Synthesis and Delayed Fluorescent Properties of *p-Nido*-Carborane-Triarylborane Conjugates with a Methyl-Substituted Phenylene Linker

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A series of *p-nido*-carborane-triarylborane conjugates (*nido*-1-3) in which a methyl group is introduced at the *ortho*-position to the carborane cage in the phenylene linker was prepared and characterized. All compounds exhibit broad low-energy absorptions ($\lambda_{abs} = ca. 350-400 \text{ nm}$) attributable to the intramolecular charge transfer transition from the *nido*-carborane donor to the (MePh)BMes₂ acceptor. Electrochemical studies confirm that oxidation occurs at the *nido*-carborane while the boryl moieties are responsible for the reduction. All *nido*-compounds show broad green emissions in tetrahydrofuran (THF) with good photoluminescence (PL) quantum yields ($\Phi_{PL} = 24\%-78\%$). In particular, different from the almost nonthermally activated delayed fluorescence (TADF) properties of unsubstituted *para*-conjugates, the transient PL decay curves of *nido*-1-3 show the existence of weak TADF ($\tau_d = 0.9-1.4 \ \mu s$ in THF). The TADF properties are further supported by the very small singlet-triplet energy splitting below 0.15 eV and are also observed in poly(methyl methacrylate) (PMMA) films doped with *nido*-1-3.

Keywords: Thermally activated delayed fluorescence, Nido-carborane, Triarylborane, Para-conjugates

Introduction

Carboranes, which are well-known icosahedral boron clusters, have been actively investigated in the field of boron cluster chemistry.¹⁻⁵ The unique properties of carboranes, such as three-dimensional σ-aromaticity, steric bulkiness, electronwithdrawing property through C-substitution, high thermal and chemical stability make them one of the promising candidates for novel luminophores.^{6–8} While 1,2-closocarboranes (1,2-dicarba-closo-dodecaboranes) are considered an electron-accepting auxiliary of luminophores owing to their strong inductive electron-withdrawing effect and conjugation effect,⁹⁻²³ 7,8-nido-carboranes (7,8-dicarbanido-undecaboranes) act as an electron-donating group due to their anionic nature. Hence, nido-carboranes have often been employed as a donor in intramolecular charge transfer (ICT) systems.²⁴⁻²⁷ However, in contrast with *closo*-carboranes, nido-carboranes have been less exploited in luminescent materials and thereby the photophysical properties of nido-carborane-based luminophores are still under investigation. In particular, the design of novel nido-carborane-based donoracceptor (D-A) systems will be challenging because such systems could be suitable for inducing thermally activated delayed fluorescence (TADF) owing to the steric bulkiness and electron-donating properties of nido-carboranes.²⁸ In recent years, TADF compounds are receiving great attention as an efficient emitting material in organic light-emitting diodes (OLEDs) since they can harvest nearly 100% singlet (S_1) excitons through reverse intersystem crossing (RISC) from triplet (T_1) excitons.^{29–31}

In this context, we recently reported nido-carboranetriarylborane conjugates as a new type of D-A system (Chart 1).³² It was demonstrated that the conjugates can exhibit TADF properties and the meta-substitution of the nido-carborane played a crucial role in attaining TADF. Although the TADF was weak in solution, the attachment of a steric group (R_2 = Me in Chart 1) to the 4position of the phenylene linker further enhanced the TADF properties.³³ It was revealed that the additional methyl group provides large energy barriers to cage rotation, which assists to maintain a perpendicular arrangement between the cage plane (C_{Cb}-C_{Cb}-B-B-B) and the Ph ring required for an efficient RISC. This finding prompted us to consider introducing a methyl group into the ortho-position to the cage in previous p-nido-carborane-substituted dimesitylphenylborane (PhBMes₂) compounds. In fact, the unsubstituted para-conjugates showed almost non TADF because of a substantial electronic conjugation between the donor (nido-carborane) and acceptor (PhBMes₂) moieties.³² Thus, it is anticipated that the electronic conjugation in para-conjugates could be weakened due to steric hindrance between the cage and methyl groups, which may improve the TADF properties of the para-conjugates (nido-1-3 in Chart 1). In this report, we prepared *p-nido*-carborane-triarylborane conjugates in which a methyl group is introduced at the *ortho*-position to the cage in the phenylene linker. The investigation of the photophysical properties of nido-1-3 having different 8-R groups showed enhanced TADF properties compared with



Chart 1. Meta- and para-nido-carborane-substituted triarylboranes.

those of the unsubstituted conjugates, verifying the rationality of the proposed approach.

Experimental Section

General Synthesis of *p-Nido*-Carborane-Substituted Triarylboranes, *nido*-1-3. *Closo*-carborane compounds (0.2 mmol) and tetrabutylammonium fluoride (*n*-Bu₄NF, TBAF) (1.0 mmol) were combined in tetrahydrofuran (THF) (20 mL) and the mixture was heated to reflux for 4 days. The mixture was cooled down to room temperature and the solvent was evaporated. The remaining residue was subjected to column chromatography on alumina using CH₂Cl₂/hexane (1:1, v/v) followed by acetone to afford a white powder of *nido*-carborane derivatives (*nido*-1-3). The product was further recrystallized from CH₂Cl₂/hexane.

[**Bu₄N**][1-(Mes₂B)-4-(8-H-7,8-*nido*-C₂B₉H₁₀)-5-MeC₆H₃] (*nido*-1). Yield = 65%. ¹H NMR (acetone-*d*₆): δ 7.25 (d, J = 7.8 Hz, 1H), 7.18 (s, 1H), 7.08 (d, J = 7.7 Hz, 1H), 6.82 (s, 4H), 3.5–1.5 (br, 9H, B-*H*), 3.47 (t, J = 9 Hz, 8H), 2.40 (s, 3H), 2.28 (s, 6H), 1.98 (s, 12H), 1.84 (quint, J = 9, 8H), 1.68 (s, 1H, C_{Cb}-*H*),1.44 (sext, J = 7.8, Hz, 8H), 0.99 (t, J = 7.5 Hz, 12H), -2.53 (br s, 1H, B-*H*-B). ¹³C NMR (acetone-*d*₆): δ 149.9, 140.3, 138.7, 138.1, 137.4, 133.1, 128.1, 128.0, 58.4 (Bu₄N), 23.5 (Bu₄N), 22.8, 20.3, 19.6, 19.5 (Bu₄N), 13.0 (Bu₄N). ¹¹B NMR (acetone-*d*₆): δ 79.1 (br s), -8.2 (1B), -9.7 (1B), -13.0 (1B), -15.4 (1B), -18.1 (2B), -22.9 (1B), -32.4 (1B), -35.2 (1B). mp = 228°C. Anal. Calcd for C₄₃H₇₅B₁₀N: C, 72.32; H, 10.59; N, 1.96%. Found: C, 72.16; H, 10.83, N, 2.01%.

[Bu₄N][1-(Mes₂B)-4-(8-Me-7,8-*nido*-C₂B₉H₁₀)-5-

MeC₆H₃] (*nido-2*). Yield = 83%. ¹H NMR (acetone-*d*₆): δ 7.25–7.19 (m, 2H), 7.10 (d, J = 7.8 Hz, 1H), 6.82 (s, 1H) 3.5–1.5 (br, 9H, B-*H*), 3.45 (t, J = 8.9 Hz, 8H), 2.40 (s, 3H), 2.28 (s, 6H), 1.98 (s, 12H), 1.81 (quint, J = 8.3, 8H), 1.45 (sext, J = 7.5, Hz, 8H), 1.01 (s, 3H, C_{Cb}-CH₃), 0.98 (t, J = 7.3 Hz, 12H), -2.45 (br s, 1H, B-*H*-B). ¹³C NMR (acetone-*d*₆): δ 147.6, 140.4, 139.5, 138.0, 137.1, 132.9, 129.5, 128.1, 58.5 (Bu₄N), 23.5 (Bu₄N), 22.7, 22.5, 21.0, 20.4, 19.5 (Bu₄N), 13.0 (Bu₄N). ¹¹B NMR (acetone-*d*₆): δ 78.3 (br s), -6.5 (1B), -9.9 (2B), -13.6 (1B), -15.3 (1B), -19.7 (2B), -33.2 (1B), -35.6 (1B). mp = 228°C. Anal. Calcd for $C_{44}H_{77}B_{10}N$: C, 72.57; H, 10.66; N, 1.92%. Found: C, 72.21; H, 10.81, N, 1.98%.

[Bu₄N][1-(Mes₂B)-4-(8-^{*i*}Pr-7,8-*nido*-C₂B₉H₁₀)-5-

MeC₆H₃] (*nido-3*). Yield = 59%. ¹H NMR (acetone-*d*₆): δ 7.26 (d, *J* = 7.8 Hz, 1H), 7.21 (s, 1H), 7.11–7.04 (m, 1H), 6.82 (s, 4H), 3.50–1.50 (br, 9H, B-*H*), 3.40 (t, *J* = 8.6 Hz, 8H), 2.49 (s, 3H), 2.28 (s, 6H, Mes-C*H*₃), 1.98 (s, 12H, Mes-C*H*₃), 1.81 (quint, *J* = 7.2 8H), 1.43 (sext, *J* = 7.5 Hz, 8H), 1.21 (sept, *J* = 6.6 Hz, 1H), 0.99 (t, *J* = 7.2 Hz, 12H), 0.95 (d, *J* = 2.1 Hz, 3H),), 0.58 (t, *J* = 8.3 Hz, 3H), -2.60 (br s, 1H, B-*H*-B). ¹³C NMR (acetone-*d*₆): δ 146.2, 142.6, 141.2, 140.5, 138.8, 134.7, 130.1, 128.9, 59.4 (NBu₄), 26.2, 25.3, 24.4 (NBu₄), 23.7, 23.6, 21.2, 20.4 (NBu₄), 13.8 (NBu₄). ¹¹B NMR (acetone-*d*₆): δ 78.3 (br s), -7.9 (2B), -14.2 (1B), -15.9 (2B), -18.6 (2B), -32.8 (1B), -35.1 (1B). mp = 181°C. Anal. Calcd for C₄₆H₈₁B₁₀N: C, 73.06; H, 10.80; N, 1.85%. Found: C, 73.12; H, 10.69; N, 1.88%.

Photophysical Measurements. Ultraviolet/Visible (UV/ Vis) absorption and photoluminescence (PL) spectroscopic studies were performed on a Varian Cary 100 and FS5 spectrophotometer, respectively. Photoluminescence quantum yields (PLQYs, Φ_{PL}) of all solution and film samples were measured on an absolute PL quantum yield spectrophotometer (Quantaurus-QY C11347-11, Hamamatsu Photonics, Japan) equipped with a 3.3 inch integrating sphere. Transient PL decay was recorded on a FS5 spectrophotometer (Edinburgh Instruments, Livingston, UK) using a timecorrelated single-photon counting (TCSPC) method (EPL-375 ps pulsed diode laser as a light source).

Results and Discussion

Synthesis and Characterization. The synthesis of *p*-nidocarborane-triarylborane conjugates (nido-1-3) was achieved using the analogous methods established previously for the meta-systems (Scheme 1).^{32,33} To investigate the substituent effect on the photophysical properties, we also introduced various 8-R groups such as H, Me, and ⁱPr groups into the 8-position of the nido-carborane cage. The carborane cage of the corresponding closo-1-3 was deboronated with TBAF in refluxing THF, producing nido-1-3 in good yields (59%–83%, see the SI for details). The synthesis of closo-1-3 compounds proceeded with slightly different routes depending on the 8-R group. The 8-H substituted closo-1 was prepared by the cage forming reaction between (4-ethynylphenyl)dimesitylborane (1b) and decaborane $(B_{10}H_{14})$ in the presence of excess Et_2S in refluxing toluene. In the synthesis of closo-2 and -3, a BMes₂ moiety was finally introduced into the 4bromobenzene intermediates having an 8-R (R = Me, i Pr) substituted *closo*-carborane (2b and 3b), which could be obtained via deprotonation of 8-H in 2a with NaH, followed by reaction with a respective alkyl iodide.

The formation of the *closo-* and *nido-*compounds was identified by nuclear magnetic resonance (NMR)



Scheme 1. Synthesis of *closo*-**1**-**3** and *nido*-**1**-**3**. i) Pd(PPh₃)₄, CuI, ethynyltrimethylsilane, ^{*i*}Pr₂NH, 0°C; ii) *n*-BuLi, ether, -78° C, then FBMes₂; iii) TBAF, THF, RT; iv) B₁₀H₁₄, Et₂S, toluene, r/x; v) NaH, DMF, 0°C, then RI (R = Me for **2b** and ^{*i*}Pr for **3b**); vi) TBAF, THF, r/x, 4 days.

spectroscopy and elemental analyses (see the SI for details). For *nido*-**1-3**, broad ¹H NMR resonances at $\delta - 2.3$ to -2.8 ppm can be attributed to the bridging B-H-B hydrogen of the *nido*-carborane. The ¹¹B NMR spectra showed two sets of signals, that is, a weak broad signal at δ ca. 78 ppm and sharp signals at $\delta -6$ to -36 ppm, which confirmed the presence of both tri-coordinated boron and *nido*-carboranyl boron atoms.

Photophysical and Electrochemical Properties. UV/Vis absorption and PL spectroscopic studies were performed in THF to investigate the photophysical properties (Figures 1 and 3, and Table 1). All *nido*-**1**-**3** exhibit similar strong absorptions at ca. 318 nm, which are mainly assignable to (MePh)BMes₂-centered π (Mes) $\rightarrow p_{\pi}$ (B) CT transition. In addition, a weak absorption is observed in the low-energy region of ca. 350–400 nm. This absorption can be ascribed to the ICT transition from the *nido*-carborane donor to the (MePh)BMes₂ acceptor.^{32,33}

The redox properties and the nature of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of compounds were investigated by an electrochemical study (Figure 2 and Table 1). All *nido*-**1**-3 show an irreversible oxidation (HOMO) typical for *nido*-carboranes.^{34,35} Owing to the presence of different 8-R groups, the oxidation potentials are slightly different among the compounds; *nido*-**1** bearing a less electron-donating 8-H group exhibits a larger oxidation potential ($E_{ox} = 0.56$ V) than those of the 8-alkyl substituted *nido*-**2** and -**3** whose



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Figure 1. UV/Vis absorption spectra of *nido*-1-3 in THF $(2.0 \times 10^{-5} \text{ M})$ at 298 K.

oxidations occur at similar potentials ($E_{ox} = 0.47$ V for *nido*-2 and 0.49 V for *nido*-3) (Table S1).

This result indicates that *nido*-carborane-centered HOMO level could be controlled by the 8-R group. In the case of reduction, while triarylboron-centered reductions are observed for all compounds, they are not completely reversible (quasi-reversible). Nevertheless, the reduction potentials are very similar to each other ($E_{\rm red} = -2.42$ V to -2.45 V) probably owing to the same boryl acceptor moiety. Accordingly, the band gap ($E_{\rm g}$) of compounds is governed by their HOMO levels, leading to the largest value for *nido*-1. These electrochemical results further indicate that HOMO (*nido*-carborane) and LUMO ((MePh) BMes₂) are well separated within a molecule due to the additional Me group at the *ortho*-position to the cage and the lowest-energy electronic transition involves the *nido*-carborane to boryl ICT transition.

The PL spectra of *nido*-**1**-**3** exhibit a broad emission centered at 520–535 nm in THF, which is typical for CT transition (Figure 3 and Table 1). Among the three compounds, *nido*-**1** shows the most blue-shifted emission because of the largest band gap. All compounds have good PL quantum yields (PLQY, Φ_{PL}) in oxygen-free THF ($\Phi_{PL} = 24\%$ -78%). The 8-H containing *nido*-**1** is the most emissive among the compounds, as similarly found for previous



Figure 2. Cyclic voltammograms of *nido*-**1-3** $(1.0 \times 10^{-3} \text{ M in DMF}, \text{ scan rate} = 100-200 \text{ mV/s}).$

Compd	λ_{abs}^{a} (nm)	$\lambda_{\rm PL}$ (nm)		$\Phi_{\mathrm{PL}}{}^{\mathrm{b}}(\%)$		$ au_{\mathrm{p}} \left(\Phi_{\mathrm{PF}} \right) \left[\mathrm{ns} \left(\% \right) \right]^{\mathrm{c}}$		$ au_{ m d} \left(\varPhi_{ m DF} ight) \left[\mu s \left(\% ight) ight]^{ m c}$		HOMO/LUMO ^d (eV)	$\frac{\Delta E_{\rm ST}^{\ e}}{({\rm eV})}$
		THF ^a	film ^f	THF ^a (N ₂ /air)	film ^f	THF^{a}	film ^f	THF^{a}	film ^f		
nido- 1	319	520	459	78/40	80	28.9 (94)	18.9 (97)	0.9 (6)	0.6 (3)	-5.36/-2.38	0.020
nido- 2	318	535	484	40/16	70	33.2 (94)	38.0 (89)	1.4 (6)	3.6 (11)	-5.27/-2.37	0.041
nido- 3	318	529	487	24/11	44	31.5 (90)	46.3 (98)	0.9 (10)	1.5 (2)	-5.29/-2.35	0.145

Table 1. Photophysical data of *nido*-1-3.

 $^{\rm a}$ In oxygen-free THF at 298 K (2.0 \times 10 $^{-5}$ M).

^b Absolute photoluminescence quantum yields (PLQYs).

^c Prompt (τ_p) and delayed (τ_d) PL lifetimes. Relative portions (%) of the prompt (Φ_{PF}) and delayed (Φ_{DF}) components are provided in parentheses. ^d From electrochemical oxidation (HOMO) and reduction (LUMO).

 $e^{\Delta}E_{ST} = E_S - E_T$. Singlet (E_S) and triplet (E_T) energies from the fluorescence and phosphorescence spectra in THF at 77 K.

^fSpin-coated PMMA films doped with 10 wt% of compounds.



Figure 3. PL spectra of *nido*-1-3 in N₂-filled and aerated THF (2.0×10^{-5} M) at 298 K. $\lambda_{exc} = 320$ nm for *nido*-1 and 2; 325 nm for *nido*-3. Insets: Transient PL decay curves of *nido*-1-3 in N₂-filled and aerated THF at 298 K. λ_{exc} (laser) = 375 nm.

nido-carborane-substituted triarylboranes.^{32,33} Note that the emission wavelength and PLQY of the 8-alkyl substituted nido-2 and -3 are almost comparable albeit a slightly higher PLQY for nido-2. Next, to investigate the TADF properties, transient PL decay for the CT emission of the compounds was measured in oxygen-free THF (Insets in Figure 3 and Table 1). For comparison, the decay curves in air-saturated THF are also obtained. The PL decay of all compounds exhibits microsecond-range decay components, as well as nanosecond-range prompt components. The estimated delayed emission lifetimes (τ_d) are of ca. 1 µs at 298 K. However, the intensities of the decay components are considerably weak for all compounds, exhibiting relative portions of the delayed components ($\Phi_{\rm DF}$) less than 10%. The absence of long-lived decay components and the much reduced emission intensities in aerated solutions indicates that the delayed emission of nido-1-3 can be assigned to TADF originating from the $T_1 \rightarrow S_1$ RISC process (Figure 3). Although these results are poorer than those of previous meta-systems, which showed strong delayed emission with long lifetimes,³³ they are promising when compared with the almost non-TADF properties of unsubstituted *para*conjugates.³² This in turn indicates that the introduction of a steric group (Me) into the ortho-position to the cage in the phenylene linker can enhance TADF properties by restricting

cage rotation which is favorable for maintaining a perpendicular arrangement between the cage plane and the Ph ring. Very small energy splitting (ΔE_{ST}) between the excited singlet (S₁) and triplet (T₁) states below 0.15 eV for all compounds further supports the TADF properties of *nido*-1-3 (Table 1 and Figure S4).



Figure 4. PL spectrum and transient PL decay curve (right inset) of PMMA film doped with 10% *nido*-2. $\lambda_{\text{exc}} = 320 \text{ nm}$. PLQY (%) and delayed lifetime (τ_{d}) are provided.

Finally, the photophysical properties of *nido*-1-3 were investigated in the rigid state using poly(methyl methacrylate) (PMMA) films. All PMMA films doped with 10 wt% compounds exhibit CT emission with increased PLQYs ($\Phi_{PL} = 80\%$ -44%) (Figures 4 and S5). The PL emission underwent rigidochromic blue shifts by ca. 40–60 nm in comparison with that in THF. The emission peak positions follow the same trend as that observed in THF solutions, showing the most blue-shifted peak for *nido*-1. In particular, the weak delayed fluorescence with emission lifetimes (τ_d) of 0.6–3.6 µs is also observed for all film samples, confirming the existence of TADF in the rigid state.

Conclusion

We characterized and prepared p-nido-carboranetriarylborane conjugates (nido-1-3) in which a methyl group is introduced at the ortho-position to the cage in the phenylene linker. Different from the almost non-TADF behavior of previous unsubstituted para-conjugates, nido-1-3 exhibited TADF properties in both solution and solid state irrespective of 8-R groups. All compounds showed very small $\Delta E_{\rm ST}$ values as a consequence of a perpendicular arrangement between the cage plane and the Ph ring induced by the steric hindrance between the two moieties. The results in this study demonstrate that TADF properties of nido-carborane-triarylborane D-A conjugates can be improved by employing a steric group between the donor (cage) and acceptor (PhBMes₂) groups and the proposed approach will also be useful for designing nido-carborane-based TADF compounds.

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Supporting Information. Additional supporting information may be found online in the Supporting Information section at the end of the article.

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