Photoinduced Intramolecular Electron Transfer and Triplet Energy Transfer in a Steroid-Linked Norbornadiene–Carbazole Dyad

Li-Ping Zhang,[a] Bin Chen,[a] Li-Zhu Wu,[a] Chen-Ho Tung,*[a] Hong Cao,[b] and Yoshifumi Tanimoto[b]

Abstract: Bichromophoric compound 3β-((2-(methoxycarbonyl)bicyclo[2.2.1]-hepta-2,5-diene-3-yl)carboxy)androst-5-en-17β-yl-[2-(*N*-carbazolyl)acetate] (NBD-S-CZ) was synthesized and its photochemistry was examined by fluorescence quenching, flash photolysis, and chemically induced dynamic nuclear polarization (CIDNP) methods. Fluorescence quenching measurements show that intramolecular electron transfer from the singlet excited state of the carbazole to the norbornadiene group in NBD-S-CZ occurs with an efficiency (Φ_{SET}) of about 14% and rate constant (k_{SET}) of about $1.6 \times 10^7 s^{-1}$. Phosphorescence and flash photolysis studies reveal that intramolecular triplet energy transfer and electron transfer from the triplet carbazole to the norbornadiene group proceed with an efficiency ($\Phi_{TET} + \Phi_{TT}$) of about 52% and rate constant ($k_{TET} + k_{TT}$) of about $3.3 \times 10^5 s^{-1}$. Upon selective excitation of the carbazole chromophore, nuclear polarization is detected for protons of the norbornadiene group (emission) and its quadricyclane isomer (enhanced absorption); this suggests that the isomerization of the norbornadiene group to the quadricyclane proceeds by a radical-ion pair recombination mechanism in addition to intramolecular triplet sensitization. The long-distance intramolecular triplet energy transfer and electron transfers starting both from the singlet and triplet excited states are proposed to proceed by a through-bond mechanism.

Keywords: carbazole · chromophores · electron transfer · energy transfer · isomerization · norbornadiene

Introduction

Intramolecular long-distance electron and energy transfer in bichromophoric compounds have been the subjects of intense studies.[1–6] The principal aims of these studies have been to develop a better understanding of photoharvesting systems in natural organisms,[1–6] and to provide a base for designing molecular photonic devices and synthetic solar-energy-conversion systems.[2, 5, 7, 8] It is generally accepted that in donor–{saturated hydrocarbon bridge}–acceptor systems electron transfer and triplet energy transfer can proceed by through-bond and/or through-space mechanisms, depending on the nature of the bridge.[1–10] For rigid bridge-linked donor–acceptor molecules, the through-bond mechanism appears to be favored.[1–9] Steroid,[11–16] fused norbornenyl[6, 17] and many other groups[18] have been used to constitute the bridge. By using these bridges, the mixing of the donor and acceptor orbitals with the orbitals of the bridge, which facilitates a super-exchange interaction, is provided by an "all-*trans*" arrangement of the σ bonds. In contrast, flexible bridge-linked donor–acceptor molecules adopt many conformations, and only a small number of the conformations allow orbital overlaps conducive to through-bond electron transfer and energy transfer. In this case, the electron transfer and energy transfer processes have been regarded as a through-space interaction.[19–22]

The factors that govern intramolecular energy- and electron-transfer processes in rigid donor–bridge–acceptor systems, for instance distance and orientation between the donor and acceptor, and the electronic properties of the intervening spacer have been extensively examined by Miller and Closs,[23, 24] Morrison,[11–13] Paddon-Row and Verhoevem,[6, 17, 25] Schuster,[26, 27] Zimmerman,[28] Gust and Moore,[2, 5] Wasielewski,[1, 8, 10, 29] and many others.[3, 7, 9, 14–16] We have utilized the androstene skeleton as the bridge, mounted an antenna chromophore and a norbornadiene (or quadricyclane) group on the steroidal framework, and investigated intramolecular triplet energy transfer and electron transfer within these systems.[15, 16] Although the donor and acceptor are separated by as much as about 17 Å, electron-

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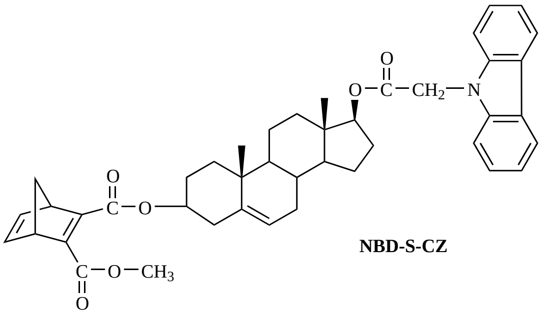
transfer and triplet energy-transfer processes occur with reasonably large rate constants by a through-bond mechanism. Our study on a norbornadiene–steroid–benzophenone system[15] has shown that the benzophenone chromophore harvests photon energy and transfers its triplet energy to the norbornadiene group with a rate constant of about $1.5 \times 10^5\,s^{-1}$ resulting in the isomerization of the later into quadricyclane group. In a study on a quadricyclane–steroid–{dibenzolmethanatoboron difluoride} system,[30] we demonstrated efficient electron transfer from the quadricyclane to the singlet excited state of the dibenzolmethanatoboron difluoride group with a rate constant of about $1.0 \times 10^9\,s^{-1}$, leading to the isomerization of the quadricyclane to the norbornadiene group. For norbornadiene–steroid–benzidine,[16] both intramolecular triplet energy transfer and singlet electron transfer occur, and the isomerization of the norbornadiene to quadricyclane group proceeds both by triplet sensitization and radical-ion pair recombination mechanisms. In the present work we have synthesized the bichromophoric compound norbornadiene–steroid–carbazole (NBD-S-CZ).



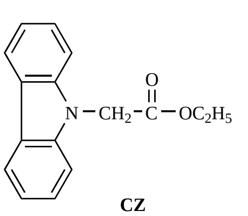
NBD-S-CZ

Emission quenching, laser flash photolysis, and chemically induced dynamic nuclear polarization (CIDNP) results suggest that, in addition to efficient triplet energy transfer and singlet electron transfer, electron transfer from the triplet excited state of the carbazole chromophore to the norbornadiene group also occurs. The data provide a new example of using an antenna chromophore to activate a remote functional group for chemical reaction by long-distance electron transfer and triplet energy transfer.

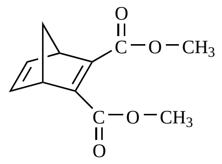
Results and Discussion

Synthesis of the norbornadiene–steroid–carbazole system (NBD-S-CZ): The synthesis of NBD-S-CZ involved three steps. Treatment of 3β-hydroxyandrost-5-en-17-one with 2-(methoxycarbonyl)bicyclo[2.2.1]hepta-2,5-diene-3-carbonyl chloride gave the norbornadiene derivative androst-5-en-17-one (NBD-S-One). After separation, NBD-S-One was reduced by a literature procedure[31] to yield a mixture of the diastereomers 3β-NBD-androst-5-en-17β-ol (NBD-S-17β-Ol) and 3β-NBD-androst-5-en-17α-ol (NBD-S-17α-Ol), with the former as the predominant product. Assignments of NBD-S-17β-Ol as the 17-C-βOH alcohol and NBD-S-17α-Ol as the 17-C-αOH alcohol were supported by ^{1}H NMR resonances at 3.32 and 3.68 ppm characteristic of 17-C-αH and 17-C-βH, respectively.[32] The isomeric alcohols NBD-S-17β-Ol and NBD-S-17α-Ol may be separated by chromatography. Since the amount of the purified NBD-S-17α-Ol was insufficient for a photochemical study, we only used NBD-S-17β-Ol as a starting material to prepare NBD-S-CZ by its treatment with 2-(*N*-carbazolyl)acetic acid.

Intramolecular electron transfer from the singlet excited state of the carbazole chromophore to the norbornadiene group in NBD-S-CZ: The absorption spectra of NBD-S-CZ and the models for the donor, ethyl 2-(*N*-carbazolyl)acetate (CZ), and for the acceptor, dimethyl bicyclo[2.2.1]hepta-2,5-diene-2,3-carbxylate (MNBD) in acetonitrile were examined. The absorption spectrum of NBD-S-CZ is essentially identical to the sum of the spectra of CZ and MNBD; this suggests the absence of a measurable interaction between the carbazole and norbornadiene chromophores of NBD-S-CZ in the ground state. Significantly, the absorption of CZ extends to longer wavelengths (with maxima at 330 and 345 nm) than does that of MNBD. The energy of the singlet excited state of the carbazole chromophore (ca. 83 kcal mol^{-1}) is lower than that of MNBD (>95 kcal mol^{-1}), as estimated from their absorption spectra. Thus singlet–singlet energy transfer from the excited carbazole chromophore to the norbornadiene chromophore is impossible. Furthermore, this factor permits the selective excitation of the carbazole moiety in the bichromophoric compound NBD-S-CZ.



CZ



MNBD

The fluorescence spectra of NBD-S-CZ and CZ in acetonitrile were studied, Figure 1. Both compounds exhibit the

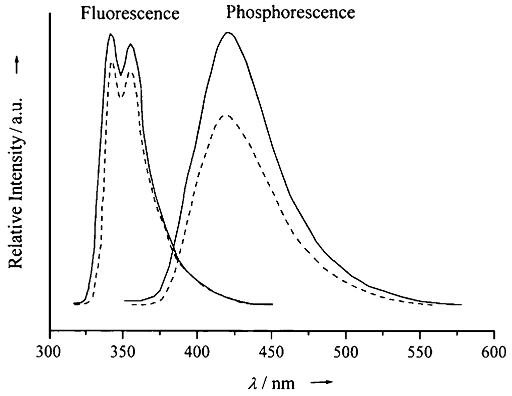


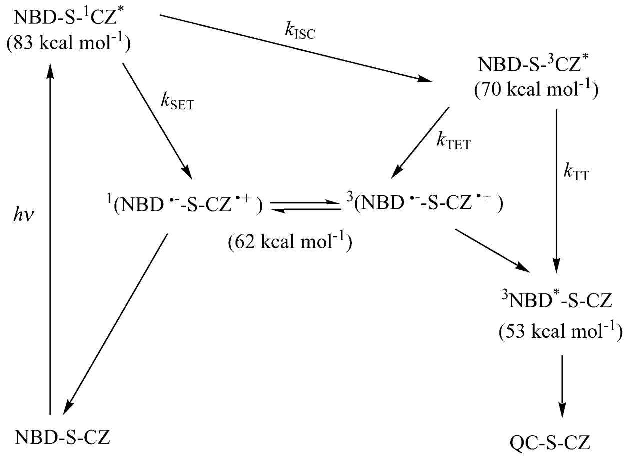
Figure 1. Emission spectra of NBD-S-CZ (----) and CZ (——). The fluorescence and phosphorescence spectra were obtained in acetonitrile at room temperature and in 2-methyltetrahydrofuran at 77 K, respectively. $\lambda_{EX} = 310$ nm, [NBD-S-CZ] = [CZ] = 1×10^{-5} M.

structured fluorescence characteristic of the carbazole chromophore with maxima at 345 and 355 nm. The parameters of the fluorescence spectra together with those of the phosphorescence spectra and cyclic voltammetry for NBD-S-CZ, CZ, and MNBD are given in Table 1. The general features of these two spectra are essentially identical. However, the fluorescence efficiency of the carbazole chromophore in NBD-S-CZ is about 15 % less than that in the model compound CZ. This observation indicates that quenching of the carbazole fluorescence by the norbornadiene group in NBD-S-CZ takes place. Measurements at different concentrations reveal that the quenching is intramolecular. The fluorescence lifetimes for NBD-S-CZ and CZ in acetonitrile were determined to be 9.0 and 10.5 ns respectively (Table 1). These data allow the calculation of the quenching constant (k_{SET}) and the quantum yield (Φ_{SET}) of the quenching, which were found to be $1.6 \times 10^7\,\mathrm{s}^{-1}$ and 14 % respectively. The value of the quenching efficiency thus obtained is comparable to that from the fluorescence efficiency measurements.

Since the possibility of singlet – singlet energy transfer being responsible for the long-distance intramolecular quenching of the carbazole fluorescence by the norbornadiene group in NBD-S-CZ is excluded on thermodynamic grounds as mentioned above, we examined the reality of electron transfer between the two chromophores as the cause of the fluorescence quenching. The free energy change (ΔG) involved in an electron-transfer process in acetonitrile can be calculated by the Rehm – Weller equation:[33, 34]

$$\Delta G\ (\mathrm{kcal\,mol^{-1}}) = 23.06\,[E_{\mathrm{ox}}(\mathrm{D}) - E_{\mathrm{red}}(\mathrm{A}) - e^2/R_{\mathrm{cc}}\varepsilon] - E_{0,0}\ (\mathrm{kcal\,mol^{-1}}) \quad (1)$$

here $\Delta E_{0,0}$ is the excited state energy, and in this case represents the singlet excited energy of the carbazole group (ca. 83 kcal mol^{-1}). E_{ox}(D) and E_{red}(A) are the redox potentials of the donor and acceptor, respectively, determined in acetonitrile. $e^2/R_{\mathrm{cc}}\varepsilon$ is the Coulombic interaction in the ion-pair state whose magnitude depends on the distance between the donor and acceptor (R_{cc}) and on the dielectric constant (ε) of the medium separating the charges. We used the Alchemy II program to calculate the energies of the two general conformations, extended and bent, of NBD-S-CZ and found that the extended conformation has the lower energy. In this conformation the center-to-center separation of the norbornadiene and carbazole groups is about 17.0 Å. Thus, we set R_{cc} equal to 17.0 Å for NBD-S-CZ. Cyclic voltammetric measurement of the model compound CZ in acetonitrile showed reversible oxidation waves with an oxidation potential E_{ox}(D) of around 1.10 V versus SCE. This value is consisted with that reported in the literature.[35] The reduction potential (E_{red}(A)) of MNBD has been reported in previous work[15, 16] to be about −1.67 V versus SCE. Calculation according to Equation (1) reveals that electron transfer from the singlet excited state of the carbazole portion of NBD-S-CZ to the norbornadiene group is exothermic by about 21 kcal mol^{-1}. Thus, we attributed the fluorescence quenching of the carbazole chromophore in NBD-S-CZ to long-distance intramolecular electron transfer from the singlet excited carbazole to the norbornadiene group as shown in Scheme 1. This conclusion is supported by the results of flash photolysis measurements. Photolysis of NBD-S-CZ by laser pulse (308 nm, 10 ns) results in instantaneous formation of a transient absorption in the region 770 – 870 nm that can be assigned to the carbazole radical cation, as reported in the next section.



Scheme 1. Photophysical and photochemical processes in NBD-S-CZ.

Intramolecular electron transfer and energy transfer from the triplet state of the carbazole chromophore to the norbornadiene group in NBD-S-CZ: Figure 1 gives the phosphorescence spectra of NBD-S-CZ and CZ in glassy 2-methyltetrahydrofuran (MTHF) at 77 K. The phosphorescence efficiency of NBD-S-CZ is much less than that of CZ; this suggests that the triplet state of the carbazole chromophore in NBD-S-CZ is quenched by the norbornadiene group. From its phosphorescence spectrum, we estimated the triplet energy of the carbazole chromophore to be about 70 kcal mol^{-1}. By using the redox potentials of CZ and MNBD in Table 1, calculation from the Rehm – Weller equation [Eq. (1)] reveals that electron transfer from the triplet excited state of the carbazole moiety to the norbornadiene group in NBD-S-CZ is thermodynamically favorable by around 8 kcal mol^{-1}. Thus, we infer that electron transfer from the triplet carbazole to the

Table 1. Spectroscopic and electrochemical properties of NBD-S-CZ, CZ, and MNBD.

Compound	Fluorescence[a] $\lambda_{\max}$ [nm]	Fluorescence[a] τ [ns]	Phosphorescence[b] $\lambda_{\max}$ [nm]	Phosphorescence[b] τ [μs][c]	E [kcal mol^{-1}] E_{s}	E [kcal mol^{-1}] E_{T}	oxidation potential[a] (V vs. SCE)	reduction potential[a] (V vs. SCE)
NBD-S-CZ	345 355	9.0	420	1.56				
CZ	345 355	10.5	420	3.25	83	70	1.10	
MNBD					> 95	53		− 1.67

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

norbornadiene group occurs. Furthermore, the triplet energy of the norbornadiene group (ca. 53 kcal mol^{-1})[15, 16] is much lower than that of the carbazole group. Thus, both electron transfer and energy transfer from the triplet state of the carbazole group to the norbornadiene group in NBD-S-CZ are thermodynamically possible.

The evidence for long-distance intramolecular triplet energy transfer and electron transfer in NBD-S-CZ based on phosphorescence efficiency and energetic consideration was further strengthened by a flash-photolysis study. Pulsed-laser photolysis of CZ in degassed acetonitrile by using 308 nm excitation light gave rise to a strong transient absorption spectrum in the region of 360–500 nm as shown in Figure 2a. This absorption can be assigned to the lowest triplet state of the carbazole chromophore by reference to the transient absorption of the triplet state of *N*-ethylcarbazole.[36–38] Furthermore, this absorption is readily quenched by penta-1,3-diene or O_2. Analysis of the transient spectrum of CZ at 400 nm as a function of time yields a lifetime of the triplet state of about 3.25 µs. In addition to the lowest triplet-state absorption, Figure 2a also shows a transient absorption spectrum in the region of 770–870 nm. This absorption band is assigned to the radical cation of the carbazole chromophore by reference to the transient absorption of the radical cation of *N*-ethylcarbazole.[36–39] This radical cation was considered to be produced by a two-photon ionization process.[36] Pulsed-laser photolysis of NBD-S-CZ under identical condition leads to absorptions of the triplet state and the radical cation of the carbazole chromophore (Figure 2b) as in the case of CZ. The lifetime of this triplet state, monitored at 400 nm, is about 1.56 µs. By comparison of the triplet lifetime of the carbazole chromophore in NBD-S-CZ to that of the model compound CZ, the quenching efficiency ($\Phi_{\mathrm{TET}} + \Phi_{\mathrm{TT}}$; Φ_{TET} and Φ_{TT} represent the efficiencies of triplet electron transfer and energy transfer, respectively) and rate constant ($k_{\mathrm{TET}} + k_{\mathrm{TT}}$; k_{TET} and k_{TT} denote the rate constants for triplet electron transfer and energy transfer, respectively) of the carbazole chromophore by the remote norbornadiene group in NBD-S-CZ are about 52% and $3.3 \times 10^5\,\mathrm{s}^{-1}$, respectively. Figure 2 clearly shows that the intensity of the radical cation absorption band relative to the triplet absorption band for NBD-S-CZ is much stronger than that for CZ. Thus, the radical cation in the case of photolysis of NBD-S-CZ is proposed to be produced mainly by electron transfer from the carbazolyl to the norbornadiene group, although two-photon ionization is also possible. By consideration of the fact that the carbazole radical cation is mainly generated during “the laser pulse”, it is clear that this cation is produced by long-distance electron transfer from the singlet excited state of the carbazole chromophore to the norbornadiene group in NBD-S-CZ. It is also possible that a fraction of the carbazole radical cation is formed from the triplet electron transfer. However, attempts to separate the contribution of the triplet electron transfer to the radical cation formation from that of the singlet electron transfer were unsuccessful.

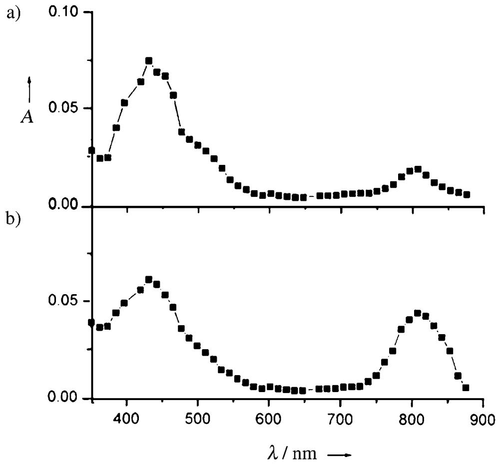


Figure 2. Transient absorption spectra observed upon laser photolysis of a) CZ and b) NBD-S-CZ in acetonitrile (2.5×10^{-5} M) 0.5 µs after the laser pulse.

CIDNP study on photosensitized isomerization of the norbornadiene group to quadricyclane in NBD-S-CZ by long-distance electron transfer: The photosensitized valence isomerization of norbornadiene to quadricyclane has been the subject of intense experimental and theoretical investigation in view of its mechanistic interests.[40–43] The isomerization mechanism involving triplet energy transfer is well understood.[44] Furthermore, MNBD is a good electron acceptor and can also undergo isomerization in the presence of an electron-donor sensitizer. Based on the observation of CIDNP effects, it has been proposed that this photosensitized isomerization involves electron transfer from the sensitizer to the norbornadiene to generate the singlet-state radical-ion pair, intersystem crossing of the resultant singlet radical-ion pair to its triplet state, and the recombination of the triplet radical-ion pair to give the triplet norbornadiene followed by rearrangement to the quadricyclane.[41, 42] For molecule NBD-S-CZ, the energy of the radical-ion pair (G), NBD$^{\bullet-}$-S-CZ$^{\bullet+}$ in acetonitrile was calculated from the redox potentials of the donor and acceptor groups ($G = E_{\mathrm{ox}}(\mathrm{D}) - E_{\mathrm{red}}(\mathrm{A}) - e^2/R_{\mathrm{cc}}\varepsilon$) to be about 62 kcal mol^{-1}. This energy lies below the triplet energy of the carbazole chromophore (ca. 70 kcal mol^{-1}), but above the triplet energy of the norbornadiene group (ca. 53 kcal mol^{-1}). Thus, we infer that the triplet radical-ion pair ^{3}(NBD$^{\bullet-}$-S-CZ$^{\bullet+}$) may undergo recombination to generate the triplet norbornadiene ^{3}NBD*-S-CZ. Therefore, the isomerization of the norbornadiene group in NBD-S-CZ might proceed both by triplet energy-transfer and by radical-ion pair recombination mechanisms. Indeed, photoirradiation with $\lambda > 300$ nm of a 2.5×10^{-4} M degassed solution of NBD-S-CZ in acetonitrile at room temperature results in valence isomerization of the norbornadiene group to quadricyclane group (QC-S-CZ).

The CIDNP method has proved to be a valuable tool for the investigation of the isomerization of norbornadiene and its derivatives to the quadricyclane valence isomers and the reverse reaction that proceed via photoinduced electron transfer and radical-ion intermediates.[41] Jones, Bargon, and their co-workers[41, 42] observed CIDNP upon irradiation of MNBD in the presence of aromatic electron-donor sensitizers in acetonitrile. Nuclear polarization was detected for selected protons of the norbornadiene (emission) and its quadricyclane valence isomer (enhanced absorption). The complementary CIDNP effects were rationalized in terms of the quenching of the sensitizer singlets by electron transfer, hyperfine induced intersystem crossing between the resultant singlet and triplet radical-ion pairs, and competition between singlet and triplet radical-ion pair recombination. The reverse electron transfer in the initially formed singlet radical-ion pairs will regenerate the reactant norbornadiene in competition with intersystem crossing to the triplet ion pairs, while the triplet ion pair on combination gives rise to the triplet state of the norbornadiene group, which in turn leads predominantly to the quadricyclane valence isomer. In the present work we irradiated a 2.5×10^{-4} M solution of NBD-S-CZ in CD_3CN in the probe of a NMR spectrometer with a 1000 W high-pressure Hg–Xe lamp through a Pyrex filter, and observed the characteristic CIDNP signals as shown in Figure 3. The signal intensities of the bridgehead and olefinic protons of the norbornadiene group during irradiation are much weaker than those before and after irradiation. This observation suggests that these protons exhibit enhanced emission. On the other hand, the corresponding protons (the bridgehead and cyclobutane protons) of the quadricyclane isomer show enhanced absorption. No polarization was observed for the bridge protons of either the norbornadiene or the quadricyclane or for protons of the carbazole moiety and the steroid spacer. The observation of the complementary CIDNP effects provides unambiguous evidence for the electron-transfer and radical-ion pair recombination mechanism in the carbazole-sensitized isomerization of the norbornadiene group to quadricyclane in NBD-S-CZ.

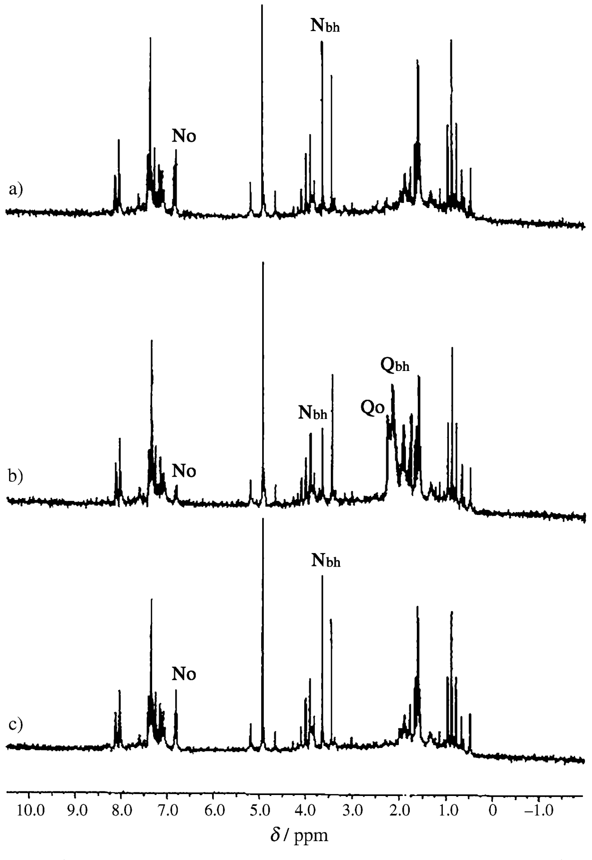


Figure 3. ^{1}H NMR spectra (80 MHz) of NBD-S-CZ (2.5×10^{-4} M) in CD_3CN. a) before irradiation, b) during irradiation, and c) after irradiation. N_o, N_{bh}, Q_o, and Q_{bh} refer the resonances of the NBD olefinic, NBD bridgehead, QC cyclobutane and QC bridgehead protons, respectively.

As mentioned above, the isomerization of the norbornadiene group in NBD-S-CZ may proceed both through triplet energy transfer and through radical-ion pair recombination mechanisms. The later mechanism involves electron transfers both from the singlet and the triplet excited states of the carbazole chromophore to norbornadiene group. The directions of the spin polarization in the isomerization of the norbornadiene to the quadricyclane group in NBD-S-CZ (the norbornadiene protons show enhanced emission, while those of the quadricyclane have enhanced absorption, Figure 3) were found to be identical to those observed by Jones and Bargon[41, 42] on irradiation of MNBD in the presence of aromatic electron-donor sensitizers. Thus, we infer that electron transfer from the singlet excited state of the carbazole chromophore to the norbornadiene group in NBD-S-CZ plays a dominant role in the norbornadiene isomerization that proceeds by the radical-ion pair recombination mechanism. However, closer inspection of Figure 3 reveals that the intensities of the CIDNP signals, particularly those associated with the norbornadiene protons, are rather weak compared with the case of the bimolecular photosensitized isomerization. This suggests that isomerization of the norbornadiene group in NBD-S-CZ through electron transfer from the triplet state of the carbazole chromophore to the norbornadiene group might also take place. According to the Kaptein rule[45, 46] and subsequent amendment,[47–49] the CIDNP effect depends on the spin multiplicity of the initially generated radical pair. The radical-ion pairs generated from the triplet electron transfer pathway and those from the singlet electron transfer pathway should give opposite polarization of signals, and they might tend to more or less cancel with each other.

Conclusion

Fluorescence quenching, flash photolysis, and CIDNP studies reveal that long-distance intramolecular triplet energy transfer and electron transfers both from the singlet and the triplet excited states of the carbazole chromophore to the norbornadiene group in NBD-S-CZ occur. Scheme 1 summarizes the photophysical and photochemical processes in NBD-S-CZ. The valence isomerization of the norbornadiene group in NBD-S-CZ proceeds via its triplet state, and this triplet state is generated by intramolecular triplet energy transfer and by recombination of the triplet radical-ion pair $^3(\text{NBD}^{\bullet -}\text{-S-CZ}^{\bullet +})$, which is produced by electron transfers both from the singlet and triplet excited state of the carbazole to the norbornadiene group. The carbazole and norbornadiene groups in NBD-S-CZ are separated by 15 σ bonds, and the center-to-center distance is about 17 Å. At such a separation between the chromophores electron transfer and triplet energy transfer by a through-space process would be very inefficient. By reference to preceding works[1–18, 23–29] on the long-distance through-bond electron and energy transfer, we infer that through-bond mechanism operates in the intramolecular electron transfers and triplet energy transfer in NBD-S-CZ.

Experimental Section

Material: Unless otherwise noted, materials were purchased from the 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 CIDNP measurements.

Instrumentation: ^{1}H NMR spectra were recorded at 300 MHz with a Varian Gemini-300 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 either on a Hitachi EM850 or a Hitachi MPF-4 spectrofluorometer. Fluorescence lifetime was determined on a Horiba NBS-1100 single-photon counting instrument.

Fluorescence and phosphorescence measurements: Fluorescence was measured in acetonitrile at room temperature. The samples were purged with nitrogen for at lest 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 5×10^{-5} Torr. The excitation wavelength both for fluorescence and phosphorescence spectra was 310 nm. For comparison of the emission efficiency of NBD-S-CZ with CZ, the spectra were run with solutions with identical optical density at the excitation wavelength. The relative emission efficiencies were measured from the peak areas of the emission spectra.

Redox potentials of carbazole and norbornadiene chromophores: The redox potentials of CZ and MNBD were determined by cyclic voltammetry in acetonitrile with a glassy carbon working electrode and an Ag/AgCl/KCl (saturated) reference electrode in the presence of tetrabutylammonium hexafluorophosphate (0.1M) as the supporting electrolyte.

Laser flash photolysis: The laser flash-photolysis system has been described elsewhere.[50] The pump light source was an XeCl excimer laser (Lumonics 500, 308 nm, 10 ns). The probe light source was a xenon arc lamp (Ushio, UXL-500-0). The probe light transmitting through the sample cell was fed to a detection system that consisted of a monochromater (Ritsu, MC-10L), photomultiplier (Hamamatsu, R928), digital oscilloscope (Tektronix, 2400), and microcomputer. The decay curves were analyzed by using nonlinear least-squares fitting.

CIDNP Measurements: CIDNP experiments were performed at 80 MHz on a Bruker AC-80 spectrometer equipped with a photo-CIDNP probe. The solution of NBD-S-CZ (2.5×10^{-4} M) in CD_3CN was irradiated in situ with $\lambda > 300$ nm light by a SQX 1000 W high pressure Hg–Xe lamp with a Pyrex glass filter.

3*β*-((2-(Methoxycarbonyl)bicyclo[2.2.1]hepta-2,5-diene-3-yl)carboxy)androst-5-en-17*β*-yl-(2-(*N*-carbazolyl)acetate) (NBD-S-CZ): The synthesis of 3*β*-((2-(methoxycarbonyl)bicyclo[2.2.1]hepta-2,5-diene-3-yl)carboxy)-androst-5-en-17*β*-ol (NBD-S-17*β*-Ol) has been described previously.[15] Treatment of NBD-S-17*β*-Ol with 2-(*N*-carbazolyl)acetic acid gave NBD-S-CZ. A 50 mL round bottom flask was equipped with a magnetic stir bar and a condenser with a nitrogen inlet tube. The apparatus was flame dried under dry nitrogen and charged with NBD-S-17*β*-Ol (150 mg, 0.3 mmol), 2-(*N*-carbazolyl)acetic acid (165 mg, 0.74 mmol), 1,3-dicyclohexylcarbodiimide (200 mg), toluene sulfonic acid (500 mg) and anhydrous pyridine (50 mL). The mixture was stirred at room temperature for 24 h, then was poured into water (200 mL). The solution was neutralized with dilute HCl, and a white precipitate was observed. After filtration, the solid was extracted with chloroform. Evaporation of the solvent afforded a yellow product, which was purified by column chromatography on silica with ethyl ether/petroleum ether (2:3 *v*/*v*) to give NBD-S-CZ (32%). M.p. 181–184 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.95-8.10$ (m, 2H; ArH), 7.20–7.50 (m, 6H; ArH), 6.95 (dd, 2H; NBD olefinic H), 5.40 (dd, 1H; steroid olefinic H), 4.95 (s, 2H; N-CH_2-COO), 4.25 (m, H; NBD bridgehead H), 4.15 (m, H; NBD bridgehead H), 3.90 (s, 3H; O-CH_3), 3.55 (m, 1H; 3α-H), 3.32 (t, 1H; 17β-H), 2.05–2.45 (m, 2H; NBD bridge H), 2.0–1.1 (m, 19H), 1.00 (s, 3H; 19-CH_3), 0.9 (s, 3H; 18-CH_3); elemental analysis calcd (%) for $C_{43}H_{47}NO_6$ (673): C 76.67, H 6.98, N 2.08; found: C 76.43, H 6.41, N 1.94.

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