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# Energy Transfer Mechanism from BODIPY to o-Carborane via Through-Bond Channel

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2013년 10월 18일

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이 논문을 이학석사학위신청 논문으로 제출함.

2013년 10월

조 선 대 학 교 대 학 원

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# 박상하의 석사학위논문을 인준함



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#### Abstract

## Energy Transfer Mechanism from BODIPY to o-Carborane via Through-Bond Channel

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전자주개-스페이서-전자받개의 시리즈 세 묶음은 합성되어져왔고 충분히 특징지어져왔다. 전자주개와 전자받개 유닛 모두 boron dipyrromethene (BODIPY)염료로부터 만들어지지만, 그 들은 각각의 콘쥬게이션 길이에서 유사하고, 그것 때문에 서로 상당히 다른 광학적 특성을 제공한다.

이 시리즈의 안정한 특성은 각각의 서브유닛이 단색광에 의해 선택적으로 들뜬다는 것이다. 매우 효과적인 전기적 에너지 이동(EET)은 확장된 BODIPY를 기반으로 한 핵에서 그것의 대응 물질인 기존의 BODIPY염료에서 첫 번째로 들뜬 singlet 위치에서 발생하는데, 그러나 속도상 수는 이격거리에 따라서 비선형의 전개를 이끈다. 에너지 이동은 BODIPY-carborane 한 쌍에 있는 end-on BODIPY유닛의 입체구조에 따라 통제된다. 에너지 이동 과정은 고정된 입체구조 를 피하면서 전자주개 BODIPY와 전자받개 o-carborane 유닛 사이의 상호작용 결합을 통해 촉 진된다.

### 1. Introduction

o-Carborane has become a three-dimensional platform that can provide rich photochemistry when photo-active functional groups are placed at the carbon atom of the cage framework.<sup>1</sup> Diphenyl-o-carborane is a central photophysical motif and in particular, the conformation posed by the two diphenyl groups attached to o-carborane determines the electron accepting capability of this unit.<sup>2</sup> So torsional angle ( $\phi$ ) is a buoy determining energy transfer process. Chart 1 illustrates the conformational effect of the diphenyl groups of the o-carborane backbone. Keeping close to 90°, carborane can function as an effective electron acceptor.<sup>3</sup> Previous example represented by carbazole end-on donor further elaborates efficient energy transfer to the core rigid o-carborane backbone<sup>4</sup> as long as donor unit has conformational freedom. Within the rigid and efficient electron accepting diphenyl-o-carborane core,<sup>5</sup> two carbazolyl groups can rotate freely allowing successive energy transfer resulting in distinctive charge separation.<sup>6</sup>



Figure 1. Torsional angle ( $\phi$ ) determines electron accepting capability and when it reaches 90° it

Figure 1. Torsional angle ( $\phi$ ) determines electron accepting capability and when it reaches 90 it becomes rigid.

Thus, it has been established that free conformation of donor units is the key for the maximum energy transfer.<sup>7</sup> Also, for the motivation of the energy utilization, lower energy photosensitization<sup>8</sup> is much more challenging. To this end, chemically robust and easy prepared BODIPY units are to be the next agenda for synthesis and investigation for the energy transfer resorting finally to the o-carborane core.<sup>9</sup> For comparison of energy transfer efficiency, three types of BODIPY compounds were prepared as shown in Chart 2; one with o-carborane electron acceptor<sup>10</sup> and the other without o-carborane. Type 1 is reference BODIPY compounds with or without acetylene unit. Type 2 is di-substituted BODIPY compounds connected either by one or two acetylenic unit also serving

precursors to the cop responding o- carborane derivatives. Type 3 is the o-carborane based BODIPY dyads with or without internal acetylenic unit.



Figure 2. Three types of BODIPY compounds.

### 2. Results and Discussion

As shown in Scheme 1-3, all Compound symmetric and asymmetric formed PB-En-PB and PB-2En-PB was prepared by the decaborane and diethyl sulfide at elevator temperature 80 °C. All products were isolated by flash column chromatography, and showed the signals in their <sup>1</sup>H, <sup>13</sup>C, <sup>11</sup>B, and <sup>19</sup>F NMR spectra (Figure 7-14), respectively.



Scheme 1. Synthesis of PB and PB-En



Scheme 2. Synthesis of PB-En-PB and PB-2En-PB



Scheme 3. Synthesis of PB-CB and PB-En-CB

Photophysical properties of all complexes are summarized in Table 1. From the PL spectra, decrease of the BODIPY centered emission was noted when o-carborane unit is incorporated into the dyads. PB (1) gave higher BODIPY based fluorescence with QY (quantumyield) of 0.62 whereas weak electron acceptor acetylene unit PB-En (2) showed lowered QY of 0.54. Ongoing from Type 1 to Type 2, QY decrease to 0.41 due to the limitation of conformational freedom on BODIPY units exerted to each other, vide infra. Also, from the geometry optimization, it has been noted that BODIPY conformational flexibility is very important in controlling energy transfer.<sup>11</sup> Therefore, in order to avoid steric congestion created by the juxtaposition BODIPY units, longer separation between the two BODIPY units was devised and illustrated for PB-En-PB (3) and PB-2En-PB (4). It became clear that from the PL spectra when BODIPY fluorophores are engaged to the o-carborane reduced QY of 0.23 was observed. This is a clear indication that o-carborane functions as an electron acceptor and end-on BODIPY conformational flexibility governs the overall energy transfer process to the rigid o-carborane based photochemistry. Furthermore, while the room temperature emission life times of carborane functionalized complexes (5 and 6) are shorter than those of BODIPY compounds without o-carborane (1-4), at 77 K emission lifetimes become similar within the range of 10 ns. Thus, quenching process is dominant in emission relating to flexibility

of end-on BODIPY units and minimized with temperature.



**Figure 3.** X-ray structure of **6**. Hydrogen atoms are omitted for clarity, (30% probability for thermal ellipsoids).

To substantiate the structure-conformational flexibility issue, structure of the Asy-PB-CB (6) was established through X-ray crystallography and its structure is now shown in Figure 1. Structure of 6 reveals that the tortional angle ( $\phi$ ) of the one phenyl ring at the o-carborane gets close to 90° implying significant phenyl  $\pi^*$  and C-C  $\sigma^*$  orbital interactions.

PL spectrum of **6** now shows similar emission energy of the BODIPY origin, but significantly lower emission QY. BODIPY unit is fairly large compared to the o-carborane framework. Therefore, one can imagine much severe steric is imposed on the bis-BODIPY complex of **5**, which in turn accounts for the less depressed emission due to the insufficient energy transfer from BODIPY to the core o-carborane. All can be related to the structural rigidity arisen from the proximity location of the bulky two BODIPY units to the rigid environment of the

diphenyl-o-carborane framework. Figure S14 summary energies of HOMO and LUMO of the each BODIPY complexes studied. It is evident that HOMO and LUMO energies come from the BODIPY units regardless of the structural changes imposed on the base structure with or without o-carborane.

Comparing CV of **5** and **6**, from the reduction there are two peaks which can be identified one as BODIPY and the other as phenyl-o-carborane. The CV data of all compounds have similar oxidation and reduction potentials except for **5** and **6** being shown in successive BODIPY and o-carborane reduction peaks. Taking oxidation and reduction peaks with potentials, BODIPY units and o-carborane. Complying with energies from the CV data, steady-state photochemical data all fitted well to the BODIPY based transitions, having two distinctive absorptions belongs to the S1 and S2 excited states.



Figure 4. CV spectra of 5 and 6.

One critical issue that comes from the existence of the core o-carborane is that how much energy has been transferred from the BODIPY units and how efficiently that process has been undertaken. Moreover, for estimate Photo-Induced Electron Transfer (PET), the Rehm-Weller equation is calculated. The oxidation and reduction value is used in CV data and the  $E_{0.0}$  is

estimated by cross point between absorption and emission spectrum (~2.30 eV)  $w_p$  is supposed to very small value compare to oxidation/reduction potentials. The  $\Delta G^*$  of **1~5** is shows positive value (0.005~0.045). In case of **6**, although the  $\Delta G^*$  of **6** is negative value, it is too small (-0.055). according to Rehm-Weller calculation, the PET process is not available so the reduced emission of BODIPY is occurred by energy transfer not electron transfer.



Figure 5. Absorption and Emission spectrum of 5(black line) and 6(red line),  $\lambda_{ex} = 380$  nm.

Figure 3 shows UV and PL spectra of 5 and 6, and  $S1\rightarrow S0$  transition is distinctive yet  $S2\rightarrow S0$  transition is much suppressed. Also, for 6, higher energy transition is noted confirming the acetylenic absorption and excitation spectrum of 5 and 6 overlapped well to the absorption spectra indicating effective energy transfer is occurred from acetylene unit to the end-on BODIPY unit which means that the emissions of 5 and 6 are originated by  $S1\rightarrow S0$ .

Ground state electronic structures are much dependent on the BODIPY structure. Indeed, DFT calculations estimated HOMO and LUMO energies for **5** and **6**. In particular, the structure optimized for **6** is identical to that found in X-ray crystallography. HOMO and LUMO energies are virtually from BODIPY contribution only implying o-carborane not intervening LUMO stabilization which has been well established previously. These results conform well to the CV

data of **5** and **6** for HOMO and LUMO in oxidation and reduction, respectively. One thing remains to be investigated is that conformational flexibility driven by the two bulky BODIPY units with respect to the rigid core diphenyl-o-carborane backbone.

To determine the degree of the conformational flexibility, DFT calculations were performed on the angle dependence on the BODIPY groups and these results are now shown in the Figure 4. As can be seen from the angle dependence, **5** does not proceed all the way to 180° free rotation due to thesteric constraint forced on the rotational operation. However, **6** is conformationally flexible structure because two BODIPY units are now miss-matched not forcing steric constraint to each other. Figure 4 describes the angle dependent energies governed from LUMOs of **5** and **6**. Most distinctive difference is that **5** cannot optimize energies all the way through 180° whereas asymmetric thus off-tracked steric reduced **6** give rises to the maximum conformational stability in Figure 4(a). It is obvious to assume that o-carborane is well manifested as an efficient electron acceptor as long as rigid diphenyl-o-carborane unit is well reserved under the condition of the electronic energy transfer is well facilitated from the electron donating BODIPY units. These flexibility of the BODITY units on functionalized o-carborane makes the quenching pathway due to electron accepting ability of o-carborane, so the k<sub>nr</sub> is increased on Sy-PB-CB and Asy-PB-CB. Although the k<sub>rad</sub> of **5** and **6** is larger than (1) ~ (4), the Q. Y of **5** and **6** is lower than others due to large k<sub>nr</sub>.

(a)





**Figure 6.** (a) Theoretical calculations for energetically stabilized BODIPY orientations of Sy-PB-CB and Asy-PB-CB. (b) The LUMO of Sy-PB-CB and Asy-PB-CB depending on torsion angles of  $10^{\circ}$ ,  $60^{\circ}$ , and  $90^{\circ}$ 

#### 3. Experimentals

**General Procedures.** All manipulations were performed under a dry nitrogen atmosphere using standard Schlenk techniques or in a Vacuum Atmosphere Glovebox. Toluene, tetrahydrofuran (THF) and were hexane distilled under nitrogen from sodium/benzophenone. Dichloromethane was dried with CaH<sub>2</sub>. Other reagents were obtained commercially and used without further purification. Glassware, syringes, magnetic stirring bars, and needles were dried in a convection oven for overnight. Decaborane (B<sub>10</sub>H<sub>14</sub>) was purchased from KatChem and used after sublimation. The BODIPY-Eyn and BODIPY-2Eyn ligands were synthesized according to literature procedure. <sup>1</sup>All <sup>1</sup>H (400.1 MHz), <sup>13</sup>C (100.5 MHz), <sup>11</sup>B (128.4 MHz) and <sup>19</sup>F (376 MHz) NMR, respectively. <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts were measured relative to internal residual peaks from the lock solvent (99.9% CDCl<sub>3</sub>) and then referenced to Me<sub>4</sub>Si (0.00ppm). All <sup>11</sup>B NMR chemical shifts were referenced to BF<sub>3</sub>·O(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> (0.0 ppm) with a negative sign indicating an up-field shift. Elemental analyses were performed using a Carlo Erba Instruments CHNS-O EA1108 analyzer. All melting points were uncorrected.

**Synthesis** All compounds symmetric and asymmetric formed PB-En-PB and PB-2En-PB were prepared by the decaborane and diethyl sulfide at elevator temperature 80 °C. All products were isolated by flash column chromatography, and showed the signals in their <sup>1</sup>H, <sup>13</sup>C, <sup>11</sup>B and <sup>19</sup>F NMR spectra, respectively.

**Synthesis of Sy-PB-CB compound.** PB-En-PB (0.57 g, 0.73 mmol) and B<sub>10</sub>H<sub>12</sub>(SEt)<sub>2</sub> (0.17 g, 0.72 mmol) were dissolved in dry toluene (15 mL) and the resulting mixture was stirred under N<sub>2</sub> for 2 h at 40 °C and then overnight at 80 °C. The organic layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3×30 mL) and dried over magnesium sulfate. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography using CH<sub>2</sub>Cl<sub>2</sub>/hexane (1:1) as the eluent. **1** was obtained as a dark red powder (0.28 g, 43%). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.48-7.46 (d, J = 8.16 Hz, 4H), 7.08-7.06 (d, J = 7.96 Hz, 4H), 2.44 (s, 12 H), 2.15-2.09 (m, 8H), 1.02 (s, 12H), 0.81-0.76 (m, 12H). <sup>11</sup>B NMR (CDCl<sub>3</sub>): δ 0.54, -2.68, -7.21, -8.82. <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 154.7, 138.3, 137.8, 133.5, 131.9, 131.1, 130.4, 129.1, 129.0, 83.6, 17.2, 14.5, 12.7, 12.2. <sup>19</sup>F NMR (CDCl<sub>3</sub>) :  $\delta$  -145.7 (d, J = 32 Hz, BF<sub>2</sub>), -145.9 (d, J = 32 Hz, BF<sub>2</sub>). HRMS(FAB) calcd for C<sub>50</sub>H<sub>42</sub>B<sub>10</sub>N<sub>2</sub>: 778.9919. Found: 778.9907 [M]<sup>+</sup>. Anal. Calcd for C<sub>50</sub>H<sub>42</sub>B<sub>10</sub>N<sub>2</sub>: C, 77.09; H, 5.43; B, 13.88; N, 3.60. Found: C, 77.04; H, 5.42; N, 3.58.

Synthesis of Asy-PB-CB compound. A procedure analogous to that used for the preparation of Sy-PB-CB was used, starting material BP-2En-BP (1.35 g, 1.67 mmol) and B<sub>10</sub>H<sub>12</sub>(SEt)<sub>2</sub> (0.48 g, 2.0 mmol) was obtained as a deep red powder (0.78 g, 51%). <sup>1</sup>H NMR (CDCl3):  $\delta$  7.85-7.83 (d, J = 7.96 Hz, 2H), 7.31-7.30 (d, J = 7.12 Hz, 3H), 7.18-7.16 (d, J = 8.72 Hz, 1H), 7.16-7.14 (d, J = 7.76 Hz, 2H), 2.44 (s, 12 H), 2.22-2.11 (m, 8H), 1.12 (s, 6H), 1.11 (s, 6H), 0.92-0.82 (m, 12H). <sup>11</sup>B NMR (CDCl3):  $\delta$  0.59, -3.34. -9.46. <sup>13</sup>C NMR (CDCl3):  $\delta$  154.6, 138.7, 138.3, 138.1, 138.0, 137.8, 133.3, 133.0, 132.2, 131.7, 130.4, 129.0, 128.9, 120.4, 84.0, 82.9, 82.0, 77.4, 69.2, 17.3, 17.2, 14.8, 14.7, 12.7, 12.1, 12.0. <sup>19</sup>F NMR (CDCl3):  $\delta$  -145.6 (d, J = 36 Hz, BF2), -145.8 (d, J = 32 Hz, BF2). HRMS(FAB) calcd for C<sub>50</sub>H<sub>42</sub>B<sub>10</sub>N<sub>2</sub>: 778.9919. Found: 778.9907 [M]+. Anal. Calcd for C<sub>50</sub>H<sub>42</sub>B<sub>10</sub>N<sub>2</sub>: C, 77.09; H, 5.43; B, 13.88; N, 3.60. Found: C, 77.04; H, 5.42; N, 3.58.

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Figure 8. <sup>13</sup>C-NMR spectrum of Sy-PB-CB



Figure 9. <sup>11</sup>B-NMR spectrum of Sy-PB-CB.



Figure 10. <sup>19</sup>F-NMR spectrum of SyPB-CB.









Figure 14. <sup>19</sup>F-NMR spectrum of Asy-PB-CB.

Table 1. Crystal data and structure refinement for Asy-PB-CB.

Empirical formula	$C_{51}H_{59}B_{12}C_{12}F_4N_4$
Formula weight	1004.64
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, P 21/n
Unit cell dimensions	$a = 12.955(2)$ Å $\alpha = 90^{\circ}$
	$b = 16.894(3)$ Å $\beta = 100.016(4)$ °
	$c = 25.673(5)$ Å $\gamma = 90^{\circ}$
Volume	5533.0(17) Å <sup>3</sup>
Z, Calculated density	4, 1.206 Mg/m <sup>3</sup>
Absorption coefficient (m)	0.169 mm <sup>-1</sup>
<i>F</i> (000)	2092
Crystal size	0.3 x 0.15 x 0.15 mm
range for data collection	1.61 to 28.41°
Limiting indices	$-17 \le h \le 17, -22 \le k \le 22, -34 \le l \le 33$
Reflections collected / unique	$56353 / 13834 [R_{int} = 0.0439]$
Completeness to $\theta = 28.41$	99.4%
Refinement method	Full-matrix least-squares on $F^2$
Data / restraints / parameters	13834 / 0 / 686
Goodness-of-fit on $F^2$	1.005
Final R indices $[I > 2s (I)]$	$R_1 = 0.0814, \ wR_2 = 0.2338$
R indices (all data)	$R_1 = 0.1441, \ wR_2 = 0.2927$
Largest diff. peak and hole	1.161 and -0.789 e. Å <sup>-3</sup>

<sup>a</sup> $R_1 = a ||F_0| - |F_c||$  (based on reflections with  $F_0^2 > 2sF^2$ ), <sup>b</sup> $wR_2 = [a [w(F_0^2 - F_c^2)^2]/a [w(F_0^2)^2]]^{1/2}; w = 1/[s^2(F_0^2) + (0.095P)^2]; P = [max(F_0^2, 0) + 2F_c^2]/3 (also with <math>F_0^2 > 2sF^2$ )



Figure 15. Absorption(left) and Emission(right) spectrum of complexes in CH<sub>2</sub>Cl<sub>2</sub>(10mM)



Figure 16. Fluorescence decay profiles for complexes in CH<sub>2</sub>Cl<sub>2</sub>atroomtemperatureexcitedat408nm.



Figure 17. Low temperature (77K) emission spectrum in MeTHF excited at 355 nm.



Figure 18. Cyclic voltammograms of complexes taken at a sweep rate of 0.1 V/s for 0.5 mM  $CH_2Cl_2$  solution containing 0.1 M TBAP.