

Intramolecular triplet energy transfer in benzophenone- {crown ether}-naphthalene system

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Dedicated to Professor Zhi-Tang Huang on his 75th birthday
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Abstract

Bichromophoric compound benzophenone-{crown ether}-naphthalene (Bp-C-Np) was synthesized and its photophysics was examined. Steady state and time-resolved spectroscopic measurements indicate that intramolecular energy transfer from the triplet state of the benzophenone chromophore to the naphthyl group in Bp-C-Np occurs with efficiency of ca. 33% and rate constant of ca. $3.3 \times 10^5 \text{ s}^{-1}$. This long-distance triplet energy transfer is proposed to proceed via a through-bond exchange mechanism.

Keywords: Triplet energy transfer, flash photolysis, phosphorescence quenching

Introduction

Intramolecular long-distance 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 for photoharvesting systems in 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 triplet energy transfer can proceed via 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 groups¹⁸ have been used to constitute the bridge. In contrast, in flexible bridge-linked donor-acceptor molecules triplet energy transfer process has been regarded as a through-space interaction.¹⁹⁻²² In the present work we report the intramolecular triplet energy transfer for a compound (**Bp-C-Np**) in which a benzophenonyl group (**Bp**, donor) is connected with a naphthyl group (**Np**, acceptor) via

a metal ion-complexed crown ether spacer (Chart 1). Results indicate that efficient energy transfer from the triplet state of the benzophenonyl to the naphthyl group occurs.

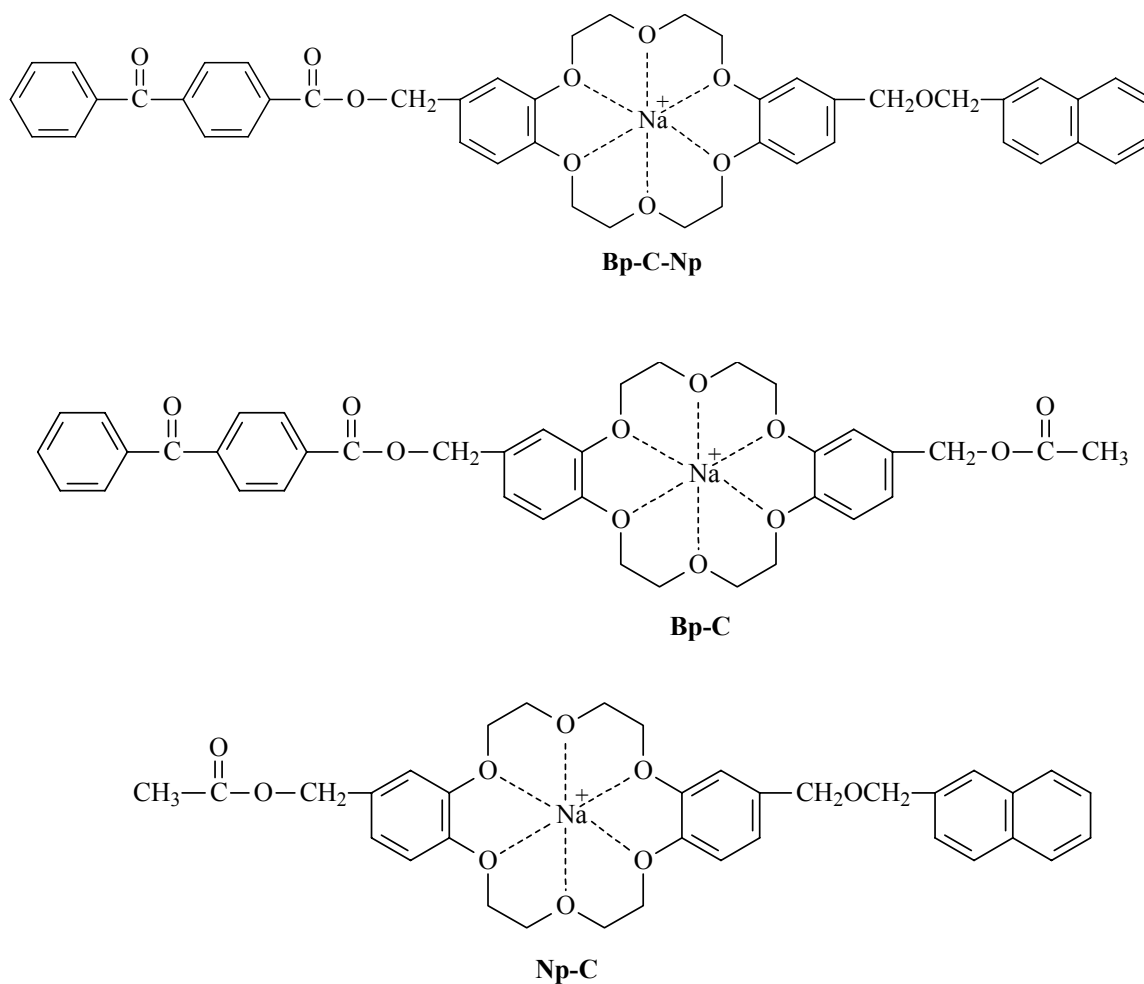


Chart 1

Results and Discussion

Phosphorescence Quenching

The absorption spectrum of **Bp-C-Np** in benzene is essentially identical with the sum of the spectrum of the models for the donor, **Bp-C**, and for the acceptor, **Np-C** as shown in Figure 1, indicating the absence of measurable interaction between the **Bp** and **Np** chromophores of **Bp-C-Np** in the ground state. Significantly, the absorption of the **Bp** group extends to longer wavelength than does that of the **Np** group, suggesting that singlet-singlet energy transfer from the excited **Bp** chromophore to the **Np** group is endothermic. Furthermore, this fact permits the

selective excitation of the **Bp** moiety in the bichromophoric compound **Bp-C-Np** at longer wavelength.

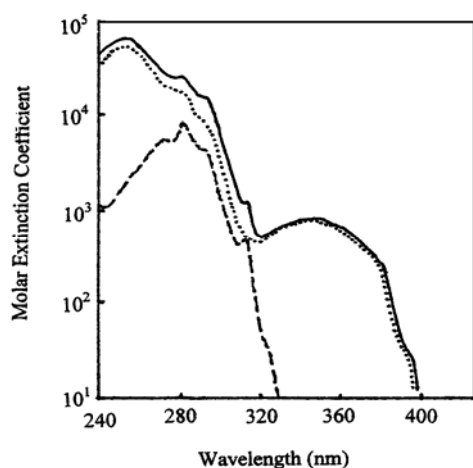


Figure 1. Absorption spectra of **Bp-C-Np** (—), **Bp-C** (···) and **Np-C** (---) in acetonitrile.

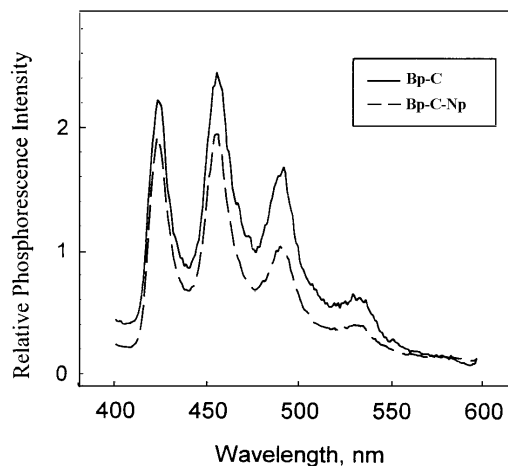


Figure 2. Phosphorescence spectra of **Bp-C-Np** (---) and **Bp-C** (—) in methylcyclohexane at 77 K $\lambda_{\text{ex}} = 350$ nm, $[\text{Bp-C-Np}] = [\text{Bp-C}] = 2 \times 10^{-5}$ M.

Figure 2 shows the phosphorescence 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 a phosphorescence characteristic of the benzophenone chromophore with maxima at 435, 467, 504 nm and a shoulder at 545 nm. These two spectra were obtained using the solutions with identical optical density at the excitation wavelength and under identical instrument parameter setup. 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 ca. 30% less than that in the model compound **Bp-C**. The triplet energy of **Bp** group (289 kJ/mol)²³ is greater than that of **Np** group (251 kJ/mol),²⁴ and triplet-triplet energy transfer from **Bp** to **Np** groups has been well established.²⁵⁻²⁷ Thus, the above observations suggest that triplet energy transfer from the **Bp** to the **Np** group in **Bp-C-Np** operates. 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-triplet energy transfer will result in the triplet state of **Np**. However, the quantum yield of the phosphorescence for **Np** is much smaller compared with that for **Bp** and the two phosphorescence spectra are extensively overlapped. Thus, we could not detect the phosphorescence of **Np** distinctly.

Flash Photolysis

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 gives rise to a strong transient absorption spectrum with maximum at 560 nm immediately after the laser pulse as shown in Figure 3. The bleaching in the region of 400~500 nm is absolutely 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 generated.¹⁵ Secondly, this species is readily quenchable by O₂. Significantly, the triplet state absorption of the **Bp** chromophore is progressively replaced by an absorption in the region of 400~500 nm (Figure 3). The latter absorption is assigned to the lowest triplet state of the **Np** chromophore by reference to the transient absorption of the triplet state of 1-methylnaphthalene.²⁸ The decay of the **Bp** triplet state absorption (at 560 nm) occurs concomitantly with a growth in absorption of the **Np** triplet state (at 440 nm) as shown in Figure 4. 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 yields a lifetime of the triplet state (τ_1) of ca. 1.03 μ s. Similarly, the lifetime of the triplet state of the **Np** group analyzed at 440 nm is ca. 13.18 μ s. The feature of the transient absorption of the **Bp** group in the model compound **Bp-C** is identical with that in **Bp-C-Np**, and the lifetime of the triplet state (τ_2) is ca. 1.55 μ s. 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 eq 1 and 2 respectively. K_{Et} was obtained to be $3.3 \times 10^5 \text{ s}^{-1}$, and ϕ_{Et} 33%, which is comparable to that obtained by phosphorescence efficiency measurements.

$$K_{Et} = 1/\tau_1 - 1/\tau_2 \quad (1)$$

$$\phi_{Et} = 1 - \tau_1/\tau_2 \quad (2)$$

Originally, we also planned to investigate the intramolecular triplet energy transfer in **Bp-C-Np** with the spacer crown uncomplexing a metal ion. However, attempt to prepare ion-free **Bp-C-Np** was not successful, because sodium ion was already complexed into the crown in the course of the synthesis, and it was difficult to remove the ion from the crown (see [Experimental Section](#)).

It has been well established that macrocyclic polyethers complexing with metal ions are rigid and shaped like crowns.²⁹

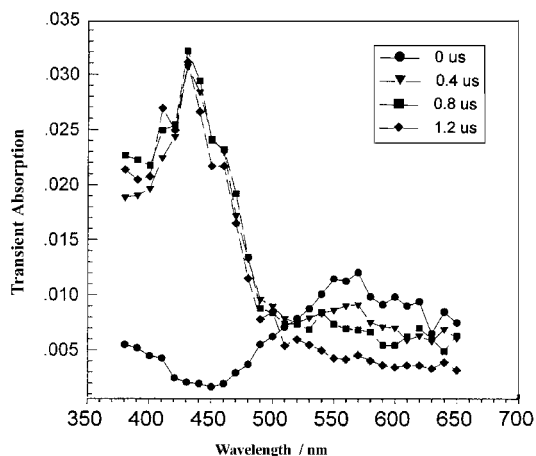


Figure 3. Transient absorption of **Bp-C-Np** in benzene, $\lambda_{ex} = 355$ nm, $[\text{Bp-C-Np}] = 5 \times 10^{-5}$ M, the spectra were obtained at 0, 0.4, 0.8 and 1.2 μs after the laser pulse respectively.

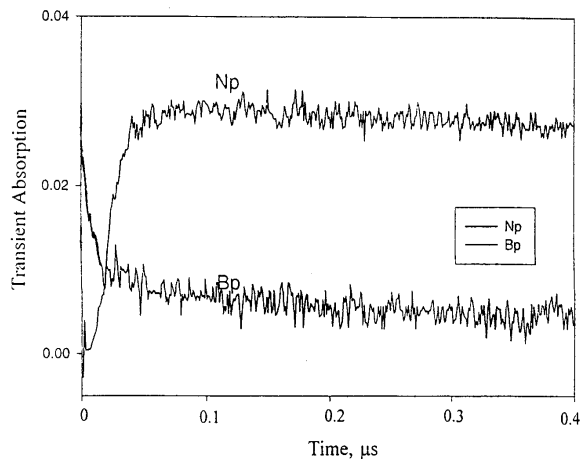


Figure 4. Oscillogram showing decay of **Bp** triplet state observed at 560 nm, and concomitant growth in absorption of the **Np** triplet state at 440 nm.

We used the Alchemy II program to calculate the energies of the various conformations of **Bp-C-Np** and found that the extended conformation has lowest energy. In this conformation the edge-to-edge distance between the **Bp** and **Np** groups, defined as the distance between the carboxyl oxygen atom of the **Bp** group and the methylene group neighbor to **Np**, is ca. 16.9 Å. At such separation between the chromophores triplet energy transfer via a through-space exchange process would be very inefficient. Thus, we infer that a through-bond exchange mechanism might operate in the intramolecular triplet energy transfer in **Bp-C-Np**. The long-distance through-bond exchange triplet-triplet and singlet-singlet energy transfer is now well preceded.¹⁻¹⁸

Experimental Section

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

Instrumentation. ^1H NMR spectra were recorded at 300 MHz with a Bruker spectrometer. MS spectra were run on a VG ZAB or VG TR-200 spectrometer. UV spectra were measured with a Hitachi UV-340 spectrometer. Steady-state emission spectra were recorded either on a Hitachi Em850 or a Hitachi MPF-4 spectrofluorimeter.

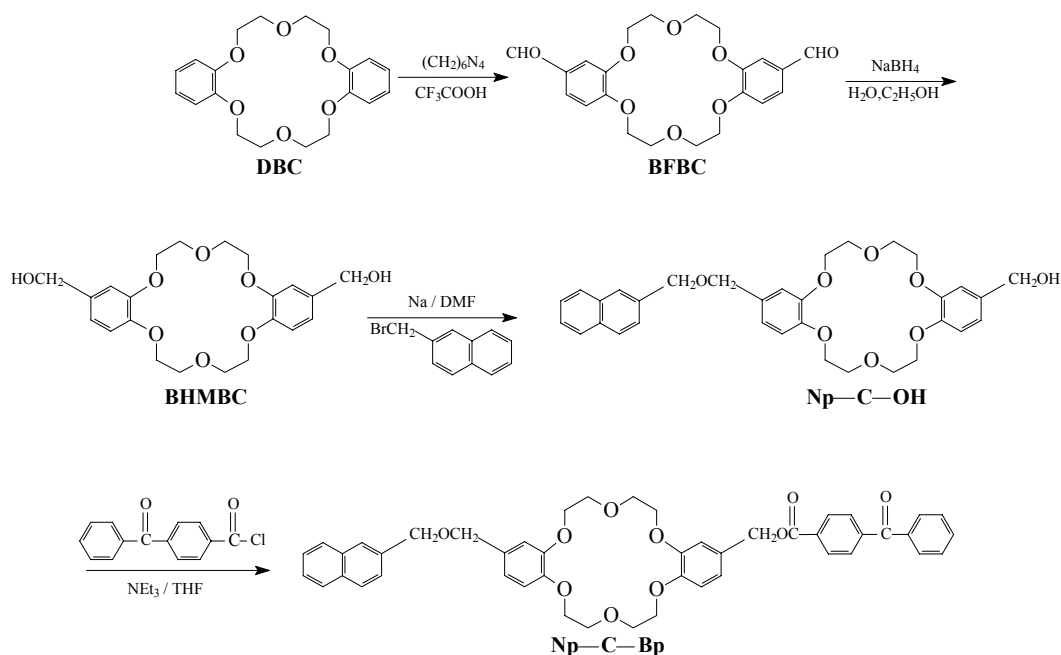
Phosphorescence Measurements. Phosphorescence studies were performed in methylcyclohexane at 77 K, and the sample solutions were degassed by at least three freeze-

pump-thaw cycles at a pressure of 5×10^{-5} Torr. The excitation wavelength was 355 nm. For comparison of the emission efficiency of **Bp-C-Np** with **Bp-C**, the spectra were run using solutions with identical optical density at the excitation wavelength and under identical instrument parameter setup.

Laser Flash Photolysis. The pump light source for the laser flash photolysis 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.

Synthesis of Bp-C-Np. **Bp-C-Np** was prepared by four steps as shown in Scheme 1. Reaction of dibenzo-18-crown-6 (**DBC**) with hexamethylenetetramine in the presence of trifluoroacetic acid gave bis(4'-formylbenzo)-18-crown-6 (**BFBC**) according to the literature method.³⁰ After separation, **BFBC** was reduced by sodium borohydride to yield bis(4'-hydroxymethylbenzo)-18-crown-6 (**BHMBC**). Reaction of **BHMBC** with 2-(bromomethyl)naphthalene in the presence of metal sodium in DMF produced (2-naphthyl-derivative-benzo)-(4'-hydroxymethylbenzo)-18-crown-6 (**Np-C-OH**). Electrospray-ionization mass spectrometry (ESI-MS) analysis revealed that the crown-ether in **Np-C-OH** complexed with a sodium ion, and this sodium ion was difficult to be removed. **Np-C-OH** (complexing sodium ion) was used as a starting material to prepare **Bp-C-Np** by its reaction with *p*-benzoylbenzoyl chloride. It was found that the crown ether in **Np-C-Bp** also complexed a sodium ion.

2,3,11,12-Bis(4'-formylbenzo)-18-crown-6 (BFBC). This compound was prepared according to the literature.³⁰ A mixture of dibenzo-18-crown-6 (**DBC**) (10.8 g, 0.03 mol), trifluoroacetic acid (0.21 mol) and hexamethylenetetramine (8.8 g, 0.02 mol) was stirred at 90 °C under nitrogen for 12 h. After the mixture was cooled, 50 ml of concentrated KOH and 200 ml of water were successively added. The product was precipitated as a brown solid. The crude product was collected by suction filtration and washed with acetone several times, resulting in white powder, yield 8.2 g (65%). ¹H-NMR δ 9.85 (2H, s, CHO), 7.5-6.9 (6H, m, ArH), 4.35-3.90 (16H, m, OCH₂CH₂O).



Scheme 1

2,3,11,12-Bis(4'-hydroxymethylbenzo)-18-crown-6 (BHMBC). 4.16 g (0.01 mol) of **DFBC** was dissolved in 50 ml of ethanol and to the solution 1.42 g (0.04 mol) of sodium borohydride was added individually. The mixture was stirred for half an hour under room temperature, and for another hour under 40 °C, then was cooled to room temperature and poured into 150 ml of water. After neutralization with sulfuric acid the mixture was extracted with 5 × 30 ml of methylene chloride. The solvent was evaporated, and 2.1 g of white solid was obtained. Yield 50%. ¹H-NMR δ 7.78-6.98 (6H, m, ArH), 4.61 (4H, s, CH₂OH), 4.35-3.95 (16H, m, OCH₂CH₂).

Np-C-OH. To the solution of 4.20 g (0.01 mol) of **BHMBC** in 25 ml of dry fresh distilled DMF was added slowly 0.1 g of sodium metal. The mixture was stirred for half an hour. Then 2.4 g (0.011 mol) of 2-(bromomethyl)naphthalene in 10 ml of DMF was added dropwise. The mixture was stirred for 4 h at room temperature, and then 100 ml of water was added. The mixture was acidified with 2 N HCl. The solid was isolated by filtration and purified by chromatography on silica eluting with chloroform /ethyl ether (1:2, V/V). Yield 0.6 g (11%). ¹H-NMR δ 8.1-7.4 (7H, m), 7.1-6.7 (6H, m), 4.85 (2H, s), 4.65 (2H, s), 4.61 (2H,s), 4.35-3.95 (16H, m); HR-ESI-MS *m/z*: calcd for C₃₃H₃₆O₈Na₁ (M+Na)⁺ 583.23, found 583.24, calcd for C₃₃H₃₆O₈ (M⁺) 560.24, found 560.34.

Bp-C-Np. *p*-Benzoylbenzoyl chloride was prepared by refluxing the solution of 1.13 g (5 mmol) of *p*-benzoylbenzoic acid and 3 ml of thionyl chloride in 10 ml of chloroform for 3 h. After the excess thionyl chloride and chloroform were evaporated under reduced pressure, the resultant benzoylbenzoyl chloride was added to a solution of 4.2 g of **Np-C-OH** in 20 ml of chloroform, then 1 ml of pyridine was added. The reaction mixture was stirred and refluxed for 4 h. To the mixture 20 ml of water was added and then the solution was extracted with 3 × 15 ml of

chloroform. Evaporation of the solvent afforded a yellow solid. The crude product was purified by column chromatography on silica eluting with chloroform /ethyl ether (1:2, V/V). Yield 10%. $^1\text{H-NMR}$ δ 8.2-7.4 (16H, m), 7.1-6.7 (6H, m), 5.3 (2H, s), 4.85 (2H, s), 4.65 (2H, s), 4.35-3.95 (16H, m); HR-ESI-MS m/z : calcd. for $\text{C}_{47}\text{H}_{44}\text{O}_{10}\text{Na}_1$ ($\text{M}+\text{Na}$) $^+$ 791.28, found 791.44, calcd for $\text{C}_{47}\text{H}_{44}\text{O}_{10}$ (M^+) 768.29, found 768.07.

Synthesis of Np-C. This compound was synthesized by the reaction of **Np-C-OH** with acetyl chloride using similar condition as the synthesis of **Np-C-Bp**. The isolated yield of the product was 40%. $^1\text{H-NMR}$ δ 8.1-7.4 (7H, m), 7.1-6.7 (6H, m), 5.3 (2H, s), 4.85 (2H, s), 4.65 (2H, s), 4.35-3.95 (16H, m), 2.05 (3H, s); HR-ESI-MS m/z : calcd for $\text{C}_{35}\text{H}_{38}\text{O}_9\text{Na}_1$ ($\text{M}+\text{Na}$) $^+$ 625.24, found 625.24, calcd for $\text{C}_{35}\text{H}_{38}\text{O}_9$ (M^+) 602.25, found 602.26.

Synthesis of Bp-C. **Bp-C** was prepared from **BHMBC** by two steps. Reaction of **BHMBC** with acetyl chloride produced **Acetyl-C-OH**. The resultant **Acetyl-C-OH** then reacted with benzoylbenzoyl chloride as in the case of synthesis of **Bp-C-Np**. $^1\text{H-NMR}$ δ 8.16-7.48 (9H, m), 7.1-6.7 (6H, m), 5.3 (4H, s), 4.35-3.95 (16H, m), 2.05 (3H, s); HR-ESI-MS m/z : calcd for $\text{C}_{38}\text{H}_{38}\text{O}_{11}\text{Na}_1$ ($\text{M}+\text{Na}$) $^+$ 693.23, found 693.24, calcd for $\text{C}_{38}\text{H}_{38}\text{O}_{11}$ (M^+) 670.24, found 670.25.

Acknowledgments

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