



2014년 2월 석사학위 논문

Carborane Dyads for Photo-Induced Electron Transfer Process

Photophysical Studies on Carbazole and Phenyl-o-Carborane Molecular Assemblies

조 선 대 학 교 대 학 원 화 학 과 김 소 연

Carborane Dyads for Photo-Induced Electron Transfer Process

Photophysical Studies on Carbazole and Phenyl-o-Carborane Molecular Assemblies

2014년 2월 25일

조 선 대 학 교 대 학 원 화 학 과 김 소 연

Carborane Dyads for Photo-Induced Electron Transfer Process

Photophysical Studies on Carbazole and Phenyl-o-Carborane Molecular Assemblies

지도교수 이 종 대

이 논문을 이학석사학위신청 논문으로 제출함. 2013년 10월

> 조 선 대 학 교 대 학 원 화 학 과 김 소 연

조선대학교 대학원

2013년 11월

위	원	조선대학교	교수	이 종 대	(인)
위	원	조선대학교	교수	임 종 국	(인)

위원장 조선대학교 교수 류설 (인)

김소연의 석사학위논문을 인준함

TABLE OF CONTENTS

TABLE OF CONTENTS	i
LIST OF FIGURES	iii
LIST OF TABLE	iv
LIST OF CHART	iv
LIST OF SCHEME	iv
ABSTRACT	V

Carborane Dyads for Photo-Induced Electron Transfer Process

1.	Introduction	7
2.	Results and Discussion	9
2.1.	Results	9
2.1.1.	Synthesis	9
2.1.2.	Steady-state photophysical properties	9
2.1.3.	Excited State properties	14
2.1.4.	Electrochemical properties	18
2.1.5.	Intermolecular properties	18
2.1.6.	DFT Calculations	19
2.2.	Discussion	20

3.	Conclusions	22
4.	Experimental Section	23
4.1.	General Procedures	23
4.2.	Synthesis of 1	23
4.3.	Synthesis of 2	24
4.4.	Synthesis of 3	24
4.5.	Synthesis of 4	25
4.6.	Fluorescence Lifetime	25
4.7.	Transient Absorption Spectroscopy	25
4.8.	Cyclic voltammetry and Spectroelectrochemistry	26
4.9.	Density Functional Calculations	26
5.	Reference	27

LIST OF FIGURES

- Figure 1 (a) UV-Vis absorption and normalized photoluminescence (PL) spectra of carborane molecules(b) Normalized PL spectra of 1 in various solvents at room temperature , respectively.
- Figure 2 Emission decay profile of 1 in various solvent(a) ~360nm region(b) longer wavelengths rather than 531 nm.
- Figure 3 Lippert-Mataga plots for charge transfer emissions of 1 (black circles) and 2 (red circles) in n-hexane (1), cyclohexane (2), ethylether (3), THF (4) and CH2Cl2 (5).
- Figure 4 Transient absorption spectra of 1 (a) and 2 (b) in Ar-purged CH2Cl2 obtained at a 10 ns-delay after 355 nm laser excitation.
- Figure 5 SEC spectra of 1 and 2 taken by electrolysis at -2.1 V of 1 (a) and 2 (b).
- Figure 6 DFT calculation results for 1
- Figure 7 DFT calculation results for 2
- Figure 8 Schematic energy diagram for [Cz]-[Ph-Cab].

LIST OF TABLES

 Table 1
 Photophysical Properties of the Cb Compounds

 Table 2
 Oxidation and Reduction Potentials of Carborane Compounds

LIST OF CHART

Chart 1 Carborane based donor-acceptor-donor triad and donor- acceptor dyad.

LIST OF SCHEME

Scheme 1 Synthetic routes for Cz-linked carborane compounds.

Carborane Dyads for Photo-Induced Electron Transfer Process

:Photophysical Studies on Carbazole and Phenyl-o-Carborane Molecular Assemblies

Kim So Yeun

Advisor : Prof. Lee Jong Dae, Ph.D, Department of Chemistry, Graduate School of Chosun University

o-carboranyl phenyl 단위와 N-carbazole (1) 또는 4-phenyl-N-carbazole (2)을 결 합하는 주개-받개 이합체를 기반으로 한 o-Carborane과 이들의 특성은 정류 상태의 광화학과 광역학적 실험들 뿐만 아니라 전기 화학 연구에 의해 잘 나타났다. 이합체 의 흡수와 전기화학적 성질들은 기본적으로 바닥상태에서 카바졸과 오쏘 카보란 단위 사이에 무시할 정도의 상호작용을 가리키는 카바졸과 페닐 오쏘 카보란 단위의 합이 다. 하지만 1 과 2의 방출 스펙트럼들은 카바졸 형광이 효과적으로 꺼지고 새로운 전 하전달(CT) 방출이 헥산에서 아세토나이트릴까지 변화하는 다양한 용매에서 큰 stoke 를 보여준다는 것을 관찰했다. 더욱이 이합체를 기본으로한 오쏘 카보란의 CT 방출 성질들은 들뜬 상태에서 (Cz)⁺(Ph-o-Cb)⁻의 전하 분리된 종을 형성하는 전하분리 단 위를 발생시키는 것을 Lippert-Mataga plot에 의해 더 분석하였다. 이 들뜬 상태는 분광전기화학(SEC)측정과 nanosecond trasient 흡수 스펙트럼에 의해 확인되었다; 카 된 라디칼 양이온과 음이온인 CT 상태를 발생시킨다. DFT 계산은 줄어든 음이온 상태 의 Ph-o-Cb 분자의 HSOMO의 국한된 수를 보여줌으로써 이 CT 종들을 잘 입증시킨다. 결론적으로 분자 조립은 페닐렌 또는 다중 페닐렌으로 분자내 방법에서 광 유발 전자 전달 과정을 밝혀내어 카바졸 그룹과 오쏘 카보란 뭉치를 연결시켜 형성되었다.

1. Introduction

Since discovery of borane and carborane clusters.¹ relentless effort has been made to understand their electronic structures² due to their unique cage structures.³ However, there have been few investigations on the excited-state properties and photochemical behavior of carborane compounds,⁴ probably because the parent carboranes or their derivatives with no π -substituent reveal little or no absorption at > 250 nm and hardly any emission. Even for their π -substituted derivatives, no detailed investigations have been made, particularly into how the carborane cage affects their excited-state behavior.⁵ Recently, a limited number of reports appeared on the unique fluorescence of the polymers containing 1.2-diaryl-substituted ortho-carborane (o-Cb) units, which was inferred from their aggregation-induced emission⁶ and charge transfer.⁷ However, no detailed analysis has been performed on the electronic nature of the fluorescence from the o-Cb unit or the possible roles of the o-Cb.⁸ Also, detailed investigation by which o-Cb cage functions as the most critical electronic alteration in the donor-acceptor systems, i.e. in the light driven charge separated bifunctional molecules, has never been properly carried out. Recently, we report the excited property of 1,2-diphenyl-o-carborane in that the o-Cb becomes an electron accepting unit when it is bonded to the diphenyl groups through the two carbon atoms of the o-Cb. Employing donor functional units to each end of the diphenyl groups of the o-Cb established the formation of the desired dyad. However, only single electron transfer event was observed even with presence of two electron donors as shown in the structure of D-A-D triad. (Chart 1) Closo-type o-Cb is known to transform to the corresponding nido-structure by two electron reduction process, and thus two electron transfers from each donor end could be facilitated at the expense of structural change of o-Cb. However, the photo-induced electron transfer

(PET) process carries single electron transfer in the carborane based D-A-D triad. ⁹

Given the fact that two donors only carried single electron transfer event, designing an 1:1 donor-acceptor assembly shown in D-A dyad and confirming the desired dyad characteristics are prime reasons of this study. Cz and o-Cb units are chemically bonded through phenyl and biphenyl linker to give 1-(4-(N-carbazolyl)phenyl)- ortho-carborane (1) and 1-(4,4'-(N-carbazolyl)biphenyl)-ortho-carborane (2), respectively. (see Chart 1) For

comparison, m- and p-carborane counterparts of 1-(4-(N-carbazolyl)phenyl)-meta-carborane (**3**) and 1-(4-(N-carbazolyl) phenyl)-para-carborane (**4**) are prepared as well. Steady-state photochemical data provide direct evidence of dyad formation between Cz and Ph-o-Cb showing a red-shifted charge-transfer (CT) band at around 510 nm. Interpretation of solvent dependent CT emission and prediction of the electron transfer by thermodynamic estimation provided a ground for the stable dyad formation. Furthermore, nanosecond transient absorption spectra and spectroelectrochemical (SEC) measurement confirmed the formation of cationic and anionic radicals at the Cz and the Ph-o-Cb centers, respectively, based on the peak analysis; from prolonged electrolysis and transient absorption spectra, 400 nm and 820 nm peaks were assigned to the radical anion, Ph-o-Cab⁺⁻ and the radical cation, Cz⁺⁺, respectively.



Chart 1. Carborane based donor-acceptor-donor triad and donor-acceptor dyad.

2. Results and Discussion

2.1. Results

2.1.1. Synthesis.

As shown in **Scheme 1**, all Cz-linked carborane compounds were synthesized from ortho-, meta-, and para-carboranes using Ulmann type coupling reactions in morderate yields. Compound **1**, **2**, **3**, and **4**, where 4-(N-carbazolyl)phenyl or 4,4'-(N-carbazolyl) biphenyl was directly linked to the carbon atom in the carborane clusters, were prepared in a single step in 30-42% yields via the coupling reaction of 1 equiv of 9-(4-bromophenyl)carbazole or 9-(4'-bromobiphenyl-4-yl)carbazole with the lithium salt of o-carborane, m-carborane, or p-carborane, in the presence of copper (I) halides. The details of these syntheses are given in the experimental section. All products were isolated by flash column chromatography and further purified by train sublimation. The formation of carbazolylphenyl-o-carborane compounds was confirmed by high- resolution mass spectrometry and elemental analyses. The compounds showed the expected signals in their ¹H and ¹³C and ¹¹B NMR spectra for the characteristic carbazole and carborane groups.



Scheme 1. Synthetic routes for Cz-linked carborane compounds.

2.1.2. Steady-state photophysical properties.

Figure 1 shows the emission spectra of Cz-linked carboranes (1-4) in various solvents upon excitation at 309 nm and three characteristic emission bands are observed. o-Cb does not exhibit any absorption band in the UV/Vis region. Therefore, upon irradiation in this wavelength region, the observed fluorescence around 360 nm is due to carbazole moieties

in the singlet excited state¹⁰ and there is no excimer emission around 420 nm region¹¹ due to the mono-substitution effects.



Figure 1. (a) UV-Vis absorption and normalized photoluminescence (PL) spectra of carborane molecules (10 μ M in hexane, at room temperature). (Inset: photograph of the molecular solution in hexane under a 350 nm hand UV lamp) (b) Normalized PL spectra

of 1 in various solvents at room temperature (excited at 309 nm), respectively.

It is noteworthy that markedly red-shifted emission bands are observed at longer wavelengths rather than 531 nm. Tentatively, red-shifted emission may be attributed to the photo-induced charge transfer (PCT) state between Cz and o-Cb. This emission showed the strong dependence on the polarity of solvent. The emission maximum shifted to longer wavelength from 531 nm in n-hexane to 696 nm in CH_2Cl_2 . On the other hand, the emission for Cz showed the red-shift of 5 nm from 360 nm with increase of solvent polarity.

Ch) (mm) [a] ^{a,b}	λ_{em}	Stokes	- (na) ^{a,c}	ъd
CU	λ_{abs} (IIII) [8]	(nm) ^a	shift(nm)	$t_{\rm F}$ (ns)	$\Psi_{ m F}$
1	291 [25739], 316 [22485], 335 [10766]	365,	20/248	0.07/0.11	0.06/0.07
		583	50/248	0.07/0.11	0.00/0.07
2	201 [25720] 226 [22495] 229 [1076]	368,	30/215	0 12/0 21	0.09/0.04
	291 [23739], 320 [22463], 336 [10700]	553		0.12/0.21	
3	202 [25720] 224 [22405] 220 [107(()	350,	12	4.51	0.22
	295 [25759], 524 [22465], 556 [10700]	362		4.31	0.55
4	202 [25720] 200 [22405] 220 [10766]	349,	12	0.26	0.22
	295 [25759], 508 [22485], 559 [10/00]	361		9.30	0.32

Table 1. Photophysical Properties of the Cb Compounds

^aMeasured in Ar-saturated hexane solution (10 μ M) at room temperature. ^bMolar extinction coefficient (ϵ , M⁻¹ cm⁻¹). ^cTaken by excitation at 309 nm. For lifetimes monitored at different wavelengths. ^dRelative to 9,10-diphenylanthracene or rhodamine B as standards.



Figure 2. Emission decay profile of 1 in various solvent (a) \sim 360nm region (b) longer wavelengths rather than 531 nm. (Excitation wavelength is 309 nm)

The PCT emissions showed outstanding solvatochromic properties. The solvent-polarity effect can be analyzed in terms of difference in the dipole moments in the ground and excited states, and it has been found that the larger dipole-moment change causes larger

peak shift. This phenomenon can be analyzed by a Lippert-Mataga plot, which is essentially a plot of the Stokes' shift of the fluorescence emission versus the solvent polarity. The Mataga-Lippert equation for the solvatochromic shifts is expressed as follows:

$$\overline{v}_a - \overline{v}_f = \frac{2(\mu_e - \mu_g)^2}{hca^3} \Delta f, \qquad \Delta f = \left(\frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}\right)$$

where μ_e and μ_g are the dipole moments in the excited and ground states, respectively, *c* is the velocity of light, *h* is Plank's constant, and *a* is the radius of the Onsager cavity around the fluorophore. The solvent dielectric constant (ε) and refraction index (*n*) are included in the term, Δf . The Onsager radius was calculated from the optimized structure obtained by a DFT calculation using B3LYP/6-31G(d,p) method. The Onsager radius (7.25 Å) was taken as half of the longest diameter of **1**. As shown in **Figure 3**, the Stokes shift of a series of solvent polarity changes linearly against the Δf , from which increases in the dipole moments ($\Delta \mu$) of 28.0 D for photoinduced charge-transfer complex were estimated. Since the dipole moment (μ_g) in ground state was established of 4.5 D by the theoretical calculation,¹² the dipole moment (μ_e) in excited state is 32.5 D. Since 4.8 D is the dipole moment of 32.5 D is thus comparable to a unit charge separation of 6.77 Å, which is a distance comparable to the distance between carbazole nitrogen atom and o-carborane carbon atom. Therefore, we may hypothesize that the intramolecular PET process takes place from Cz to the C-C bond of Cb. In case of **1**,

the dipole moment was determined as 31.0 D.



Figure 3. Lippert-Mataga plots for charge transfer emissions of 1 (black circles) and 2 (red circles) in n-hexane (1), cyclohexane (2), ethylether (3), THF (4) and CH_2Cl_2 (5).

2.1.3. Excited State properties.

In order to prove the occurrence of PET process in **1** and **2**, the laser flash photolysis was carried out. Transient absorption spectra of **1** and **2** were measured in Ar-saturated CH_2Cl_2 upon 355 nm laser excitation as shown in **Figure 4**. The spectra contain a band centered at 838 nm. It is well known that Cz^{++} have a transient absorption band around 800 nm.¹³ In view of the absence of an absorption band of o-Cb in the UV above 200 nm, 355 nm laser excitation has allowed the excitation of Cz-ph moiety. The PET process from either the singlet or triplet excited state Cz leads to the formation of carbazole radical cation (Cz⁺⁺) and acceptor radical anions (o-Cb⁺⁻).¹⁴ The decay times from both (Cz)-Phn-o-Cb monitored at 830 nm are few nanoseconds, which indicate the charge recombination (CR) time between Cz⁺⁺ and Cb⁺⁻.







Figure 4. Transient absorption spectra of 1 (a) and 2 (b) in Ar-purged CH_2Cl_2 obtained at a 10 ns-delay after 355 nm laser excitation.

To provide explicit evidence for the above arguments based on the Mataga-Lippert plots, we conducted laser-flash photolysis experiments for **1** and **2**. As shown in **Figure 4**, two characteristic absorptions appeared at 400 and 830 nm upon irradiation of laser pulses at 355 nm. Both the 400 and 830 nm transients decayed commonly within a few nanoseconds, roughly in accord with the observed CT emission lifetime. Therefore, the transient spectrum must be due to the excited state of **1**. The 830 nm transient can be attributed to the radical cation of the Cz unit (Cz⁺⁺), because the radical cations of various carbazole compounds generally show characteristic absorptions at ~800 nm. In order to assign the 400 nm bands, spectroelectrochemical (SEC) measurements were performed for **1** under constant-voltage conditions at 1.8 V, a potential corresponding to the one-electron reduction of **1**. As shown in **Figure 5**, a 400 nm peak appeared under keeping the spectral shape after prolonged electrolysis, being thus assignable as the spectrum of the radical anion of 1 (1⁺). It should be noted that this absorption is closely related to the spectrum reported for the radical anion of 1-phenyl-o-Cab (Ph-o-Cab⁺).



Figure 5. SEC spectra of 1 and 2 taken by electrolysis at -2.1 V of 1 (a) and 2 (b). (Inset: anionic state carborane geometry and HSOMO obtain by DFT caluclation.)

These spectroscopic observations strongly indicate that the excited state of **1** is a charge-separated state consisting of the carbazole radical cation (Cz^{+}) and the acceptor radical anion (Ph-o-Cab⁺), an assignment in accord with the arguments based on the Mataga-Lippert plots. This assignment is again in line with the TD-DFT calculation results which show the localized populations of the highest singly-occupied molecular orbital (HSOMO) on the Cz unit in the oxidized cationic state and on the Ph-o-Cab moiety in the reduced anionic state.

The CT emissions of all compounds reveal similar solvent-dependent behavior, such that increasing the solvent polarity decreases their intensity to virtually nil in acetonitrile, whereas the lifetime is initially lengthened to a maximum in toluene and then shortened as the solvent polarity is further increased. This behavior might be interpreted in terms of the solvation-induced electronic changes of the CT state, which would lead to different solvent dependences of the radiative and non-radiative rate constants.¹⁵ This means that the CT state is not formed instantaneously upon the excitation of the Cz chromophore, but by way of the excited-singlet Cz ($^{1}Cz^{*}$). If this is the case, the rate constant for the formation of the CT state estimated from the Cz fluorescence lifetime of 1 (120 ± 10 ps) is $\sim 8'10^{9}$ s⁻¹, which is not far from the value for electron transfer over a distance of ~ 7 Å with a driving force of ~ 1 eV.

2.1.4. Electrochemical properties.

The electrochemical properties of carboranes were examined by cyclic voltammetry (CV). **Table 2** summarizes the CV results, which were obtained in CH₂Cl₂ containing 0.1 M tetrabutylammonium perchlorate (TBAP) at a scan rate of 0.1 Vs⁻¹. All scans are shown in **Figure 4**. The potential values of the first redox wave in both the positive and negative directions represent E_{ox} and E_{red} , respectively. All carboranes exhibited reversible oxidation peaks. Moreover, a distinct cathodic reduction process was recorded when the electrode potential was swept continuously between 0.0 and -2.5 V.

Entry	oxidation (V vs SCE)				reduction (V vs SCE)					
Liitti y	E_{pa1}	$E_{\rm pa2}$	E_{pc1}	E_{pc2}	$E_{\text{onset}}^{\text{ox}}$	E_{pa1}	E_{pa2}	E_{pc1}	E_{pc2}	$E_{1/2}^{red}$
1	0.76	- ^[b]	0.68	0.45	0.72	-1.75	-1.81	-2.01	- ^[b]	-1.88
2	0.75	- ^[b]	0.67	0.44	0.71	-1.63	-1.72	-1.95	- ^[b]	-1.79
3	0.77	- ^[b]	0.69	0.47	0.73	-	-	-	-	-
4	0.75	- ^[b]	0.66	0.46	0.72	-	-	-	-	-

Table 2. Oxidation and Reduction Potentials of Carborane Compounds^[a]

^[a]CVs were recorded at room temperature in Ar purged CH₂Cl₂/0.1 M TBAP. ^[b]Not observed.

2.1.5. Intermolecular properties.

To confirm the intermolecular behavior of compounds, the quenching of 9-ethylcarbazole (EtCz) fluorescence by Ph-o-Cb was performed. The unique excited behavior of the o-Cb compounds reported herein implies the existence of unusual effects of the o-Cb cage on the electronic systems. While the parent o-Cb is completely inert under the usual photochemical and electrochemical conditions, the bonding of the π -electronic system (i.e. the phenyl group) with one or two of the carbon atoms of o-Cb causes a drastic change in its electronic nature, making the molecule an efficient electron acceptor.¹⁶

As shown in **Figure S1**, we confirmed that Ph-o-Cb quenches the fluorescence of EtCz at a diffusion-controlled rate, an observation in accord with the extensive quenching of the carbazole fluorescence observed with 1-4. However, the intermolecular fluorescence quenching is not accompanied by any new emission, indicating that the emission from the CT state would require a structure favorable for electronic coupling between the positively and negatively charged units.

2.1.6. DFT Calculations.

Figure 6-7 shows the optimized structures of complexes. We undertook DFT calculations to see whether 1) the frontier orbitals are located on different parts of the molecule in 1 and on the same part of the molecule in 3 and 4, so that new emission could be explained by a charge-transfer state; and whether 2) the key role of the carboranyl fragment can be ascertained in this luminescent process.



Figure 6. DFT calculation results for **1**; energy levels and isodensity plots for HOMO-LUMOs.

In the ground state, theoretical calculations using the DFT at the B3LYP/6-31G(d,p) level of theory with Gaussian 09 were used and the DFT calculated results show that the structure of 4-((N-carbazolyl)phenyl (D) does not suffer appreciable variations with the different carborane cores (A). Whenever possible, optimized calculated geometries were compared to experimental ones, and only minor discrepancies were found for the bond lengths. The electronic ground states of 1-4 were studied by examining the molecular orbital energy levels for each compound. The contributions for each isolated subunit and MO energies are collected in **Figure 6** and **Figure 7**.



Figure 7. DFT calculation results for **2**; energy levels and isodensity plots for HOMO-LUMOs.

2.2. Discussion

The experimental results shown above clearly indicate that activated processes are responsible for the quenching of carbazole fluorescence. The transient absorption experiments demonstrate that the activated process involved in the fluorescence quenching is PET from the Cz to Ph-o-Cb. For the quenching of carbazole fluorescence, it is reasonable to assume the participation of PET from ${}^{1}Cz^{*}$ to the Ph-o-Cb, although attempts failed to observe the formation of Cz^{*+} and Ph-o-Cb⁻⁻ after irradiation at 309 nm laser pulses. This is because the laser intensity at 309 nm in our setup is too low to allow reliable detection of transient species.

In order to confirm the feasibility of the PET mechanism in the excited states of the carboranes, we evaluated the driving forces (ΔG_{PET}) for the PET processes based on the Rhem-Weller equation using the oxidation potential of the Cz ($E_{ox}(Cz^{*+/0}) = 0.89$ V vs. Fc⁺/Fc), the reduction potential of the Ph-o-Cb ($E_{red}(Ph-o-Cb^{0/-}) = -2.26(1)$, -2.17(2) V vs. Fc⁺/Fc) for 1 and 2, respectively, and the excitation energies of ${}^{1}Cz^{*}$ ($E_{0\in \mathcal{D}0}(Cz) = 3.54$ eV). The coulomb terms in ΔG_{PET} are assumed to be negligibly small (≤ 30 meV). The ΔG_{PET} value calculated for the PET process from ${}^{1}Cz^{*}$ to Ph-o-Cb is highly negative

(-0.42(1), -0.48(2) eV) for **1** and **2**, respectively. The large k_f^q values might arise from the high driving force ($\Delta G_{PET} = -1.5 \text{ eV}$) close to the solvent reorganization energy.



Figure 8. Schematic energy diagram for [Cz]-[Ph-Cab]. CR indicates the charge recombination.

The k_f^q values are different between 1 and 2, probably reflecting the distance dependences of the PET processes. According to the energy minimized geometries of 1 and 2 obtained by the semi-empirical PM3 method, the average distances between the carbazole and carborane parts were estimated to be ~12 Å for 1 and ~16 Å for 2, a difference that can give an appreciable effect on the PET processes. It should be, however, stressed that the estimated distances are only intuitive for an understanding of the distance dependences of k_f^q and k_p^q . It appears that the k_f^q values are unusually large for the "long-range" PET with a distance exceeding 10 Å.

3. Conclusions

New types o-carborane based donor-acceptor dyad complexes were prepared and their unique photophysical properties were studied to show that facile photo-induced electron transfer (PET) process occurred in intramolecular manner. The notable observation is that the spectroscopic and electrochemical properties of the dyads are essentially the sum of their constituent chromophores, indicating negligible interaction of the constituent chromophores in the ground state between carbazole and o-carborane unit. However, emission studies show a dramatically quenching of carbazole fluorescence and appear unique charge transfer emission. Accordingly, we confirmed that Ph-o-Cb quenches the fluorescence of carbazole at a diffusion-controlled rate, an observation in accord with the extensive quenching of the carbazole fluorescence. However, the intermolecular fluorescence quenching is not accompanied by any new emission, indicating that the emission from the CT state would require a structure favorable for electronic coupling between the positively and negatively charged units.

4. Experimental Section

4.1. General Procedures.

All manipulations were performed under a dry nitrogen or argon atmosphere using standard Schlenk techniques. Ethylene glycol dimethyl ether (DME) and toluene were distilled under nitrogen from sodium/benzophenone. The elemental analyses were performed using a Carlo Erba Instruments CHNS-O EA 1108 analyzer. High Resolution Tandem Mass Spectrometry (Jeol LTD JMS-HX 110/110A) was performed at the Korean Basic Science Institute (Seoul). The ¹H, ¹¹B, and ¹³C NMR spectra were recorded on a Varian Mercury 300 spectrometer operating at 300.1, 96.3, and 75.4 MHz, respectively. All ¹¹B chemical shifts were referenced to BF₃·O(C_2H_5)₂ (0.0 ppm) with a negative sign indicating an up-field shift. All proton and carbon chemical shifts were measured relative to the internal residual CHCl₃ from the lock solvent (99.9% CDCl₃). The absorption and photoluminescence spectra were recorded on a SHIMADZU UV-3101PC UV-VIS-NIR scanning spectrophotometer and a VARIAN Cary Eclipse fluorescence spectrophotometer, respectively. The fluorescence lifetimes were measured by a time correlated single photon counting spectrometer. The emission quantum yields (Φ PL) of the carborane compounds were calculated by means of the comparative method of William1 for samples of five different concentrations (1 μ M \sim 5 μ M) using 9,10-diphenylanthracene (Φ PL = 0.95) and Rhodamine B (Φ PL = 1.00) as a reference standard. o-Carborane, m-carborane, p-carborane, carbazole, N,N-dimethylaniline, 1,1'-bis(diphenylphosphino)ferrocene (dppf), and all other reagents were purchased and used as received. 9-(4-bromophenyl)carbazole and 9-(4'-bromobiphenyl-4-yl)carbazole were prepared using the methods reported in the literature.

4.2. Synthesis of 1.

9-(4-bromophenyl)carbazole and o-carborane were coupled using the literature protocol. A solution of o-carborane (1.44 g, 10 mmol) in 15 mL of dry DME was added dropwise to a 2.5 M solution of n-BuLi in n-hexane (4.2 mL, 10.5 mmol) at -5 °C under N₂. The mixture was stirred for 30 min, then dry CuCl (1.1 g, 11.1 mmol) was added in one portion, and the final mixture was stirred at room temperature for 1 h. Pyridine (6 mL) and 9-(4-bromophenyl)carbazole (3.86 g, 12 mmol) were added in one portion and the

resulting mixture was refluxed for 16 hours. After the removal of the solvent with a rotary evaporator under reduced pressure, the residue was diluted with water and extracted with CH₂Cl₂. The combined organic layer was dried over anhydrous MgSO₄ and filtered. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography using CH₂Cl₂/hexane (1:4) as the eluent. **1** was obtained as a white powder (0.89 g, 23%) and further purified by train sublimation in 79% yield. ¹H NMR (CDCl₃): δ 8.14 (d, 2H), 7.81 (d, 2H), 7.63 (d, 2H), 7.50 (d, 2H), 7.41 (t, 2H), 7.25 (t, 2H). 3.98 (s, 1H), 3.72-1.60 (br, 10H, B-H).¹¹B NMR(CDCl₃): δ -2.5, -8.80, -9.85, -13.3. ¹³C NMR (CDCl₃): δ 141.1, 139.7, 138.3, 134.6, 126.2, 125.7, 123.4, 120.3, 120.0, 110.1, 61.0, 78.3. HRMS(FAB) calcd for C₂₀H₂₃B₁₀N: 385.5133. Found: 385.5127 [M]⁺. Anal. Calcd for C₂₀H₂₃B₁₀N: C, 62.31; H, 6.01; N, 3.63. Found: C, 62.29; H, 6.00; N, 3.61.

4.3. Synthesis of 2.

A procedure analogous to that used for the preparation of **1** was used, but instead starting from 9-(4'-bromobiphenyl-4-yl)carbazole (4.78 g, 12 mmol). **2** was obtained as a white powder (1.47 g, 32%) and further purified by train sublimation in 71% yield. ¹H NMR (CDCl₃): δ 8.16 (d, 2H), 7.78 (d, 2H), 7.68-7.60 (m, 6H), 7.49-7.40 (m, 4H), 7.31 (t, 2H),

4.02 (s, 1H). 3.82-1.61 (br, 10H, B-H). ¹¹B NMR(CDCl₃): δ -8.4, -15.2, -17.3. ¹³C NMR (CDCl₃): δ 141.2, 136.8, 136.5, 136.1, 136.0, 135.7, 134.7, 134.1, 126.1, 125.9, 122.3, 121.1, 120.2, 111.1, 79.8. HRMS(FAB) calcd for C₂₆H₂₇B₁₀N: 461.6093. Found: 461.6088 [M]⁺. Anal. Calcd for C₂₆H₂₇B₁₀N: C, 67.65; H, 5.43; B, 23.42; N, 3.03. Found: C, 67.50; H, 5.40; N, 2.99.

4.4. Synthesis of 3.

A procedure analogous to that used for the preparation of **1** was used, but instead starting from m-carborane. **3** was obtained as a white powder (0.89 g, 23%) and further purified by train sublimation in 51% yield. ¹H NMR (CDCl₃): δ 8.14 (d, 2H), 7.71 (d, 2H), 7.56 (d, 2H), 7.43 (d, 4H), 7.33 (m, 2H), 4.03 (s, 1H), 3.72-1.60 (br, 10H, B-H).¹¹B NMR(CDCl₃): δ -7.34, -8.91, -14.41, -16.05, -17.99. ¹³C NMR (CDCl₃): δ

140.4, 139.7, 132.1, 129.5, 127.1, 126.4, 123.9, 120.8, 109.8, 60.6. HRMS(FAB) calcd for $C_{20}H_{23}B_{10}N$: 385.5133. Found: 385.5130 [M]⁺. Anal. Calcd for $C_{20}H_{23}B_{10}N$: C, 62.31; H, 6.01; N, 3.63. Found: C, 62.20; H, 5.98; N, 3.64.

4.5. Synthesis of 4.

A procedure analogous to that used for the preparation of **1** was used, but instead starting from p-carborane. **4** was obtained as a white powder (0.89 g, 23%) and further purified by train sublimation in 63% yield. ¹H NMR (CDCl₃): δ 8.10 (d, 2H), 7.73 (d, 2H), 7.46 (d, 2H), 7.26-7.19 (m, 6H), 3.81-1.70 (br, 10H, B-H). ¹¹B NMR(CDCl₃): δ -8.48, -16.40. ¹³C NMR (CDCl₃): δ 140.3, 140.0, 132.5, 129.3, 126.6, 126.5, 123.9, 120.7, 120.6, 109.5, 84.8. HRMS(FAB) calcd for C₂₀H₂₃B₁₀N₁: 385.5133. Found: 385.5131 [M]⁺. Anal. Calcd for C₂₀H₂₃B₁₀N₁: C, 62.31; H, 6.01; N, 3.63. Found: C, 62.26; H, 6.07; N, 3.65.

4.6. Fluorescence Lifetime.

The lifetime measurements were performed by means of a single photon counting method using a streakscope (Hamamatsu Photonics, C4334-01), a polychromator (Acton Research, SpectraPro150), and a Ti:sapphire laser (Spectra-Physics, Tsunami 3941-M1BB, fwhm 100 fs) pumped with a diode solid-state laser (Spectra-Physics, Millennia VIIIs). For excitation of the samples, the output of the Ti:sapphire laser was converted to the second harmonic (400 nm) with a harmonic generator (Spectra-Physics, GWU-23FL). The instrument response function was determined by analyzing temporal profiles of the scattered laser light to give a time resolution of approximately 20 ps after deconvolution. The observed temporal emission profiles were well fitted to a single- or double-exponential function. The residuals were less than 1.1 % for each system.

4.7. Transient Absorption Spectroscopy.

Nanosecond transient absorption measurements were carried out by employing the technique of laser flash photolysis. The third harmonic generation (THG, 355 nm) of a Q-switched Nd:YAG laser (Continuum, Surelite II, pulse width of 4.5 ns) was used as the excitation light. A Xenon lamp (ILC Technology, PS 300-1) was focused onto the sample

solution as the probe light for the transient absorption measurements. The temporal profiles were measured with a monochromator (DongWoo Optron, Monora 500i) equipped with a photomultiplier (Zolix Instruments Co., CR 131) and a digital oscilloscope (Tektronix, TDS-784D). The transient absorption spectra were measured by ICCD (Ando Technology, iStar) with a gate time of 1.6 ns at 10 ns time-delay. The reported signals were the averages of 500 events. The sample solutions were argon-saturated.

4.8. Cyclic voltammetry and Spectroelectrochemistry.

The cyclic voltammetry experiments were performed using a BAS 100 electrochemical analyzer. A three-electrode cell system containing a platinum disk, a platinum wire, and Ag/AgNO₃ as the working, counter, and reference electrodes, respectively, was used. All data were obtained for Ar-purged CH_2Cl_2 solution containing 0.1 M tetrabutylammonium perchlorate (TBAP) at a scan rate of 0.1 Vs⁻¹. Spectroelectrochemical (SEC) measurements were performed to measure the UV-vis absorption spectra of the one electron reduced species (OER) of **1-4** using strands of 0.1 mm diameter Pt wire. In a porous glass tube (2 mm i.d., 3 mm o.d., 40 mm length) as the working electrode, a Pt wire coiled around the porous glass tube as the counter electrode, and an Ag/AgNO₃ reference electrode. A THF solution containing **1-4** (0.5 mM) and TBAP (0.1 M) in a quartz cell was purged with Ar for 10 minutes. Immediately after electrolysis using a BAS 100 electrochemical analyzer, the UV-vis absorption spectra were measured.

4.9. Density Functional Calculations.

All calculations were performed with the Gaussian 09 package¹⁷ to perform the geometry optimizations, spectra analysis, and excited state evaluations. The ground-state geometries of all compounds, as well as their cationic and anionic molecules, were optimized at the density function theory (DFT) level. The characterization of the low-lying excited singlet states relies on the time-dependent DFT (TD-DFT) calculation that is performed on the basis of the ground-state geometry by B3LYP density functional theory (DFT), using a 6-31G(d,p) basis set. The various properties of all compounds, such as HOMOs, LUMOs, energy gaps, ionization potentials, electron affinities, and reorganization energies are obtained from the computed results and are compared to the available experimental data.

5. References

 a) R. N. Grimes, *Carboranes, 2ndEdition*; Acadamic Press: Mar-2011. b) V. I. Bregadze, *Chem. Rev.* 1992, 92, 209. c) J. Ko, S. O. Kang, *Adv. Organomet. Chem.* 2001, 47, 61.
 a) B. T. King, S. Korbe, P. J. Schreiber, J. Clayton, A. Nemcova, Z. Havlas, K. Vyakaranam, M. G. Fete, I. Zharov, J. Ceremuga, J. Michl, *J. Am. Chem. Soc.* 2007, 129, 12960. b) T. T. Fister F. D. Vila, G. T. Seidler, L. Svec, J. C. Linehan, J. O. Cross, *J. Am. Chem. Soc.* 2008, 130, 925. c) F. Z. L. i. Mamena, L. Teruel, M. S. Galletero, A. Corma, H. Garcia, *Chem. Commun.* 2008, 499.

a) V. Manero, J. M. Oliva, L. Serrano-Andres, D. J. Klein, *j. Chem. Theory. Comput.* 2007, 3, 1399. b) L. Serrano-Andres, D. J. Klein, P. v. R. Schleyer, J. M. Oliva, *j. Chem. Theory. Comput.* 2008, 4, 1338.

4. H. Kunkely, A.Vogler, Inorganica Chimica Acta 2004, 357, 4607.

 a) B. P. Dash, R. Satapathy, E. R. Gaillard, J. A. Maguire, N. S. Hosmane, J. Am. Chem. Soc. 2010, 132, 6578. b) B. P. Dash, R. Satapathy, E. R. Gaillard, K. M. Norton, J. A. Maguire, N. Chug, N. S. Hosmane, *Inorg. Chem.* 2011, 50, 5485.

6. a) K. Kokado, Y. Chujo, *Macromolecules* 2009, 42, 1418. b) K. Kokado, Y. Tokoro, Y. Chujo, *Macromolecules* 2009, 42, 2925. c) K. Kokado, Y. Tokoro, Y. Chujo, *Macromolecules* 2009, 42, 9238. d) J. J. Peterson, M. Werre, Y. C. Simon, E. B. Coughlin, K. R. Carter, *Macromolecules*, 2009, 42, 8594. e) K. Kokado, A. Nagai, Y. Chujo, *Macromolecules* 2010, 43, 6463.

7. a) K. Kokado, Y. Chujo, J. Org. Chem. 2011, 76, 316. b) J. J. Peterson, A. R. Davis,
 M. Werre, E. B. Coughlin, K. R. Carter, ACS Appl. Mater. Interfaces, 2011, 3, 1796.

a) K.-C. Son, Y.-J. Lee, M. Cheong, J. Ko, S. O. Kang, J. Am. Chem. Soc. 2006, 128, 12086.
 b) J.-D. Lee, S.-K. Kim, T.-J. Kim, W.-S. Han, Y.-J. Lee, D.-H. Yoo, M. Cheong, J. Ko, S. O. Kang, J. Am. Chem. Soc. 2008, 130, 9904.
 c) J.-D. Lee, H.-Y. Kim, W.-S. Han, S. O. Kang, Organometallics 2010, 29, 2348.
 d) J.-D. Lee, W.-S. Han, T.-J. Kim, S. H. Kim, S. O. Kang, Chem. Commun. 2011, 1018.

9. K.-R. Wee, W.-S. Han, D. W. Cho, S. Kwon, C. Pac, S. O. Kang, *Angew. Chem. Int. Ed* **2012**, *51*, 2677.

10. a) J. R. Platt, J. Chem. Phys. 1949, 17, 484. b) G. E. Johnson, J. Phys. Chem. 1974, 78, 1512.

11. a) V. E. Lippert, Z. Elektrochem. 1957, 61, 962. (b) N. Mataga, Y. Kaifu, M. Koizumi, Bull. Chem. Soc. Jpn. 1956, 29, 465.

12. a) H. Masuhara, S. Ohwada, N. Mataga, A. Itaya, K. Okamoto, S. Kusabayashi, J.

Phys. Chem. **1980**, *84*, 2363. b) Y. Tsujii, A. Tsuchida, Onogi, Y. Yamamoto, M. *Macromolecules* **1990**, *23*, 4019.

13. M. A. Fox C. Nervi, A. Crivello, P. J. Low, Chem. Commun. 2007, 2372.

14. N. Nakashima, M. Murakawa, N. Mataga, Bull. Chem. Soc. Jpn. 1976, 49, 854.

a) E. S. Alekseyeva, M. A. Fox, J. A. K. Howard, J. A. H. MacBride, K. Wade, *Appl. Organometal. Chem.* 2003, *17*, 499. b) J. M. Oliva, N. L. Allan, P. v. R. Schleyer, C. Viňas, F. Teixidor, *J. Am. Chem. Soc.* 2005, *127*, 13538. c) B. W. Hutton, F. MacIntosh, F. Herisse, S. A. Macgregor, D. McKay, V. Petrie-Armstrong, G. M. Rosair, D. S. Perekalin, H. Tricas, A. J. Welch, *Chem. Commun.* 2008, 5345.

a) W. R. Heineman, W. B. Jensen, *Electrochemistry, Past and Present, Chapter 30*,
 1989, 442-457. b) O. Ishitani, M. W. George, T. Ibusuki, F. P. A. Johnson, K. Koike, K. Nozaki, C. Pac, J. J. Turner, J. R. Westwell, *Inorg. Chem.* **1994**, *33*, 4712-4717.

17. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A.Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L.Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, Revision B.01, Gaussian, Inc., Wallingford CT, 2010.