traces b and c). Similar behavior was previously reported for a variety of aromatic donor–viologen systems.[12] The fluorescent donor group is included in the cavity of β-cyclodextrin, so both intra- and intermolecular quenching by the pyridinium moiety and solvent molecules are greatly decelerated and the excited state is retained longer. In contrast, fluorescence enhancement is moderate in the case of γ-cyclodextrin (Figure 4, trace c). This result may be rationalized by a loose fitting of the donor group to a larger γ-cyclodextrin cavity, which can not completely prevent the quenching attack of the pyridinium moiety or solvent molecules. ^{1}H NMR spectroscopic analysis of the complexes also supports this conclusion, as the aromatic protons are much more deshielded in the presence of β-cyclodextrin than in the presence of γ-cyclodextrin (see the Supporting Information).

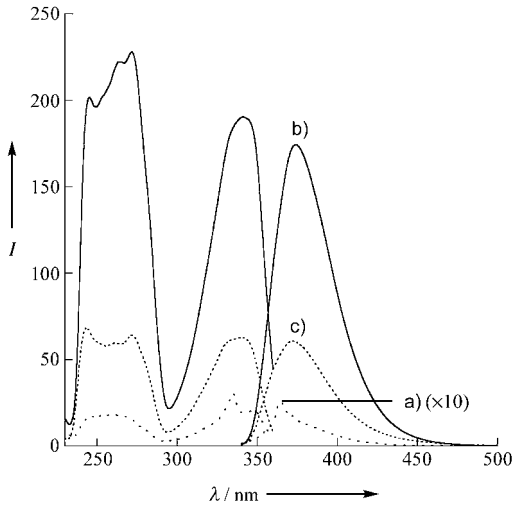

Figure 4. Fluorescence emission and excitation spectra of **1** (0.1 mM) at ambient temperature: a) in methanol (ten times expansion); in the presence of b) β- and c) γ-cyclodextrin (0.5 mM) in water.

Upon the addition of β- or γ-cyclodextrin (5 mM) to an aqueous solution of **1** (1 mM), large negative Cotton effects were induced in the ^1L_b (≈340 nm) and ^1L_a (≈240 nm) regions of the naphthalene chromophore (Figure 3, traces e and f). This result is consistent with the empirical rules[13] and indicates that the longer axis of the naphthalene moiety is parallel to the axis of the cyclodextrin cavity. Interestingly, the CT band exhibited larger negative Cotton effects with unusually large *g* factors of −0.00028 and −0.00008 for the β- and γ-cyclodextrin complexes, respectively. The strong CD for the CT band, particularly in the presence of β-cyclodextrin, is quite puzzling, since the cavity is formally fitted to the size of naphthalene and the included naphthalene moiety does not appear to form a CT complex even with the tethered pyridinium moiety. By combining all the results from the UV/Vis, fluorescence, NMR, and CD spectral examinations, we tentatively rationalize this interesting chiroptical behavior of the β-cyclodextrin complex of **1** as being a consequence of a shallow penetration or perching of the acceptor moiety into the β-cyclodextrin cavity, which is already occupied by the more hydrophobic naphthalene moiety, to afford a less face-to-face, twisted CT complex. It is thus inferred that the naphthalene moiety is accommodated in the β-cyclodextrin cavity and the remaining acceptor moiety is forced to form a tilted CT complex, which is closely located and/or twisted relative to the donor moiety and hence exhibits a stronger Cotton effect. However, the donor–acceptor pair is more face-to-face and less tightly packed in a larger γ-cyclodextrin cavity, which results in a less intense Cotton effect.

As formulated by Hush (mostly for transition-metal complexes), the electronic coupling element (H_{ab}) is related to the charge-transfer transition according to Equation (1),[14]

$$H_{ab}[\mathrm{cm}^{-1}] = 0.0206(\nu_{max}\,\Delta\nu^{1/2}\,\varepsilon)^{1/2}/r \qquad (1)$$

in which ν_{max} and $\Delta\nu^{1/2}$ are the peak position and full width at half maximum (in wavenumbers) of the CT band, ε is the molar extinction coefficient at the CT-band maxima, and r is the effective separation of relevant redox centers in the complex.[15] The electronic coupling element H_{ab} was estimated for the CT transition of **1** under various conditions to give the values listed in Table 1. Notably, the CT interaction in the dimer is almost twice as large as that in the monomer. The H_{ab} value for the β-cyclodextrin complex is also appreciably larger than that of the uncomplexed monomer, probably as a result of the stronger intramolecular donor–acceptor interactions of **1** within the hydrophobic cyclodextrin cavities, or a slightly larger separation between donor and acceptor.

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Table 1: Anisotropy (g) factors and electronic coupling elements (H_{ab}) of monomeric and dimeric CT complexes and the β-cyclodextrin inclusion complex.

CT species	Conditions	H_{ab}[a]	λ_{max}[b]	g factor [$\times 10^3$]
A	[**1**] = 10 mM in MeCN, 25 °C	0.65	420	≈ −0.1
C	[**1**] = 1 mM in water, 25 °C	0.72	380	−0.3
B	[**1**] = 1 mM in CH_2Cl_2, −95 °C	1.23	480	−1.6

[a] Electronic coupling element [10^3 cm^{-1}], calculated by the Marcus–Hush equation [Eq. (1)], with the assumtion $r = 3.5$ Å. [b] Absorption maximum of the CT band [nm].

It has thus been demonstrated for the first time that donor–acceptor dyads, such as **1**, form both intramolecular monomeric and intermolecular dimeric CT complexes depending on the conditions employed, and that their CT bands give anomalously large g factors of up to 0.002. Such an enhancement in g factor upon CT interaction is of theoretical/mechanistic interest and also of practical use as a tool for enhancing the efficiency of absolute asymmetric synthesis with circularly polarized light.[16]

Received: September 22, 2004
Revised: January 21, 2005
Published online: March 22, 2005

Keywords: anisotropy · charge transfer · circular dichroism · cyclodextrins · donor–acceptor systems

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