Angewandte
International Edition Chemie

DOI: 10.1002/anie.201109069

Carborane Clusters

Carborane Photochemistry Triggered by Aryl Substitution: Carborane-Based Dyads with Phenyl Carbazoles**

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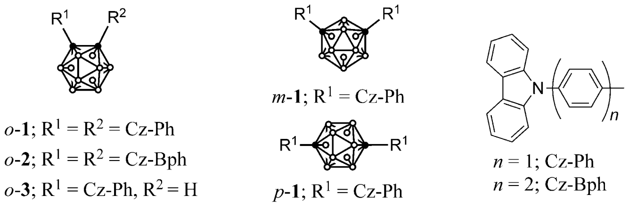
Since the discoveries of boranes and carborane clusters,[1] relentless effort has been made to understand their electronic structures,[2] particularly those of carborane compounds, because of their unique cage structures.[3] However, there have been few investigations on the excited-state properties and photochemical behavior of carborane compounds,[4] probably because the parent carboranes and their derivatives without π substituent show little or no absorption at >250 nm, nor any emission. Even for their π-substituted derivatives, furthermore, no detailed investigations have been performed, particularly into how the carborane cages affect their excited-state behavior.[5] Recently, a limited number of reports appeared on the unique fluorescence of polymers containing diaryl-substituted 1,2-carborane (*o*-Cab) units, which was inferred from their aggregation-induced emission[6] and charge transfer.[7] However, no detailed analysis has been performed on the electronic nature of the fluorescence from the *o*-Cab unit or the possible roles of the *o*-Cab cage. As an important part of our research projects on carborane chemistry,[8] we performed a detailed investigation on the excited-state properties of a series of aryl-substituted carboranes with the carbazole (Cz) end group (Scheme 1), using steady-state and time-resolved spectroscopic methods. The Cz group was used as an effective chromophore for spectroscopic studies, because rich spectroscopic data of Cz are available and because they are typical molecules acting as an electron donor. We report herein the observations on the emission behavior of the Cab compounds and discuss the implications of the effects of the carborane cage on the electronic and material properties of the molecules.

The Cab compounds were prepared in moderate yields (31–35%) using explored synthetic protocols and their structures were firmly identified by their spectroscopic data,



o-**1**; $R^1 = R^2$ = Cz-Ph
o-**2**; $R^1 = R^2$ = Cz-Bph
o-**3**; R^1 = Cz-Ph, R^2 = H
m-**1**; R^1 = Cz-Ph
p-**1**; R^1 = Cz-Ph
n = 1; Cz-Ph
n = 2; Cz-Bph

Scheme 1. Structures of the carborane compounds. The solid and open circles in the cage represent the carbon and boron atoms, respectively.

including the X-ray structures of *o*-**1**, *o*-**2**, and *p*-**1** (see the Supporting Information for details). As shown by the ORTEP structures of *o*-**1**, *o*-**2**, and *p*-**1** in Figure S1 in the Supporting Information, the Cz ring is disposed perpendicularly to the phenylene ring and the C–C distance of *o*-**1** (1.725 Å) is significantly longer than that of the nonsubstituted *o*-Cab (1.629 Å).[9]

As shown in Figure 1a and Table 1, the absorption spectra of *o*-**1**, *m*-**1**, and *p*-**1** are similar, commonly showing the longest absorption maximum at around 336 nm characteristic of the π,π* transition of the Cz chromophore.[10] This can be reasonably understood from the structures that indicate little conjugation between the Cz ring and the perpendicularly situated phenylene ring. However, a slight difference can be found in the 300–330 nm region; the intense band of *o*-**1** at around 324 nm seems to arise as a result of the red shift of the band of *m*-**1** and *p*-**1** at around 305 nm, possibly because of the slight electronic perturbations caused by the deformation of the *o*-Cab cage. By contrast, the emission of *o*-**1** is highly different from those of *m*-**1** and *p*-**1** which are almost identical each other with the spectra, lifetimes, and quantum yields characteristic of the excited-singlet Cz emission. In the case of *o*-**1**, a broad emission appears at 531 nm along with extensive quenching of the Cz fluorescence. This broad red-shifted emission can be attributed to the charge-transfer (CT) state, as shown by the remarkable solvatochromic shifts of the emission displayed in Figure 1b. Similar solvent-dependent CT emissions were observed for the other *o*-Cab compounds, *o*-**2** and *o*-**3** (see Figures S3 and S4 in the Supporting Information).

Figure 2a shows the Mataga–Lippert plots for the solvatochromic shifts of the CT emissions of *o*-**1** and *o*-**2** versus the solvent-polarity parameter (Δf). From the slopes of the linear plots, the differences in the dipole moments ($\Delta\mu$) between the ground-state and CT states were estimated to be around 28.0 D for *o*-**1** and around 60 D for *o*-**2**. Taking the dipole moment (μ_g) in the ground state to be 2.0 D for *o*-**1** and 1.1 D for *o*-**2**, as obtained by theoretical calculations,[11] the dipole

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[**] This research was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science, and Technology (MEST) of Korea (grant number 2011-0018595) and by the Center for Next Generation Dye-Sensitized Solar Cells (grant number 2011-0001055). We thank Prof. Tetsuro Majima, Associate Prof. Mamoru Fujistuka, and Takumi Kimura for their assistance during the pulse radiolysis studies in SANKEN. We also acknowledge Youlchon Chemical Co. for its financial support to C.P.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201109069.

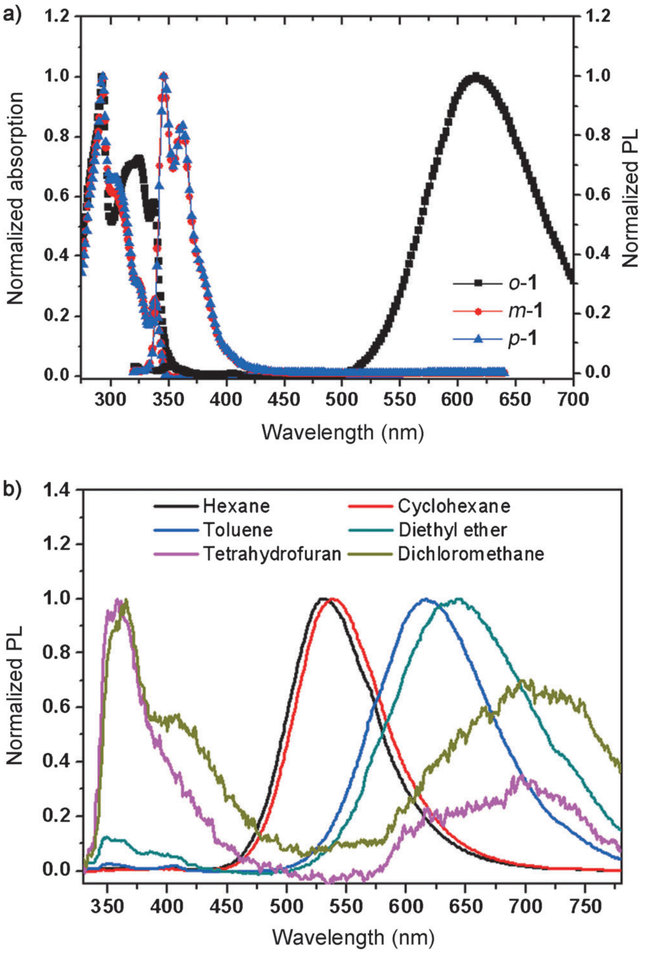

Figure 1. a) Absorption (<350 nm) and emission (>350 nm) spectra of *o*-**1** (black), *m*-**1** (red), and *p*-**1** (blue) in toluene. b) Emission spectra of *o*-**1** in various solvents.

Table 1: Photophysical properties of the Cab compounds.

Cab	λ_{abs} [nm][a]	λ_{em} [nm][a,b]	τ_F [ns][a]	Φ_F[a]	E_{ox}/E_{red}[c] [V]
o-**1**	293, 325, 338	360, 410, 531	2.83	0.06	0.72/−1.88
o-**2**	291, 326, 338	365, 583	3.41	0.05	0.71/−1.79
o-**3**	293, 324, 338	350, 360, 595	1.28	0.04	0.73/–[d]
m-**1**	293, 308, 339	349, 361	6.26	0.32	0.74/–[d]
p-**1**	293, 310, 339	350, 362	6.37	0.33	0.64/–[d]

[a] Measured in Ar-saturated toluene solution (5 μM) at room temperature. [b] Taken by excitation at 290 nm. For lifetimes monitored at different wavelengths, see Table S3 in the Supporting Information. [c] Oxidation and reduction potentials measured for Ar-saturated dichloromethane solution by cyclic voltammetry (V versus SCE). [d] No wave observed.

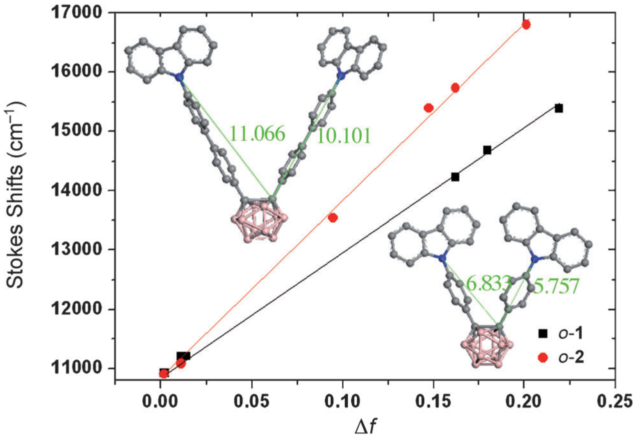

Figure 2. Mataga–Lippert plots for CT emissions of *o*-**1** (black) and *o*-**2** (red).

moment (μ_e) in the excited state should be around 30 D for *o*-**1** and around 62 D for *o*-**2**. If we take 4.8 D as the dipole moment between the unit charges separated by 1 Å, the excited-state dipole moment values correspond to the completely charge-separated states with dipole lengths of around 6.3 Å for *o*-**1** and around 13 Å for *o*-**2**, which are comparable to the distances found between the nitrogen atom of Cz and the center of the C–C bond of *o*-Cab (6.8 Å for *o*-**1** and 11.1 Å for *o*-**2**). This implies that complete charge separation should occur in the excited state of *o*-**1** and *o*-**2**. This is again true for *o*-**3** as shown by the solvent-dependent shifts of the CT emission.

To provide explicit evidence for the above arguments based on the Mataga–Lippert plots, we conducted laser-flash photolysis experiments for *o*-**1**. As shown in Figure 3a, two characteristic absorptions appeared at 415 and 830 nm upon irradiation of laser pulses at 355 nm. Both the 415 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 *o*-**1**. The 830 nm transient can be attributed to the radical cation of the Cz unit ($Cz^{\bullet+}$), because the radical cations of various carbazole compounds generally show characteristic absorptions at around 800 nm.[12] This assignment was firmly supported by the pulse radiolysis of *o*-**1** in 1-chlorobutane, which showed a transient at 830 nm (see Figure S11 in the Supporting Information). To assign the 415 nm bands, spectroelectrochemical (SEC) measurements were performed for *o*-**1** under constant voltage conditions at −1.8 V, a potential corresponding to the one-electron reduction of *o*-**1**. As shown in Figure 3b, a 415 nm peak appeared under keeping the spectral shape after prolonged electrolysis, being thus assignable as the spectrum of the radical anion of *o*-**1** (*o*-$\mathbf{1}^{\bullet-}$). A similar spectrum was also obtained by pulse radiolysis of *o*-**1** in DMF (see Figure S12 in the Supporting Information). This absorption is closely related to the spectrum reported for the radical anion of 1,2-diphenyl-*o*-Cab (Ph_2-*o*-$Cab^{\bullet-}$).[13] These spectroscopic observations strongly indicate that the excited state of *o*-**1** is a charge-separated state consisting of the carbazole radical cation ($Cz^{\bullet+}$) and the acceptor radical anion (Ph_2-*o*-$Cab^{\bullet-}$), 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 units in the oxidized cationic state and on the Ph_2-*o*-Cab moiety in the reduced anionic state (Figure 3a inset).

The CT emissions of *o*-**1** to *o*-**3** show similar solvent-dependent behavior, such that increasing the solvent polarity decreases their intensity to virtually nil in acetonitrile,

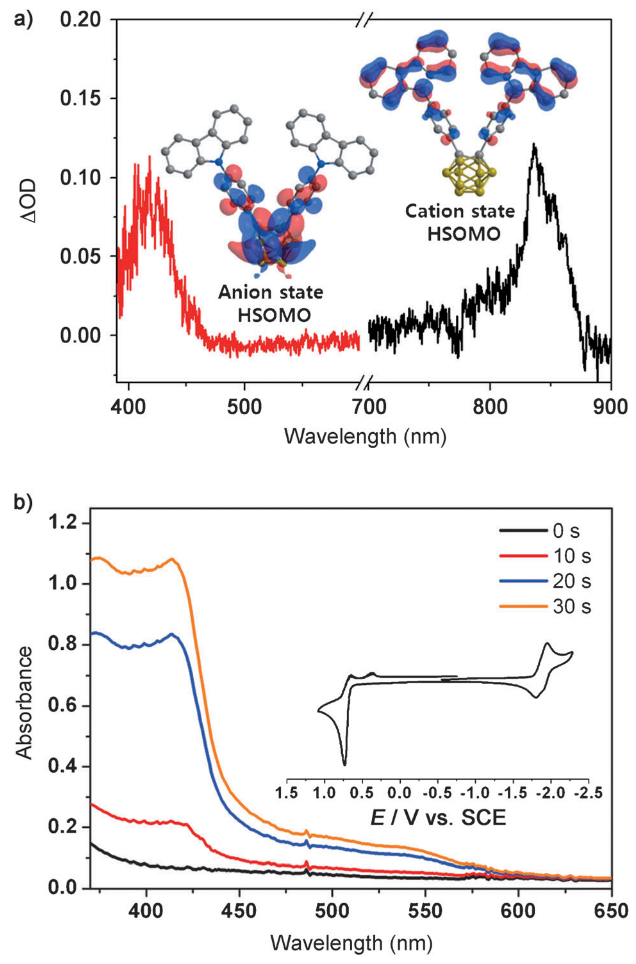

Figure 3. a) Transient absorption spectra of *o*-**1** in Ar-purged CH_2Cl_2 obtained at a 10 ns-delay after 355 nm laser excitation (Inset: cationic and anionic highest singly occupied molecular orbitals (HSOMOs) of *o*-**1**). b) Spectroelectrochemical (SEC) spectra of *o*-**1** taken by electrolysis at −1.8 V and cyclic voltammetry (CV) spectrum of *o*-**1**.

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 dependencies of the radiative and nonradiative rate constants.[14]

Another notable observation is that both the Cz fluorescence and excimer emission[15] can be detected for *o*-**1**, though they are very weak or masked by the CT emission in the low-polarity solvents. This means that the CT state is not formed instantaneously upon 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 *o*-**1** (120 ± 10 ps) is around 8×10^9 s^{-1}, which is not far from the value for electron transfer over a distance of around 7 Å with a driving force of around 1 eV.

The unique excited behavior of the *o*-Cab compounds reported herein implies the existence of unusual effects of the *o*-Cab cage on the electronic systems. While the parent *o*-Cab 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-Cab causes a drastic change in its electronic nature, making the molecule an efficient electron acceptor.[16] As shown in Figure S11 in the Supporting Information, we confirmed that 1,2-Ph$_2$-*o*-Cab quenches the fluorescence of ethylcabzole at a diffusion-controlled rate, an observation in accord with the extensive quenching of the Cz fluorescence observed with *o*-**1**. 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. We are presently conducting a further investigation on the excited states of the present and other diaryl-substituted *o*-Cab molecules using more sophisticated spectroscopic methods and theoretical calculations. In contrast to the *o*-Cab cage, the *m*- and *p*-counterparts act as an insulator that completely separates the two Cz-Ph electronic systems. This is, conversely, beneficial to the use of *m*-**1** and *p*-**1** as host materials for phosphorescent organic light-emitting diodes, because the solid films have suitable glass-transition temperatures, reasonable hole mobilities, and sufficiently high triplet-energy levels. We intend to apply *m*-**1** and *p*-**1** to blue-phosphorescent devices.

Experimental Section

Synthesis: 1,2-Bis(4-(*N*-carbazolyl)phenyl)-*ortho*-carborane (*o*-**1**), 1,2-bis(4-(*N*-carbazolyl)biphenyl)-*ortho*-carborane (*o*-**2**), 1-(4-(*N*-Carbazolyl)phenyl)-*ortho*-carborane (*o*-**3**), 1,7-bis(4-(*N*-carbazolyl) phenyl)-*meta*-carborane (*m*-**1**), and 1,12-bis(4-(*N*-carbazolyl)-phenyl)-*para*-carborane (*p*-**1**) were synthesized from 9-(4-bromophenyl)carbazole, as shown in Scheme S1 in the Supporting Information. *o*-**1** was obtained in two steps, through the reaction of di(4-(*N*-carbazolyl)phenyl)acetylene with decaborane, in an overall yield of 35 %. *o*-**2** was prepared by the Suzuki coupling reaction between 1,2-bis(4-bromophenyl)-*ortho*-carborane and two equivalents of 4-(carbazol-9-yl)phenylboronic acid. On the other hand, *o*-**3**, *m*-**1**, and *p*-**1** were prepared in a single step in moderate yields through the coupling reaction of 9-(4-bromophenyl)carbazole with the lithium salt of *o*-carborane or *m*-carborane or *p*-carborane, in the presence of copper(I) halides. All products were isolated by flash column chromatography and further purified by train sublimation in moderate yields. The formation of *o*-**1**, *o*-**2**, *o*-**3**, *m*-**1**, and *p*-**1** was confirmed by X-ray single-crystal structure, high-resolution mass spectrometry, and elemental analyses. The compounds showed the expected signals in their ^{1}H, ^{11}B and ^{13}C NMR spectra for the characteristic phenylcarbazole and carborane groups.

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/AgNO$_3$ as the working, counter, and reference electrodes, respectively, was used. All data were obtained for an Ar-purged CH_2Cl_2 solution containing 0.1 M tetrabutylammonium perchlorate (TBAP) at a scan rate of 0.1 V s^{-1}. Spectroelectrochemical[17] (SEC) measurements were performed to measure the UV/Vis absorption spectra of the one-electron-reduced species (OER) of *o*-**1** using strands of 0.1 mm diameter Pt wire. In a porous glass tube (2 mm inside diameter, 3 mm outside diameter, 40 mm length) as the working electrode, a Pt wire coiled around the porous glass tube as the counter electrode, and an Ag/AgNO$_3$ reference electrode. A THF solution containing *o*-**1** (0.5 mM) and

TBAP (0.1M) in a quartz cell was purged with Ar for 10 min. Immediately after electrolysis using a BAS 100 electrochemical analyzer, the UV/Vis absorption spectra were measured.

Laser flash photolysis: 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 full width at half maximum, fwhm) 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 (Dong-Woo 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 saturated with argon.

Received: December 22, 2011

Keywords: boranes · cage compounds · electron transfer · photophysics

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