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# Heptacyclo[6.6.0.0$^{2,6}$.0$^{3,13}$.0$^{4,11}$.0$^{5,9}$.0$^{10,14}$]tetradecane: a new type of spacer for mediating electron transfer processes

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**Abstract**—A series of derivatives of the titled compound with donor and acceptor substituents were prepared. Efficient fluorescence quenching was observed for the molecules in which donor and acceptor π-chromophores are coplanar. Charge recombination of the radical ion pairs resulted in broad charge transfer bands centered at ca. 510 nm. Twisting the donor and acceptor chromophores 90° with respect to each other seemed to retard the electron transfer process. 

Designing molecular devices is a topic of current interest with extensive investigations. Light induced electron transfer processes (ET) play a central role in many designs, such as molecular rectifiers[1] and switches,[2] electrochemical sensors,[3] photovoltaic cells,[4] nonlinear optical materials,[5] photosyntheses,[6] etc. Some of these devices require a molecular spacer between the donor (D) and the acceptor (A) chromophores, so that the flow of electrons can be regulated.[7] A wide range of selections for spacer groups have been reported previously to accommodate various purposes.[8] The use of the title compound, heptacyclo[6.6.0.0$^{2,6}$.0$^{3,13}$.0$^{4,11}$.0$^{5,9}$.0$^{10,14}$]tetradecane (HCTD), as a spacer group has been proposed before;[9] however, thus far no report on its spectroscopic properties has been published. The geometry of this molecule has the virtue of high symmetry ($D_{2d}$) as well as structural rigidity.[10] The D and A chromophores can be aligned linearly across a σ-skeleton, and their relative orientation can be adjusted to allow their π-orbitals to be either coplanar (0° dihedral angle) or perpendicular (90° dihedral angle) with respect to each other.[11] These unique features are seldom found in other spacer groups.[12] In this report, we describe a preliminary result on the observation of ET processes in compounds **2**–**4** by analyzing their emission spectra.

The syntheses utilized HCTD-6-ol-11-one (**1**) as the starting material.[13] The formation of catechol ketal at C(11) yielded **2a** in 96% yield; subsequent oxidation with PCC transformed **2a** to **2b** in 87% yield. The preparation of **2c** (93%) and **2d** (74%) followed a similar sequence by using benzenedithiol.[14] Dehydrations of **2b** and **2d** with malononitrile proceeded smoothly in refluxed benzene in the presence of base, and the isolated yields of **3a** and **3b** were 93 and 92%, respectively. The geometry of both compounds belongs to point group $C_{2v}$, so that both their NMR ($^1$H and $^{13}$C) and IR absorption signals are quite simple.[15] The central HCTD moiety, besides C(6) and C(11), showed only four peaks in either $^1$H or $^{13}$C NMR spectroscopy. Compound **4b** is also of $C_{2v}$ symmetry, which was prepared in order to examine the geometrical effect of ET. The benzenedithiol moiety of **4b** was twisted 90° with respect to that of **3b** by the insertion of an ethylene moiety. The synthesis of **4b** commenced with HCTD-6,11-dione,[13] which was first converted to **4a** in 22% yield.[16] Dehydration of **4a** with malononitrile yielded **4b** in 93% yield.[15] Structures **2**–**4** were confirmed by their spectroscopic character, and all samples were recrystallized before being subjected to UV absorption and fluorescence analyses. Compounds **3b** and **4b** are stable while stored in an inert atmosphere, but slowly decompose in solution upon exposure to air.

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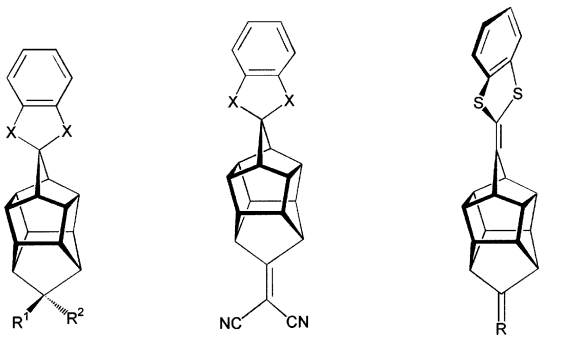


**2a)** $R^1 = H$; $R^2 = OH$; X = O
**b)** $R^1$ & $R^2 = O$; X = O
**c)** $R^1 = H$; $R^2 = OH$; X = S
**d)** $R^1$ & $R^2 = O$; X = S

**3a)** X = O
**b)** X = S

**4a)** R = O
**b)** $R = C(CN)_2$

The absorption spectra of **2a**, **3a**, **3b** and **4b** are shown in Fig. 1. The 280 nm maximum of **2a** and **3a** are assigned to a $\pi-\pi$ absorption of catechol, whereas for **3b** the strong band at 230 nm was derived mainly from the dicyanoethylene. Excitation of **2a** at 280 nm yielded significant fluorescence at 310 nm (Fig. 2) without a large Stokes shift. This emission was almost completely (>98%) quenched in **3a**, as an unequivocal evidence for an efficient ET process across the σ-framework of HCTD.[17] More evidence for the formation of the charge separated state of **3a** was the observation of a broad CT band centered at 510 nm.[18] The maximum of CT band was solvent dependent, and its intensity was more pronounced in THF than in hexane or methanol.[19]

A broad CT band was also observed for **3b**, centered at ca. 510 nm as shown in Fig. 2. The aromatic chro-

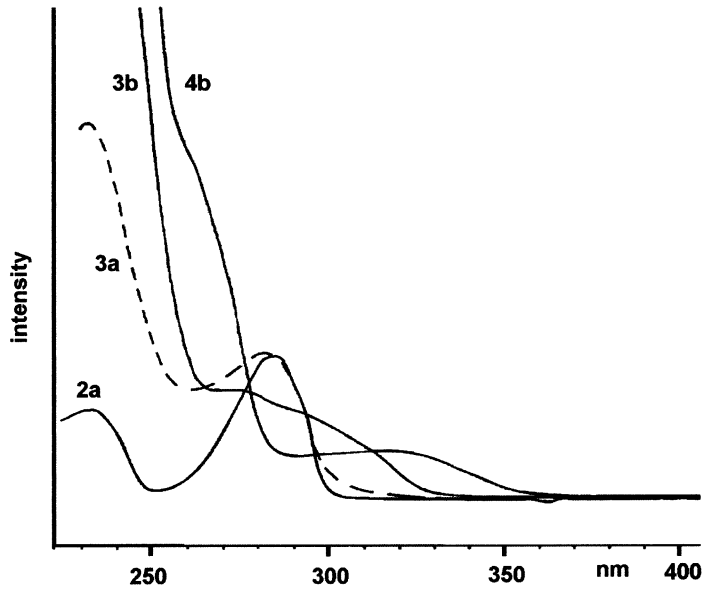


**Figure 1.** Absorption spectra of compounds **2a**, **3a**, **3b**, and **4b** in THF.

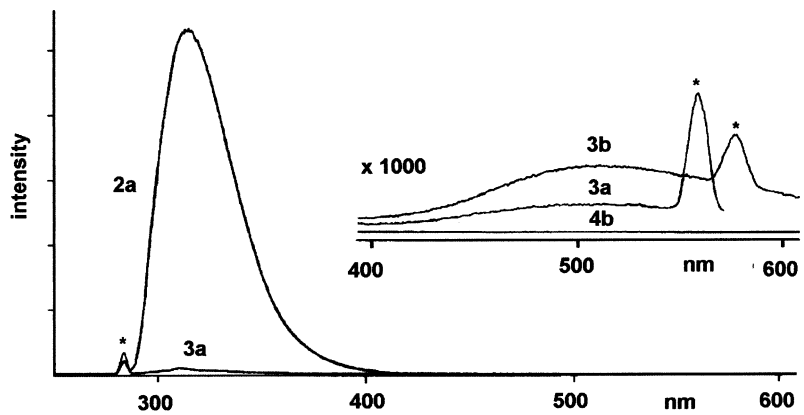


**Figure 2.** Emission spectra of **2a** and **3a** in THF at ca. 25°C, where a comparison shows that the fluorescence of **2a** at 310 nm is quenched by the dicyanoethylene in **3a**. The inset shows the CT emission bands of **3a** and **3b** in THF centered at 510 nm (relative intensities not normalized), which is absent for **4b**. Peaks marked with * are caused by excitations.

mophores (D) in both **3a** and **3b** are coplanar with the π-orbitals of dicyanoethylene (A) across the σ-framework of HCTD. Their CT processes are therefore considered more feasible than that of **4b**, in which the D and A chromophores are oriented perpendicular to each other.[20] Indeed, upon excitation at 318 nm, no CT emission was detected for **4b**. This phenomenon seems to indicate that the ET process was not effective in this molecule.

In summary, we have shown that HCTD can be utilized as a unique spacer group for regulating photo-induced ET processes. In cases where D and A chromophores are coplanar, ET processes proceeded with high efficiency. Further analyses on the symmetry effect of D and A chromophores are currently under investigation.

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15. Physical data for **3a**: mp 345°C (decomp.); $\nu_{max}/cm^{-1}$ (KBr) 2982, 2225, 1629, 1488; $\delta_H$ ($CDCl_3$, 200 MHz) 2.64 (m, 2H), 2.85 (m, 4H), 3.04 (m, 4H), 3.23 (m, 2H), 6.76 (m, 4H); $\delta_C$ ($CDCl_3$, 50 MHz, $^1$H-decoupled) 52.13, 52.44, 52.56, 53.94, 75.48, 109.01, 112.18, 122.01, 135.73, 148.01, 196.72; *m*/*z* (EI) 352 ($M^+$, 100%), 315 (4), 274 (6), 247 (20), 231 (40). Physical data for **3b**: mp 341°C (decomp.); $\nu_{max}/cm^{-1}$ (KBr) 2971, 2230, 1637, 1446; $\delta_H$ ($CDCl_3$, 200 MHz) 2.82 (m, 4H), 2.99 (m, 2H), 3.09 (m, 4H), 3.27 (m, 2H), 7.00 (m, 2H), 7.20 (m, 2H); $\delta_C$ ($CDCl_3$, 50 MHz, $^1$H-decoupled) 51.93, 53.62, 55.06, 60.23, 75.46, 87.30, 112.09, 122.97, 126.14, 138.02, 195.64; *m*/*z* (EI) 384 ($M^+$, 65%), 347 (5), 330 (10), 315 (25). Physical data for **4b**: mp 337°C (decomp.); $\nu_{max}/cm^{-1}$ (KBr) 2966, 2230, 1630, 1447; $\delta_H$ ($CDCl_3$, 200 MHz) 2.75 (m, 4H), 2.88 (m, 4H), 2.92 (m, 2H), 3.24 (m, 2H), 7.00 (m, 2H), 7.10 (m, 2H); $\delta_C$ ($CDCl_3$, 50 MHz, $^1$H-decoupled) 51.95, 53.16, 53.34, 55.30, 75.14, 112.17, 114.06, 122.09, 126.22, 136.86, 142.37, 197.10; *m*/*z* (EI) 396 ($M^+$, 100%), 347 (5), 330 (4), 315 (10).
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