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# Remote Activation of the Quadricyclane Group in a Quadricyclane−Steroid−{Dibenzoylmethanatoboron Difluoride} System by Intramolecular Electron Transfer[†]

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A bichromophoric compound, 3$\beta$-((2-(methoxycarbonyl)quadricyclane-3-yl)carboxy)androst-5-en-17$\beta$-yl-{3,3-dibenzoylmethanatoboron difluoride} propionate (QC−S−$BF_2$) was synthesized, and its photochemistry was examined using both steady-state and time-resolved techniques. Fluorescence quenching and lifetime measurements indicate that intramolecular electron transfer from the QC group to the singlet excited state of the $BF_2$ chromophore in QC−S−$BF_2$ occurs with efficiency of ca. 25% and rate constant of ca. $1.0 \times 10^9$ $s^{-1}$. Selective excitation of the $BF_2$ chromophore results in the valence isomerization of the quadricyclane group to norbornadiene group with quantum yield of ca. 5.8%.

## Introduction

There has been extensive recent interest in the photoinduced intramolecular electron transfer in multichromophoric molecules.[1−12] It has been well established[13] that in rigid donor−{saturated hydrocarbon spacer}−acceptor (D−S−A) systems electron transfer may occur by means of a through-space mechanism, if the distance between D and A is small enough to allow for direct overlap between the frontier orbitals of the donor and acceptor. On the other hand, when the D and A centers are too far apart for direct orbital overlap to be important, electron transfer may occur via through-bond interactions.[13−15] Previous studies on through-bond electron transfer have primarily chosen A and D to be chemically stable during the electron-transfer process and mainly concerned photophysical processes, although a few investigations[8−12,16] have focused on acceptors (donors) designed to undergo fast and irreversible chemical reactions as a tool to provide information on the dynamics of intramolecular electron transfer. In an effort to get deeper insight into the through-bond electron transfer, we have utilized the androstene skeleton as the spacer and mounted a norbornadiene moiety as the electron acceptor and a remote benzidine group as the electron donor on the steroidal framework.[10] Irradiation of the benzidine chromophore resulted in the conversion of the norbornadiene group into its valence isomer, quadricyclane. Both through-bond triplet energy transfer and through-bond singlet electron transfer were found to be operating in this photoisomerization. Because the isomerization of norbornadiene can occur only via its triplet state, in the electron-transfer-initiated isomerization, the rearrangement mechanism of the norbornadiene group must involve electron transfer from the singlet excited state of the benzidine to the norbornadiene, intersystem crossing of resultant radical-ion pairs, and recombination of the triplet radical-ion pairs to give triplet norbornadiene followed by rearrangement to the valence isomer. The requirement of the population of the triplet state and the involvement of the multisteps result in a low quantum yield for the electron-transfer-initiated isomerization. This made it difficult to analyze the dynamics of the through-bond electron transfer in an accurate manner on the basis of the photochemical reaction, although the rates and quantum efficiencies of the long-distance intramolecular triplet energy transfer and singlet electron transfer were determined by steady-state and time-resolved spectroscopies. In the present work, we still use an androstene skeleton as the spacer and incorporate a quadricyclane group and a dibenzoylmethanatoboron difluoride chromophore into the spacer (QC−S−$BF_2$) as shown in Chart 1. In this molecule, the $BF_2$ group is a powerful electron acceptor[17] and the QC group is an electron donor. Because the radical cation of quadricyclane can easily undergo isomerization,[1] one might expect that the through-bond electron-transfer-initiated isomerization of the QC group in QC−S−$BF_2$ would proceed with high efficiency. Indeed, excitation of the $BF_2$ chromophore in QC−S−$BF_2$ resulted in the isomerization of the QC group into the norbornadiene group with a higher quantum yield. The efficiency and absolute rate constant for the long-distance singlet electron transfer were also examined by steady-state and time-resolved spectroscopies.

## Results and Discussion

**Fluorescence Quenching: Intramolecular Electron Transfer from the Quadricyclane to the Singlet Excited State of the Dibenzoylmethanatoboron Difluoride Chromophore in QC−S−$BF_2$.** The absorption spectra of QC−S−$BF_2$ and the models for the electron donor, MQC (Chart 1), and for the electron acceptor, Et$BF_2$ (Chart 1), in acetonitrile were examined and are shown in Figure 1. The spectrum of QC−S−$BF_2$ is essentially identical to the sum of the spectra of MQC and Et$BF_2$, indicating the absence of measurable interaction between

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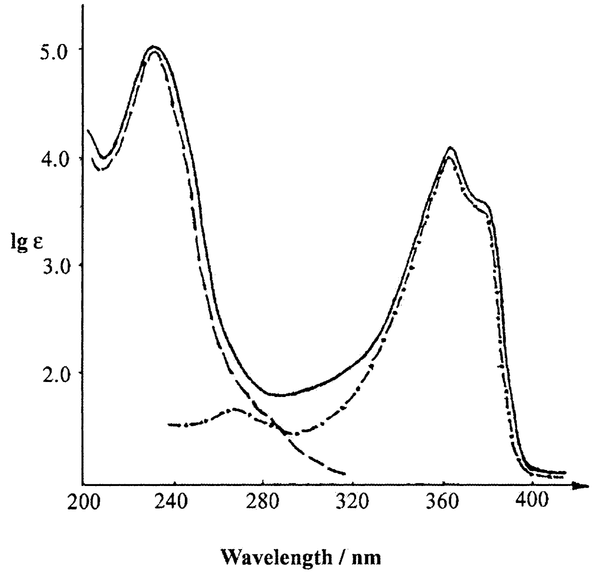
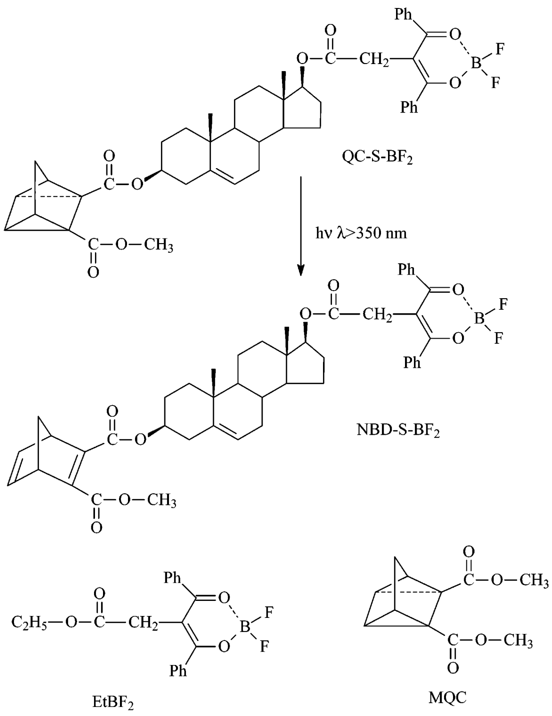


**Figure 1.** Absorption spectra of QC−S−BF$_2$ (—), MQC (− − −), and EtBF$_2$ (− • −) in acetonitrile.

**CHART 1**



the QC and BF$_2$ chromophores in QC−S−BF$_2$ in the ground states. Significantly, the BF$_2$ group exhibits strong absorption in the wavelength range of ca. 320−400 nm, where the QC group shows no absorption. This fact permits the selective excitation of the BF$_2$ moiety in the bichromophoric compound QC−S−BF$_2$.

The emission spectra of QC−S−BF$_2$ and EtBF$_2$ are given in Figure 2. Both compounds in acetonitrile at room temperature show fluorescence characteristic of the BF$_2$ chromophore with maxima at 403 and 418 nm and a shoulder at 430 nm. The fluorescence quantum yields of these compounds were also determined and are given in Table 1. Evidently the fluorescence quantum yield of the BF$_2$ chromophore in QC−S−BF$_2$ is ca. 26% less than that in the model compound EtBF$_2$. This observation indicates that quenching of the BF$_2$ fluorescence by the QC group in QC−S−BF$_2$ operates. Measurements at different concentrations reveal that the quenching is intramolecular. The fluorescence lifetimes for QC−S−BF$_2$ ($\tau$) and EtBF$_2$ ($\tau_0$) were measured to be ca. 0.24 and 0.32 ns, respectively (Table 1). These data allow the calculation of the quenching constant ($k_{\mathrm{SET}}$) and the quenching efficiency ($\phi_{\mathrm{SET}}$)[18] according to eqs 1 and 2, respectively:

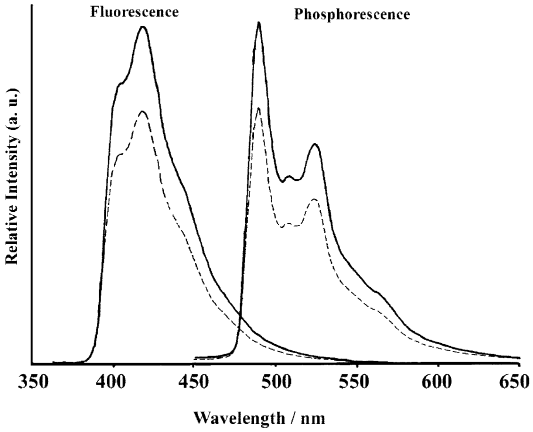


**Figure 2.** Emission spectra of QC−S−BF$_2$ (− − −) and EtBF$_2$ (—). The fluorescence and phosphorescence spectra were obtained in acetonitrile at room temperature and in 2-methylhydrofuran at 77 K, respectively: $\lambda_{\mathrm{ex}} = 355$ nm; [QC−S−BF$_2$] = [EtBF$_2$] = $2 \times 10^{-5}$ M.

$$k_{\mathrm{SET}} = \frac{1}{\tau} - \frac{1}{\tau_0} \tag{1}$$

$$\phi_{\mathrm{SET}} = 1 - \frac{\tau}{\tau_0} \tag{2}$$

$k_{\mathrm{SET}}$ and $\phi_{\mathrm{SET}}$ were obtained to be ca. $1.0 \times 10^9$ s$^{-1}$ and ca. 0.25, respectively. The value of the quenching efficiency thus obtained is consisitent with that from the fluorescence quantum yield measurements.

The energy of the singlet excited state of the BF$_2$ chromophore is lower than that of the QC group, as estimated from their absorption spectra (Table 1). Thus, singlet energy transfer from the excited BF$_2$ chromophore to the QC group is thermodynamically impossible. Therefore, we examined the reality of electron transfer between the excited-state BF$_2$ and the QC group in QC−S−BF$_2$ responsible for the long-distance intramolecular fluorescence quenching. The free-energy change ($\Delta G$) involved in a photostimulated electron-transfer process can be estimated by the Rehm−Weller equation:[19]

$$\Delta G\ (\mathrm{kcal/mol}) = 23.06[E(\mathrm{D/D}^{+\bullet}) - E(\mathrm{A/A}^{-\bullet}) - e^2/(r\epsilon)] - E_{00}\ (\mathrm{kcal/mol}) \tag{3}$$

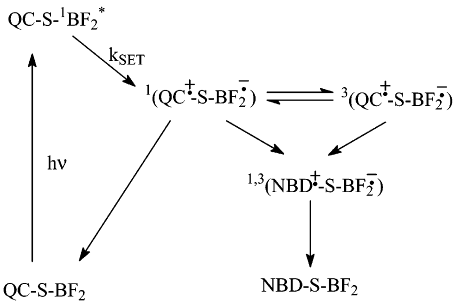
where $E_{00}$ is the excited-state energy and in this case represents the singlet excited-state energy of the BF$_2$ group (70.9 kcal/mol). $E(\mathrm{D/D}^{+\bullet})$ and $E(\mathrm{A/A}^{-\bullet})$ are the redox potentials of the donor and acceptor in acetonitrile solution, respectively; $e^2/(r\epsilon)$ is the Columbic interaction in the ion-pair state, the magnitude of which depends on the distance between the donor and acceptor ($r$) and on the dielectric constant ($\epsilon$) of the medium separating the charges. We used the Alchemy II program to calculate the energies of the general conformations, extended and bent, of QC−S−BF$_2$ and found that the extended conformation has the lowest energy. In this conformation, the center-to-center distance between the QC and BF$_2$ group (Chart 1) is

**TABLE 1: Spectroscopic and Electrochemical Properties of QC−S−BF$_2$, EtBF$_2$, and MQC**

| | absorption | | fluorescence[a] | | | phosphorescence[b] | | $E$ (kcal/mol) | | oxidation potiential[a] | reduction potiential[a] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| compound | $\lambda_{max}$ (nm) | log $\epsilon$ | $\lambda_{max}$ (nm) | $\Phi_F$ | $\tau$ (ns) | $\lambda_{max}$ (nm) | $\tau$ ($\mu$s)[c] | $E_s$ | $E_T$ | (V vs SCE) | (V vs SCE) |
| QC−S−BF$_2$ | 230 | 5.0 | 403 | 0.26 | 0.24 | 489 | 7.5 | | | | |
| | 360 | 4.1 | 418 | | | 508 | | | | | |
| | 385 | 3.6 | 430 | | | 524 | | | | | |
| | | | | | | 560 | | | | | |
| EtBF$_2$ | 360 | 4.1 | 403 | 0.35 | 0.32 | 489 | 7.5 | 70.9 | 58.4 | | −0.87 ± 0.03 |
| | 385 | 3.6 | 418 | | | 508 | | | | | |
| | | | 430 | | | 524 | | | | | |
| | | | | | | 560 | | | | | |
| MQC | 230 | 5.0 | | | | | | >85 | >69 | 1.62 ± 0.03 | |

[a] In acetonitrile. [b] In glassy MTHF at 77 K. [c] Determined by T−T transient absorption.

**SCHEME 1**



ca. 19 Å. Thus, we set $r$ to be 19 Å for QC−S−BF$_2$. It is likely that other conformations of this molecule will be populated within the lifetime of the excited state of the BF$_2$ chromophore. However, analysis of eq 3 shows that at this distance small change in $r$ will result in only a minor impact on $\Delta G$. Because the steroid skeleton acts as the medium separating the changes, we set the $\epsilon$ value to be the dielectric constant of cyclohexane ($\epsilon = 2.015$ D). The oxidation potential of MQC, $E$(QC/QC$^{+\bullet}$), and the reduction potential of EtBF$_2$, $E$(BF$_2$/BF$_2^{-\bullet}$), were determined in acetonitrile by the cyclic voltammetry method to be ca. +1.62 ± 0.03 and −0.87 ± 0.03 V with respect to SCE, respectively. Calculation according to eq 3 reveals that electron transfer from the QC group to the singlet excited BF$_2$ portion of QC−S−BF$_2$ in acetonitrile is exothermic by ca. 17 kcal/mol. Thus, the fluorescence quenching of the BF$_2$ chromophore in QC−S−BF$_2$ was attributed to the long-distance intramolecular electron transfer from the QC group to the singlet excited BF$_2$ as shown in Scheme 1. This electron transfer initiated the isomerization of QC, as reported below.

**Phosphorescence and Flash Photolysis: Exclusion of Triplet Electron Transfer and Energy Transfer.** To search for evidence of intramolecular triplet electron transfer and energy transfer in QC−S−BF$_2$, the phosphorescence spectra of QC−S−BF$_2$ and EtBF$_2$ in glassy 2-methyltetrahydrofuran (MTHF) at 77 K were examined and are given in Figure 2. Both spectra show distinct vibronic transitions with maxima at ca. 489, 508, and 525 nm and a shoulder at ca. 560 nm. The phosphorescence efficiency of the BF$_2$ group in QC−S−BF$_2$ is ca. 25% less than that in EtBF$_2$. The reduction of the phosphorescence in QC−S−BF$_2$ may be attributed either to the direct quenching of the triplet state of the BF$_2$ chromophore by the QC group via intramolecular triplet electron transfer or triplet energy transfer or to the quenching of BF$_2$ singlet excited state via intramolecular electron transfer as mentioned in the above section, which results in the reduction of the triplet quantum yield. To clarify the reason for the reduction of phosphorescence of the BF$_2$ group in QC−S−BF$_2$ as compared with that in EtBF$_2$, we performed a laser flash photolysis study. Pulsed-laser photolysis of QC−S−BF$_2$ in degassed acetonitrile using 355 nm excitation light gives rise to a strong transient absorption spectrum with maximum at ca. 670 nm as shown in Figure 3. This absorption is assignable to the lowest triplet state of the BF$_2$ chromophore on the basis of the observation that this absorption is readily quenchable by O$_2$. Analysis of the transient spectrum at 670 nm as a function of time yields a lifetime of the triplet state of ca. 7.5 $\mu$s. The transient absorption of the model compound EtBF$_2$ is identical with that of QC−S−BF$_2$, and the lifetime of its triplet state is the same with that of QC−S−BF$_2$ within experimental error. Thus, the triplet state of BF$_2$ in QC−S−BF$_2$ is not quenchable by the QC group, and the phosphorescence reduction of the BF$_2$ group in QC−S−BF$_2$ as compared with that in EtBF$_2$ originates from the intramolecular singlet electron transfer, which leads to the decrease in the BF$_2$ triplet state yield.

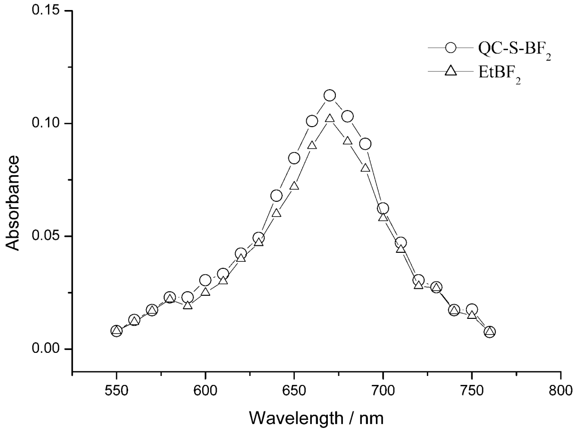


**Figure 3.** Transient absorption spectra of BF$_2$ triplet state formed upon laser photolysis of QC−S−BF$_2$ (○) and EtBF$_2$ (Δ) in acetonitrile 0.5 $\mu$s after the laser pulse.

**Photosensitized Isomerization of the Quadricyclane to the Norbornadiene Group in QC−S−BF$_2$.** Photochemical interconversion of norbornadiene and quadricyclane has been the subject of intense experimental and theoretical investigation in view of its mechanistic significance.[1,20,21] The forward reaction occurs only from the triplet state of norbornadiene. In this case, the triplet norbornadiene can be populated by triplet energy transfer[11] or by triplet radical-ion pair recombination in electron-transfer sensitization.[1,20,21] On the other hand, the back reaction originates from the radical cation of quadricyclane and can be initiated by photoinduced electron transfer using electron-deficient sensitizers. BF$_2$ chromophore is a potent electron acceptor and can sensitize the photoisomerization of quadricyclane to norbornadiene with high efficiency via singlet electron transfer.[17] Thus, study of the intramolecular photosensitized isomerization of the QC group in QC−S−$BF_2$ may provide evidence for the remote singlet electron transfer.

Irradiation with $\lambda > 350$ nm light of a $2.5 \times 10^{-5}$ M degassed solution of QC−S−$BF_2$ in acetonitrile at room temperature results in valence isomerization of the quadricyclane group to norbornadiene group (NBD−S−$BF_2$) as shown in Chart 1. Under this condition, only the $BF_2$ chromophore absorbs the light. Thus, the isomerization of the quadricyclane to the norbornadiene group must be attributed to the sensitization via singlet electron transfer. The yield of the isomerization product is 100% on the basis of the consumption of the starting material. The assignment of the product as the norbornadiene derivative relies mainly on its $^1$H NMR spectrum, which is in close agreement with that reported in the literature.[10,11,20,21] Measurements of product formation at different substrate concentrations demonstrate that the isomerization of the QC group in QC−S−$BF_2$ is induced by intramolecular photosensitization. On the basis of the experimental results mentioned above, the primary photophysical and photochemical processes in QC−S−$BF_2$ can be expressed by Scheme 1. The quantum yield of this intramolecular photosensitized isomerization, $\phi_{iso}$(QC−S−$BF_2$), can be calculated by eq 4

$$\phi_{iso}(\mathrm{QC{-}S{-}BF_2}) = \phi_{SET}\phi_{iso}(\mathrm{QC^{+\bullet}/NBD^{+\bullet}})\phi_{BET} \quad (4)$$

where $\phi_{iso}(\mathrm{QC^{+\bullet}/NBD^{+\bullet}})$ represents the efficiency of the isomerization from $\mathrm{QC^{+\bullet}}$ to $\mathrm{NBD^{+\bullet}}$ and $\phi_{BET}$ is the efficiency of the charge recombination in $\mathrm{NBD^{+\bullet}{-}S{-}BF_2^{-\bullet}}$. The value of $\phi_{iso}$(QC−S−$BF_2$) was determined to be ca. 0.058. The value of $\phi_{SET}$ is ca. 0.25 as mentioned above. It has been established that $\mathrm{NBD^{+\bullet}}$ cannot be isomerized to $\mathrm{QC^{+\bullet}}$ because of the unfavorable energetics for this transformation.[1] Thus, we assume $\phi_{BET}$ in $\mathrm{NBD^{+\bullet}{-}S{-}BF_2^{-\bullet}}$ to be unity. This in turn gives $\phi_{iso}(\mathrm{QC^{+\bullet}/NBD^{+\bullet}})$ to be ca. 0.23 according to eq 4. It is known that in the isomerization of quadricyclane in polar solvents via intermolecular electron-transfer photosensitization, reversible electron transfer is an important pathway for the radical-ion pair and substantially diminishes the yield of isomerization.[1] In our case, although a polar solvent (acetonitrile) is used, 23% of QC radical cation generated by intramolecular electron transfer is isomerized to $\mathrm{NBD^{+\bullet}}$. The high efficiency for this radical cation isomerization is probably due to the separation of $\mathrm{QC^{+\bullet}}$ and $\mathrm{BF_2^{-\bullet}}$ groups in $\mathrm{QC^{+\bullet}{-}S{-}BF_2^{-\bullet}}$, which suppresses the charge recombination.

As mentioned above, the $BF_2$ and QC chromophores in QC−S−$BF_2$ are separated by 15 $\sigma$-bonds, and the center-to-center distance between the two chromophores in the extended QC−S−$BF_2$ conformation is ca. 19 Å. At such separation between the chromophores, electron transfer via a through-space process would be very inefficient. With reference to the precedent works,[1−15] it is proposed that through-bond mechanisms operate in the photoinduced intramolecular singlet electron transfer in QC−S−$BF_2$ and in the charge recombination in $\mathrm{NBD^{+\bullet}{-}S{-}BF_2^{-\bullet}}$.

## Conclusions

Spectroscopy and photosensitized reaction experiments reveal that excitation of the $BF_2$ chromophore in QC−S−$BF_2$ results in a remote intramolecular singlet electron transfer from the QC to $BF_2$ group with an efficiency of ca. 25% and a rate constant of $1.0 \times 10^9$ s$^{-1}$. The generated radical cation of QC undergoes the isomerization to the norbornadiene radical cation with an efficiency of ca. 23%, which subsequently leads to the formation of NBD−S−$BF_2$ by the recombination of the radical-ion pair in $\mathrm{NBD^{+\bullet}{-}S{-}BF_2^{-\bullet}}$. The photoinduced intramolecular electron transfer in QC−S−$BF_2$ and the charge recombination in $\mathrm{NBD^{+\bullet}{-}S{-}BF_2^{-\bullet}}$ are proposed to proceed via a through-bond mechanism.

## Experimental Section

**Material.** Unless otherwise noted, materials were purchased from Beijing Chemical Work and were used without further purification. Spectral-grade 2-methyltetrahydrofuran and acetonitrile were used for absorption and emission spectra, flash photolysis, redox potential measurements, and steady-state photoirradiation measurements.

**Synthesis of the Quadricyclane−Steroid−{Dibenzoylmethanatoboron Difluoride} System (QC−S−$BF_2$).** The synthesis of QC−S−$BF_2$ involved three steps. Reaction of 3$\beta$-((2-(methoxycarbonyl)bicyclo[2.2.1]hepta-2,5-diene-3-yl)carboxy)-androst-5-en-17$\beta$-ol (NBD−S−17$\beta$-ol)[22] with 3,3-dibenzoylpropionyl chloride gives NBD−S−17$\beta$-yl-(3,3-dibenzoylpropionate) (NBD−S−diketone), which was used as a starting material to prepare NBD−S−$BF_2$ by its reaction with boron fluoride. QC−S−$BF_2$ was obtained by photoirradiation of NBD−S−$BF_2$ with $\lambda < 280$ nm light. The synthesis procedure and identification are given in the Supporting Information.

**Instrumentation.** $^1$H NMR spectra were recorded at 300 MHz with a Brucker spectrometer. MS spectra were run on a VG ZAB spectrometer. UV spectra were measured with a Hitachi UV-340 spectrometer. IR spectra were run on a Perkin-Elmer 983 spectrometer. Steady-state emission spectra were recorded on either a Hitachi Em850 or a Hitachi MPF-4 spectrofluorimter. Fluorescence lifetime was determined on a Horiba NBES-1100 single-photon-counting instrument. HPLC was performed on a Varian VISTA 5500 liquid chromatograph with a Lichrosorb RP 18 column.

**Fluorescence and Phosphorescence Measurements**. Fluorescence was measured in acetonitrile at room temperature. The samples were purged with nitrogen for at least 30 min before measurements. Phosphorescence studies were performed in 2-methyltetrahydrofuran at 77 K, and the sample solutions were degassed by at least three freeze−pump−thaw cycles at a pressure of $5 \times 10^{-5}$ Torr. The excitation wavelength both for fluorescence and for phosphorescence spectra was 355 nm. It was found that the feature of the emission spectra was independent of the excitation wavelengths. For comparison of the emission efficiency of QC−S−$BF_2$ with Et$BF_2$, the spectra were run using solutions with identical optical density at the excitation wavelength. The relative emission efficiencies were measured from the peak areas of the emission spectra. The fluorescence quantum yields of the $BF_2$ group in Et$BF_2$ and QC−S−$BF_2$ were determined in acetonitrile relative to quinine bisulfate in 1 N sulfuric acid.[23]

**Redox Potentials of $BF_2$ and QC.** The redox potentials of Et$BF_2$ and MQC were determined by cyclic voltammetry in acetonitrile, using a glassy carbon working electrode and a Ag/AgCl/KCl (saturated) reference electrode in the presence of 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte.

**Laser Flash Photolysis.** The laser flash photolysis system has been described elsewhere.[24] The pump light source was the third harmonic (355 nm) of an Nd:YAG laser (Spectra-Physics, GCR-11-1). The probe light source was a xenon arc lamp (Vshio, UXL-500-0). The probe light transmitting through the sample cell was fed to a detection system, which consists of a monochromator (Ritsu, MC-10L), photomultiplier (Hamamatsu, R928), digital oscilloscope (Tektronix, 2440), and microcomputer. The decay curves were analyzed by using nonlinear least-squares fitting.

**Photoirradiation and Product Analysis.** Photoirradiation was carried out in a Pyrex reactor, and the solution of QC−S−$BF_2$ (ca. $1 \times 10^{-5}$ M) in acetonitrile was purged with nitrogen. A 450-W Hanovia high-pressure mercury lamp was used as the excitation source. After irradiation, the solvent was evaporated from the samples under reduced pressure. The product was separated from the starting material by preparative thin-layer chromatography, eluted with ethyl acetatel/petroleum ether (1/2.5 in volume), and characterized by $^1$H NMR and mass spectroscopes (see Supporting Information). Product yields were determined by analysis of the $^1$H NMR spectra and by HPLC analysis. Quantum yield for intramolecular photosensitization isomerization of the quadricyclane group in QC−S−$BF_2$ was determined by using a benzophenone/benzhydrol system as the actinometry ($\phi = 0.74$ in benzene).[25] In this measurement, we control the conversion of QC−S−$BF_2$ to NBD−S−$BF_2$ to be less than 20% to suppress the reversed isomerization.[26]

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**Supporting Information Available:** Synthesis procedures and data of melting points, elemental analysis, mass spectroscopies, infrared spectroscopies, and $^1$H NMR of 3$\beta$-((2-(methoxycarbonyl)bicyclo[2.2.1]hepta-2,5-diene-3-yl)carboxy)-androst-5-en-17$\beta$-yl-(3,3-dibenzoylpropionate) (NBD−S−diketone), 3$\beta$-((2-(methoxycarbonyl)bicyclo[2.2.1]hepta-2,5-diene-3-yl)carboxy)androst-5-en-17$\beta$-yl-{3,3-dibenzoylmethanatoboron difluoride} propionate (NBD−S−$BF_2$), and 3$\beta$-((2-(methoxycarbonyl)quadricyclane-3-yl)carboxy)androst-5-en-17$\beta$-{3,3-dibenzoylmethanatoboron difluoride} propionate (QC−S−$BF_2$). This material is available free of charge via the Internet at http://pubs.acs.org.

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(26) The triplet energy of the NBD group in NBD−S−$BF_2$ (ca. 53 kcal/mol)[10] is lower than that of the $BF_2$ chromophore (58.4 kcal/mol), suggesting that photosensitized isomerization of NBD−S−$BF_2$ to QC−S−$BF_2$ via intramolecular triplet energy transfer is thermodynamically possible. We also measured the oxidation potential of the NBD group in acetonitrile ($E$(NBD/NBD$^{+\bullet}$) = +1.45 V with respect to SCE) by the cyclic voltammetric method. Calculation according to eq 3 shows that electron transfer from the NBD group to the singlet excited state of the $BF_2$ group is endothermic by ca. 5 kcal/mol.