Intramolecular Triplet Energy Transfer in Donor–Acceptor Molecules Linked by a Crown Ether Bridge

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Abstract: Bichromophoric compounds BP-C-NP and BP-C-NBD were synthesized with benzophenone chromophore (BP) as the donor, and 2-naphthyl (NP) and norbornadiene group (NBD) as the acceptor, respectively. Their intramolecular triplet energy transfer was examined. The bridges linking the donor and acceptors in these molecules involve a crown ether moiety complexing a sodium ion. Phosphorescence quenching, flash photolysis and photosensitized isomerization experiments indicate that intramolecular triplet energy transfer occurs with rate constants of about 3.3×10^5 and 4.8×10^5 s^{-1} and efficiencies of about 33 and 42% for BP-C-NP and BP-C-NBD, respectively. Theoretical calculations indicate that these molecules adopt conformations below room temperature which allow their two-end chromophores conducive to through-space energy transfer.

Keywords: crown compounds · donor–acceptor systems · energy transfer · norbornadiene · through-space interactions

Introduction

Triplet–triplet energy transfer has been extensively examined.[1] The mechanism for triplet energy transfer is usually described by Dexter electron exchange interaction, which requires overlap of the electron clouds for the donor and acceptor chromophores.[2] Recently, there has been increasing interest in long-distance intramolecular triplet energy transfer in bichromophoric molecules.[3–20] It is generally accepted that in donor-{saturated hydrocarbon bridge}–acceptor molecules, triplet energy transfer can proceed via through-bond and/or through-space mechanisms, depending on the nature of the bridge. For rigid bridge-linked donor–acceptor molecules, the through-bond mechanism appears to be favored.[3–9] Steroids,[6,9] fused norbornyl,[5] and many other groups[3,4,7,8,12] 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. By contrast, the flexible bridge-linked donor–acceptor molecules adopt many conformations, and only a small fraction of the conformations allow the σ bonds in "all-*trans*" arrangement conducive to through-bond energy transfer. However, rapid conformational equilibrium makes a sufficient fraction of such molecules within the lifetime of the donor triplet state experience conformations that allow the two end chromophores close enough for orbital overlap and through-space energy transfer.[10,11f,21–23] Such conformations may not be those with the lowest energies, therefore their population may not be large. However, in room temperature liquid solution unhindered rotational motion of the σ bonds in the bridge will allow the chromophores to sample a wide variety of conformations possessing both good and poor overlap. As long as the rate of interconversion between the conformers is comparable with the triplet energy transfer rate, energy transfer by through-space mechanism can be expected.

Previous studies on through-space triplet energy transfer have primarily utilized "fully flexible" tethers (polymethy-

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lene or polyethylene glycol chains) to link the donor and acceptor, in which the energy transfer relies on the rapid conformational equilibrium. In the present work we use benzophenone (BP) as the donor and 2-naphthyl (NP) or bornadiene group (NBD) as the acceptor; the linkage was achieved by a bridge that involves crown ether moiety (complexing a sodium ion and with chloride anion) as shown in Schemes 1 and 2, BP-C-NP and BP-C-NBD. Efficient intra-

Scheme 1.

Scheme 2.

molecular triplet energy transfer in such molecules were evidenced by phosphorescence quenching, flash photolysis and photosensitized isomerization experiments. It is known that the molecule of macrocyclic polyether complexing a metal ion is rigid and shaped like a crown.[25] The relatively rigid crown ether moiety in these molecules restricts the rotational motion of the σ bonds in the bridge and thereby prevents the conformers from rapid interconversion. On the other
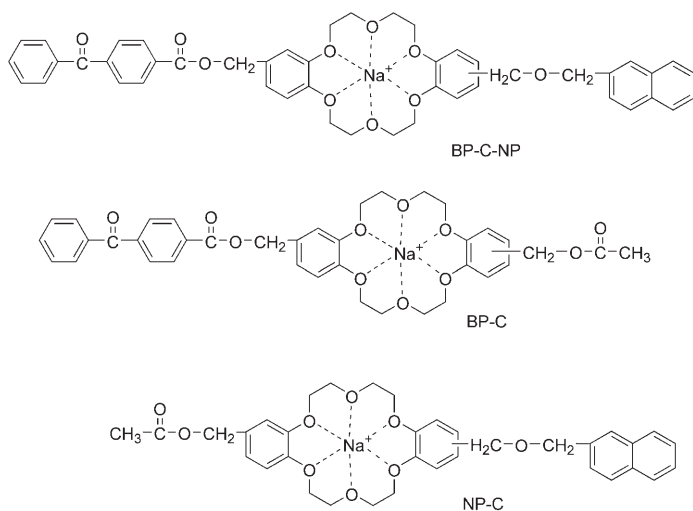
hand, calculations indicate that for these molecules in the conformations with the lowest energies (therefore most probably populated) the two end chromophores are separated only by about 3.8–4.2 Å. Thus, intramolecular triplet energy transfer may proceed efficiently via a through-space mechanism.
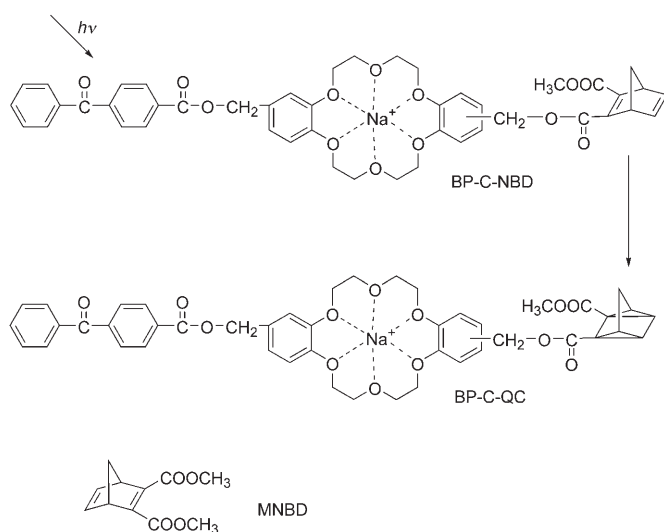
Results and Discussion

Syntheses of BP-C-NP and BP-C-NBD: BP-C-NP contains two isomers (*syn*-BP-C-NP and *anti*-BP-C-NP) due to the different substitution positions of the BP and NP groups at the crown-dibenzo moiety. Calculations show that the separation between donor (BP) and acceptor (NP) in the *syn*-BP-C-NP conformer—which has the lowest energy and is responsible to through-space triplet energy transfer—is almost identical with that of *anti*-BP-C-NP (see below). Indeed, flash photolysis experiments show that triplet energy transfer occurs in the two isomers with same rate and efficiency (see below). Thus, we used the mixture of the two isomers for energy transfer study. These isomers were synthesized in four steps (see Experimental Section). Reaction of dibenzo[18]crown-6 (DBC) with hexamethylene tetramine in the presence of trifluoroacetic acid gave the mixture of 2,3,11,12-bis(4′-formylbenzo)-[18]crown-6 (*syn*-BFBC) and 2,3-(4′-formylbenzo)-11,12-(5′-formylbenzo)-[18]crown-6 (*anti*-BFBC) according to the literature method.[26] The mixture of the two BFBC isomers was reduced by sodium borohydride to yield the mixture of corresponding *syn*-BHMBC and *anti*-BHMBC. Electrospray ionization mass spectrometry (ESI-MS) analysis revealed that the yielded crown ether derivatives formed a complex with a sodium ion; also it turned out that it was difficult to remove this sodium ion. Reaction of the BHMBC isomers with β-(bromomethyl)-naphthalene in the presence of metal sodium in DMF produced naphthalene derivatives (*syn*-NP-C-OH and *anti*-NP-C-OH). The isomers of NP-C-OH also formed complexes with a sodium ion, which were used as starting materials to prepare BP-C-NP by their reaction with *p*-benzoylbenzoyl chloride. The BP-C-NP obtained was a mixture of *syn*-BP-C-NP and *anti*-BP-C-NP, and formed a complex with a sodium ion in the crown moiety. BP-C-NP was dissolved in cyclohexane and the solution was washed with saturated aqueous solution of sodium chloride. Thus in the sample of BP-C-NP for energy transfer study the counter anion was chloride.

BP-C-NBD was synthesized by a similar procedure for BP-C-NP. BP-C-NBD also consists of *syn*- and *anti*-isomers, and both isomers complex with sodium ion. Again the counteranion is chloride.

Intramolecular triplet energy transfer in BP-C-NP: The absorption spectrum of BP-C-NP in benzene is essentially identical to the sum of the spectra of the models for the donor, BP-C, and for the acceptor, NP-C. The absorption of the BP group extends to a longer wavelength than does that

of the NP group. This fact permits the selective excitation of the BP moiety in the bichromophoric compound BP-C-NP at longer wavelength. Figure l shows the phosphorescence
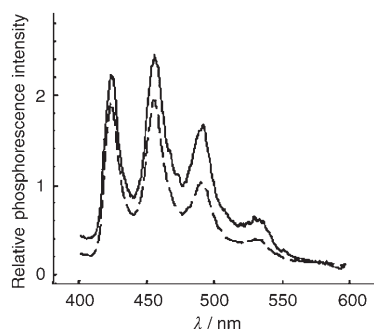

Figure 1. Phosphorescence spectra of BP-C-NP (-----) and BP-C (——) in methylcyclohexane at 77 K; $\lambda_{ex}=350$ nm, [BP-C-NP] = [BP-C] = 2×10^{-5} mol L^{-1}.

spectra of BP-C-NP and BP-C in glassy methylcyclohexane at 77 K. The excitation light wavelength used was 350 nm where only the BP chromophore absorbed. Both compounds exhibit phosphorescence characteristic of the benzophenone chromophore with maxima at 420, 458, 495 nm and a shoulder at 535 nm. The general features of the phosphorescence spectra of the BP chromophores from BP-C-NP and BP-C are essentially identical. However, the phosphorescence efficiency of the BP group in BP-C-NP is about 30 % less than that in the model compound BP-C. The triplet energy of BP group (288 kJ mol^{-1})[9a] is greater than that of NP group (251 kJ mol^{-1}),[27] and triplet energy transfer from BP to NP groups has been well established.[28] Thus, the observations mentioned above suggest that the triplet energy transfer in BP-C-NP works from the BP to the NP group. Measurements at different concentrations reveal that this triplet energy transfer is intramolecular. Originally we expected to be able to observe the phosphorescence from the NP group, because the triplet energy transfer will result in the triplet state of NP. Considering the much smaller quantum yield of the phosphorescence for NP compared with that for BP[1a] and the extensive overlap of the two phosphorescence spectra, it is not surprising that the phosphorescence of NP is not distinctly observed.

The evidence for long-distance intramolecular triplet energy transfer in BP-C-NP based on the phosphorescence efficiency is further strengthened by flash photolysis study. Pulse-laser photolysis of BP-C-NP solution in benzene with λ_{ex} at 355 nm gives rise to a strong transient absorption spectrum with maximum at 560 nm immediately after the laser pulse as shown in Figure 2. The bleaching in the region of 400–500 nm is due to the phosphorescence of the BP chromophore. The absorption spectrum with the maximum at 560 nm is assigned to the lowest triplet state of the BP chromophore on the basis of the following observations. First, this absorption is essentially identical with that of the alkyl benzophenone-4-carboxylate triplet state independently
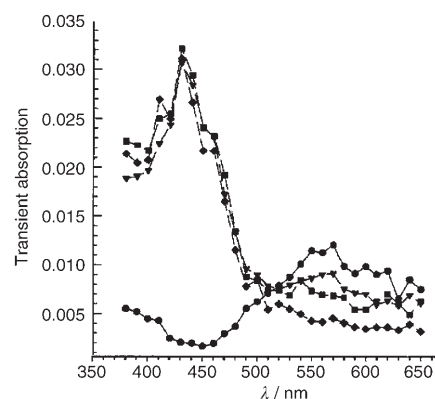

Figure 2. Transient absorption spectra of BP-C-NP in benzene; $\lambda_{ex}=$ 355 nm, [BP-C-NP] = 5×10^{-5} mol L^{-1}; the spectra were obtained at 0 (●), 0.4 (▼), 0.8 (■), and 1.2 μs (◆) after the laser pulse.

generated.[9a] Secondly, this species is readily quenchable by O$_2$. Significantly, the triplet state absorption of the BP chromophore is progressively replaced by an absorption in the region of 400–500 nm (Figure 2). The latter absorption is assigned to the lowest triplet state of the NP chromophore by comparison to the transient absorption of the triplet state of 2-substituted naphthalene.[29] The decay of the BP triplet state absorption (at 560 nm) and the growth in absorption of the NP triplet state (at 440 nm) occur in the same time scale. This observation convincingly demonstrates that triplet energy transfer from BP to NP group indeed occurs.

Analysis of the transient spectrum of BP group at 560 nm as a function of time revealed that the transient decay can be well described by a monoexponential function. This observation indicates that *syn-* and *anti-*BP-C-NP isomers undergo triplet energy transfer with same rate and efficiency. The lifetime of the triplet state of the BP group in BP-C-NP (τ_1) was about l.03 μs. Similarly, the lifetime of the triplet state of the NP group analyzed at 440 nm is about l3.18 μs. On the other hand, photolysis of the model compound BP-C also results in the transient absorption of the BP group. The feature of this transient absorption is identical with that in BP-C-NP. However, the decay of this transient absorption does not lead to growth in the absorption in the region of 400–500 nm. The lifetime of this BP triplet state (τ_2) is about l.55 μs. The shorter lifetime of the BP triplet state in BP-C-NP in comparison with that in BP-C is consistent with the proposal that a long-distance intramolecular triplet energy transfer in BP-C-NP operates. The rate constant (k_{ET}) and efficiency (ϕ_{ET}) for this energy transfer can be calculated from τ_1 and τ_2 according to Equations (1) and (2), respectively. k_{ET} was obtained to be 3.3×10^5 s^{-1}, and ϕ_{ET} 33 %, which is comparable to that obtained by phosphorescence efficiency measurements.

$$k_{ET} = \frac{1}{\tau_1} - \frac{1}{\tau_2} \quad (1)$$

$$\phi_{ET} = 1 - \frac{\tau_1}{\tau_2} \quad (2)$$

Intramolecular triplet energy transfer in BP-C-NBD: The triplet energy transfer from the BP to the NBD group in BP-C-NBD (Scheme 2) was also evidenced by phosphorescence quenching, flash photolysis as well as the photosensitized isomerization of the NBD group. The phosphorescence efficiency of the BP group in BP-C-NBD in glassy methylcyclohexane at 77 K is about 40% less than that in the model compound BP-C. This phosphorescence quenching is attributed to the intramolecular energy transfer from the triplet BP to the NBD group in BP-C-NBD, since the triplet energy transfer from alkyl benzophenone-4-carboxylate to dimethyl bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (MNBD) (triplet energy, 222 kJ mol^{-1}) is known,[9] and the efficiency of the phosphorescence quenching in BP-C-NBD is independent of the substrate concentration. Flash photolysis of BP-C-NBD solution in benzene gives rise to the transient absorption spectrum of the BP triplet state with maximum at 560 nm as in the case of the model compound BP-C. Similar to the case of BP-C-NP, the transient decay at 560 nm for BP-C-NBD can be well described by a monoexponential function, suggesting that triplet energy transfer occurs in *syn*- and *anti*-isomers of BP-C-NBD with same rate and efficiency. The lifetime of this triplet state (τ_3) was measured to be about 0.89 µs. The rate constant (k_{ET}) and efficiency (ϕ_{ET}) for this energy transfer were calculated from τ_3 and τ_2 to be about 4.8×10^5 s^{-1} and 42%, respectively, according to Equations (1) and (2).

The intramolecular triplet energy transfer in BP-C-NBD is further confirmed by the valence isomerization of the NBD group. Previous studies for intramolecular triplet energy transfer have mainly chosen the acceptor to be chemically stable during the energy transfer process and concerned photophysical processes as in the case of BP-C-NP, although a few investigations have focused on acceptors designed to undergo fast and irreversible chemical reactions as a tool to provide information on the dynamics of the energy transfer.[6,8–10] In BP-C-NBD, the NBD group can undergo valence isomerization to quadricyclane (QC) via its triplet state (Scheme 2).[9,30] Thus, study of the intramolecular photosensitized isomerization of the NBD group in BP-C-NBD may provide evidence for the long-distance triplet energy transfer. Irradiation with $\lambda > 350$ nm of a 2.5×10^{-5} M solution of BP-C-NBD in benzene at room temperature leads to valence isomerization of the NBD group to QC (BP-C-QC) as shown in Scheme 2. Under this condition only the BP chromophore absorbs the light. Thus, the isomerization of NBD to QC must be attributed to energy 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 quadricyclane derivative mainly relies on its ^{1}H NMR spectrum, which is in close agreement with that reported in the literature.[31] Measurements of product formation by ^{1}H NMR spectrum and HPLC analyses at different concentrations demonstrate that the isomerization of the NBD group in BP-C-NBD is induced by intramolecular photosensitization. On the basis of the experimental results mentioned above, the primary pho-

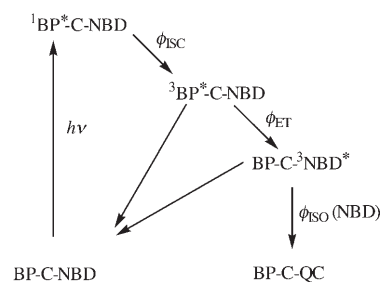tophysical and photochemical processes in BP-C-NBD can be shown by Figure 3.

Figure 3.

The quantum yield of this intramolecular photosensitization isomerization, ϕ_{ISO}(BP-C-NBD), can be calculated according to Equation (3):

$$\phi_{ISO}(\text{BP-C-NBD}) = \phi_{ISC} \cdot \phi_{ET} \cdot \phi_{ISO}(\text{NBD}) \qquad (3)$$

where ϕ_{ISC} represents the quantum yield of the intersystem crossing from the singlet to the triplet excited state of the BP group and is assumed to be unity.[1] ϕ_{ISO}(NBD) represents the quantum yield of the isomerization reaction of the NBD triplet state. ϕ_{ISO}(BP-C-NBD) was determined to be 0.074. To obtain ϕ_{ISO}(NBD), a solution of benzophenone (10^{-2} M) in benzene in the presence of MNBD (1×10^{-2} M) was irradiated at $\lambda > 350$ nm. Under these conditions we could exclusively excite benzophenone. The intersystem crossing efficiency for benzophenone is unity as mentioned above. Since the quencher (MNBD) concentration is high, we assume that all of the benzophenone triplet energy was transferred to MNBD. Thus, measurement of the yield of the isomerization product of MNBD allows determination of ϕ_{ISO}(NBD). It is found that ϕ_{ISO}(NBD)=0.19. This in turn gives ϕ_{ET} as 0.39 according to Equation (3). This value is very close to the values obtained by phosphorescence quenching (0.40) and flash photolysis experiments (0.42) mentioned above.

Mechanism of triplet energy transfer in BP-C-NP and BP-C-NBD: We used Hartree–Fock theory and an economic basis set proposed by one of the authors[32] to optimize the geometric structures of *syn*-BP-C-NP, *anti*-BP-C-NP, *syn*-BP-C-NBD and *anti*-BP-C-NBD individually, and then calculated the energies of eight minimum energy conformers of *syn*-BP-C-NP, eight conformers of *anti*-BP-C-NP, ten conformers of *syn*-BP-C-NBD and ten conformers of *anti*-BP-C-NBD by using B3LYP/6-31G* method. All calculations were conducted with a Gaussian 98 package.[33] Figure 4 shows the optimized conformers of *syn*-BP-C-NP and *anti*-BP-C-NP with their energies relative to their respective lowest energy conformers and the center-to-center distance between the donor and acceptor, defined as the distances between the carbonyl group in BP and the center of naphthalene. For *anti*-BP-C-Np conformer **1** has the lowest
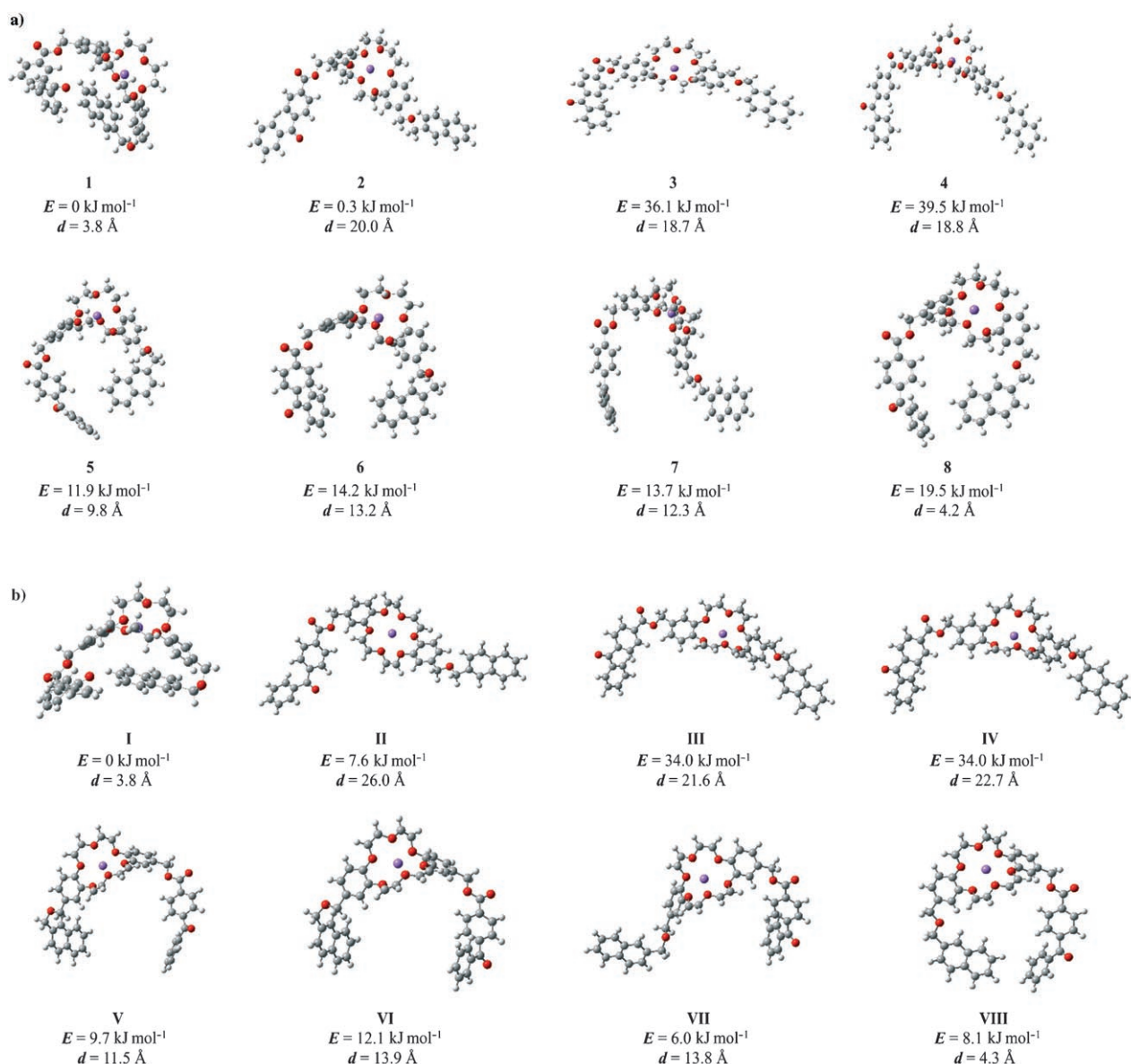
Figure 4. Schematic representation of the conformers with minimum energy for a) *anti*-BP-C-NP and b) *syn*-BP-C-NP. E and d represent their relative energy and center-to-center distance between the donor and acceptor groups, respectively.

energy; the energy of conformer **2** is only about 0.3 kJ mol^{-1} higher than conformer **1**. The other conformers have energies higher than conformer **1** by more than 11 kJ mol^{-1}. Thus, at temperatures below room temperature conformers **1** and **2** are most probably populated. In conformer **1** the center-to-center distance between donor and acceptor is about 3.8 Å. It has already been established[10,34] that triplet energy transfer can occur with rate constant as great as 10^8 s^{-1} when donor and acceptor are separated within 6 Å. Thus, we attribute the high efficient intramolecular triplet energy transfer in *anti*-BP-C-NP to conformer **1** which allow the donor and acceptor close enough for through-space interactions. Since at 77 K conformer **1** is populated, it is not surprising that the efficiency of intramolecular triplet energy transfer measured by phosphorescence (at 77 K) is almost

the same as that measured by transient absorption (at room temperature).

Similarly, for *syn*-BP-C-NP, conformer **I** has the lowest energy (Figure 4) and the other conformers have higher energies and are difficult to be populated at temperature below room temperature. Thus, conformer **I** is responsible for the intramolecular triplet energy transfer. It is significant to note that the donor–acceptor separation in conformer **I** of *syn*-isomer is identical to that in conformer **1** of *anti*-BP-C-NP. Thus, intramolecular triplet energy transfer via through-space mechanism must occur in *anti*-BP-C-NP and *syn*-BP-C-NP with similar rate and efficiency. This is consistent with the observation that the decay of the transient absorption in mixture of *anti*-BP-C-NP and *syn*-BP-C-NP is monoexponential.

Calculations for BP-C-NBD shows that the *anti*-BP-C-NBD conformer with the lowest energy and responsible for the intramolecular triplet energy transfer has the donor–acceptor separation of 4.6 Å, and that of *syn*-BP-C-NBD 4.2 Å. Thus, the intramolecular triplet energy transfer via through-space interactions in the two isomers proceeds with almost the same rate and efficiency.

Conclusion

Phosphorescence quenching, flash photolysis, and photochemical reaction studies demonstrate that intramolecular triplet energy transfer in BP-C-NP and BP-C-NBD occurs with rate constants of about 3.3×10^5 and 4.8×10^5 s^{-1} and efficiencies of about 33 and 42%, respectively. Below room temperature these molecules adopt geometries in which the donor–acceptor separations are only about 3.8–4.2 Å. Thus, the intramolecular triplet energy transfer in these molecules proceeds via a through-space mechanism. Both BP-C-NP and BP-C-NBD in this study contain *syn*- and *anti*-isomers. However, the conformer which has the lowest energy and is responsible to through-space energy transfer in the *anti*-isomer has the donor–acceptor separation identical with that for the *syn*-isomer. Thus, the two isomers undergo intramolecular triplet energy transfer with same rate and efficiency.

Experimental Section

Instrumentation: ^{1}H NMR spectra were recorded at 300 MHz with a Bruker 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 phosphorescence spectra were recorded on either a Hitachi EM850 or a Hitachi MPF-4 spectrofluorimeter.

Material: Unless otherwise noted, materials were purchased from Beijing Chemical Work and were used without further purification. Spectral-grade benzene and methylcyclohexane were used for absorption and emission spectrum, flash photolysis, and steady-state photoirradiation measurements.

Synthesis of BP-C-NP: BP-C-NP was prepared by four steps as shown in Scheme 3.

2,3,11,12-Bis(4′-formylbenzo)-[18]-crown-6 (*syn*-BFBC) and 2,3-(4′-formylbenzo)-11,12-(5′-formylbenzo)-[18]-crown-6 (*anti*-BFBC): This compound was prepared according to the literature.[26] A mixture of dibenzo[18]c-rown-6 (DBC) (10.8 g, 0.03 mol), trifluoroacetic acid (0.21 mol) and hexamethylene tetramine (8.8 g, 0.02 mol) was stirred at 90 °C under nitrogen for 12 h. After the mixture was cooled, concd NaOH (50 mL) and water (200 mL) were successively added. The product precipitated as a brown solid. The crude product was collected by suction filtration and washed with acetone several times to yield a white powder (8.2 g, 65 %). ^{1}H NMR spec-

trum showed that the product contains the *syn*- and *anti*-isomers. Separation of the isomers by chromatography was not successful. ^{1}H NMR (CDCl$_3$): $\delta = 9.85$ (s, 2H, CHO), 7.5–6.9 (m, 6H, ArH), 4.35–3.90 ppm (m, 16H, OCH$_2$CH$_2$O).

2,3,11,12-Bis(4′-hydroxymethylbenzo)-[18]crown-6 (*syn*-BHMBC) and 2,3-(4′-hydroxymethylbenzo)-11,12-(5′-hydroxymethylbenzo)-[18]crown-6 (*anti*-BHMBC): DFBC (4.16 g, 0.01 mol, mixture of *syn*- and *anti*-isomers) was dissolved in ethanol (50 mL); subsequently sodium borohydride (1.42 g, 0.04 mol) was added portionwise to this solution. The mixture was stirred for 30 min under room temperature, and for another hour under 40 °C, then was cooled to room temperature and poured into water (150 mL). After neutralization with sulfuric acid the mixture was extracted with CH$_2$Cl$_2$. The solvent was evaporated, and a white solid was obtained (2.1 g, 50 %). The product contained *syn*- and *anti*-isomers. ^{1}H NMR (CDCl$_3$): $\delta = 7.78$–6.98 (m, 6H, ArH), 4.61 (s, 4H, CH$_2$OH), 4.35–3.95 ppm (m, 16H, OCH$_2$CH$_2$).

NP-C-OH: Metal sodium (0.1 g) was slowly added to a solution of BHMBC (4.20 g, 0.01 mol; mixture of *syn*- and anti-isomers) in dry fresh distilled DMF (25 mL). The mixture was stirred for 30 min. Then, 2-(bromomethyl)naphthalene (2.4 g, 0.011 mol) in DMF (10 mL) was added dropwise. The mixture was stirred for 4 h at room temperature, then water (100 mL) was added. The mixture was acidified with 2 N HCl. The solid was isolated by filtration and purified by chromatography on silica gel with chloroform/Et$_2$O 1:2 (0.6 g, 11 %). The product was a mixture of *syn*- and *anti*-isomers. ^{1}H NMR (CDCl$_3$): $\delta = 8.1$–7.4 (m, 7H, NP-H), 7.1–6.7 (m, 6H, ArH), 4.85 (s, 2H, CH$_2$OCH$_2$), 4.65 (s, 2H, OCH$_2$), 4.61 (s, 2H, CH$_2$OH), 4.35–3.95 ppm (m, 16H, OCH$_2$CH$_2$); MS: m/z: 583.24 [M^+ +Na], 560.34 [M^+].

BP-C-NP: *p*-Benzoylbenzoyl chloride was prepared by refluxing a solution of *p*-benzoylbenzoic acid (1.13 g, 5 mmol) and thionyl chloride (3 mL) in chloroform (10 mL) for 3 h. After excess thionyl chloride and chloroform were evaporated under reduced pressure, the benzoylbenzoyl chloride obtained was added to a solution of N-C-OH (4.2 g; mixture of *syn*- and *anti*-isomers) in chloroform (20 mL), and then pyridine (1 mL) was added. The reaction mixture was stirred and heated under reflux for 4 h. To the mixture water (20 mL) was added and then the solution was extracted with chloroform. Evaporation of the solvent afforded a yellow solid. The crude product was purified by column chromatography on silica eluted with chloroform/Et$_2$O 1:2 (0.4 g, 10 %). The product was obtained as a mixture of *syn*- and *anti*-isomers. ^{1}H NMR (CDCl$_3$): $\delta = 8.6$–7.4 (m, 16H, NP-H), 7.1–6.7 (m, 6H, ArH), 5.3 (s, 2H, CO$_2$CH$_2$), 4.85 (s, 2H, CH$_2$OCH$_2$), 4.65 (s, 2H, OCH$_2$), 4.35–3.95 ppm (m, 16H, OCH$_2$CH$_2$); MS: m/z: 791.44 [M^++Na], 768.07 [M^+].

BP-C-NP was dissolved in cyclohexane and the solution was washed with saturated aq NaCl. The organic layer was separated. Evaporation of the solvent gave the sample for energy transfer study.
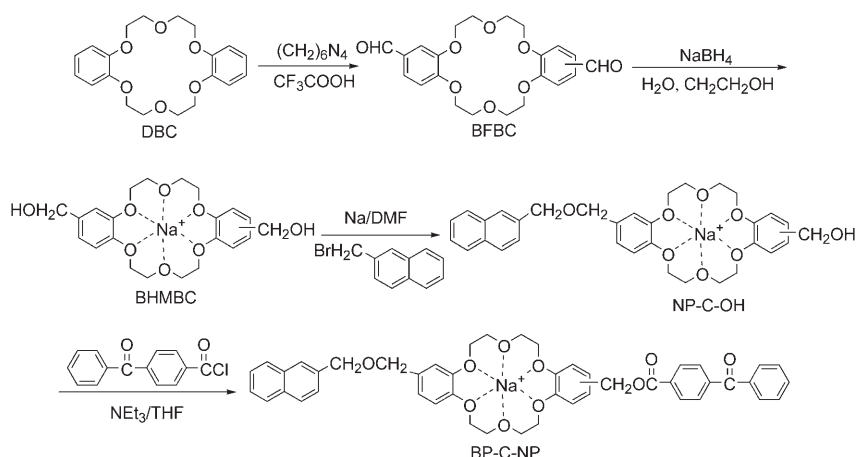
Scheme 3.

BP-C-NBD: BP-C-NBD was synthesized by the similar procedure for BP-C-NP. BP-C-NBD also contained *syn-* and *anti-*isomers and formed complexes with a sodium ion in the crown moiety. ^{1}H NMR (CDCl$_3$): $\delta =$ 8.25–7.50 (m, 9H, ArH), 7.1–6.7 (m, 8H, ArH, NBD olefinic H), 5.30 (s, 2H, CO$_2$CH$_2$), 4.55 (s, 2H, CH$_2$O$_2$C), 4.30–3.80 (m, 21H), 2.5 ppm (m, 2H, NBD bridgehead H); MS: *m/z*: 827.23 [M^++Na], 804.09 [M^+].

Phosphorescence measurements: Phosphorescence studies were performed in methylcyclohexane at 77 K. The sample solutions were degassed by at least three freeze-pump-thaw cycles at a pressure of 5×10^{-5} Torr. The excitation wavelength was 355 nm. For comparison of the emission efficiencies of BP-C-NP and BP-C-NBD with the model compound BP-C, the spectra were run by using solutions with identical optical density at the excitation wavelength. The relative emission efficiencies were measured from the peak areas of the emission spectra.

Laser flash photolysis: Transient absorption spectra were obtained on a previously described instrumentation[35] with the third harmonic out from a Nd/YAG laser (355 nm, 6 ns fwhm, 10 mJ per pulse) as the excitation source. The probe light source was a xenon arc lamp (Photon Technology International, ALH-1000). The probe light transmitting through the sample cell was fed to a detection system which consists of a monochromator (Instruments SA, H-20), photomultiplier tube (Hamamatsu, R928), digital oscilloscope (Tektronix, TDS 540), and microcomputer. The decay curves were analyzed by using nonlinear least-squares fitting.

Photoirradiation of BP-C-NBD: Photoirradiation of BP-C-NBD in benzene was carried out in a Pyrex reactor, and the samples were purged with nitrogen. A 450 W Hanovia high-pressure mercury lamp was used as the excitation source. A UVD-36B glass filter was used to cut off the light with $\lambda < 350$ nm. After irradiation the solvent was evaporated from the samples under reduced pressure. The product BP-C-QC was separated from the starting material by preparative thin-layer chromatography. ^{1}H NMR (CDCl$_3$): $\delta =$ 8.25–7.50 (m, 9H, ArH), 7.1–6.7 (m, 6H, ArH), 5.30 (s, 2H, CO$_2$CH$_2$), 5.25 (s, 2H, CH$_2$O$_2$C), 4.30–3.75 (m, 19H), 2.75–2.85 (m, 2H), 2.55 (m, 2H), 2.35 ppm (m, 2H); MS (FAB): 827.23 [M^++Na], 804.09 [M^+].

The product yield of BP-C-QC was determined by its ^{1}H NMR spectrum and HPLC analyses. The quantum yield for intramolecular photosensitization isomerization of the NBD group in BP-C-NBD (ϕ_{ISO}(BP-C-NBD)) and the efficiency of isomerization of the NBD triplet state (ϕ_{ISO}(NBD)) were determined by using a benzophenone/benzohydrol system for actinometry ($\phi = 0.74$ in benzene).[36]

Acknowledgements

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