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Fluorescence enhancement of non-fluorescent triphenylamine: A recipe to utilize carborane cluster substituents

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ABSTRACT

Carborane-substituted triphenylamines were prepared to demonstrate the effective fluorescent enhancement of triphenylamine as a typical non-fluorescent π-conjugated compound on the basis of molecular design to suppress the non-radiative decay by reduced vibronic coupling. Non-fluorescent carborane substituents work to reduce only the HOMO distribution in the non-fluorescent parent π-conjugated core, thereby leading to increase in fluorescence quantum yield by suppressing internal conversion.

To date, light-emitting molecules continue to attract great interest in conjunction with their device application such as organic light-emitting diodes (OLEDs) [1,2], and thus, various kinds of fluorescent molecules have already been so far prepared [3]. Nevertheless, given that light-emitting efficiency of non-fluorescent molecules can be enhanced by general guiding principles, many more options become available for exploitation of new fluorescent molecules. As an example of typical non-fluoescent molecules, oligoarylamines are designated, and their excited states undergo non-radiative decay with internal conversion and vibrational relaxation. As exemplified in Figure 1(a), a weak absorption band in the shoulder of an intense absorption band at about 300 nm corresponds to the HOMO–LUMO transition of trianisylamine (TAA) [4], and TAA can be substantially regarded as non-fluorescent molecule [5]. Time-dependent DFT calculations (TD-DFT) illustrates that the weak shoulder band at about 365 nm can be assigned to the transition mainly from the HOMO (31*a*) with distribution over the nitrogen p orbital and three phenyl rings to the LUMO (32*a*) without contribution of the nitrogen p orbital, thus indicating these two orbitals are related to the fluorescent process in TAA (Figure 1(b)).

Non-radiative decay mainly originates from both vibrational relaxation process and internal conversion process ($S_1 \rightarrow S_0$). Internal conversion process is, in general, caused by vibronic interaction (electron–phonon interaction). It has been demonstrated that the off-diagonal vibronic coupling constants (VCCs) between S_1 and S_0 states directly related to the rate constant of internal conversion; in fact, on the basis of the theoretical molecular design reducing off-diagonal VCCs, a newly prepared anthracene derivative exhibited suppressing effect on internal conversion process, that is, an increase in fluorescence quantum yield [6,7]. The off-diagonal VCC can be represented by the integral of the vibronic coupling density (VCD) between S_1 and S_0 states, and furthermore, the VCD equals the multiplication of the overlap density between S_1 and S_0 states and the potential derivative with respect to the normal coordinate of the vibrational mode [8,9]. According to the VCD analysis, a guiding principle to suppress non-radiative decay by the introduction of substituents is deduced: *if an excited state, which is expected to be the emitting state, originates from the excitation between a pair of molecular orbitals* (*HOMO and LUMO for the most cases*), *one of the MOs should be delocalized over the entire molecule, whereas the other should be localized on the non-fluorescent core molecular unit, presuming that the potential derivative does almost unchanged before and after the introduction of substituents* [10]. According to this guiding principle, we report here on the fluorescence enhancement of non-fluorescent triphenylamine by substitution of suitable substituents.

We have been searching for suitable one for triarylamines in the arsenal of non-fluorescent substituents, and finally, monocarba-*closo*-dodecaborate [11] ($CB_{11}H_{12}^-$; hereinafter referred to as 'carborane') has been chosen as the best one. For instance, when one of the methoxy groups in TAA is substituted by carborane, the electronic structure of the substituted TAA (**1**) was estimated by DFT and TD-DFT calculations (Figure 2). Importantly, the specific characteristics of the HOMO with the nitrogen p orbital and the LUMO without the nitrogen p orbital for TAA remained unchanged by the carborane substitution, thereby ensuring the same emission process as TAA is anticipated for **1**; in other words, the fluorophore of **1** is still the triphenylamine core. In addition, the HOMO of **1**

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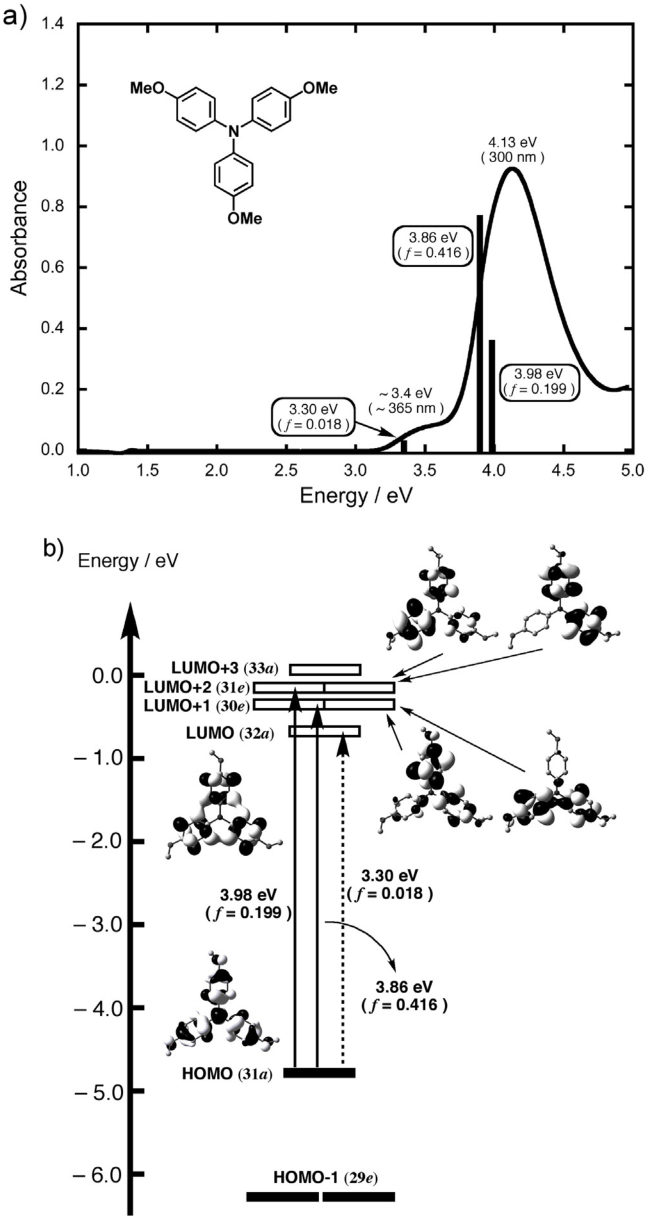

Figure 1. (a) Absorption spectrum of trianisylamine (TAA) in CH_2Cl_2 at room temperature. The black sticks designate the TD-DFT-calculated lower energy transition energies and their relative oscillator strengths at B3LYP/6-31+G*. (b) Frontier Kohn–Sham orbital energy levels for trianisylamine (TAA) at the B3LYP/6-31+G* level of theory (in C_3 symmetry). The broken and solid arrows represent the major contribution to the lowest and next-lowest energy transitions, respectively, on the basis of TD-DFT calculations.

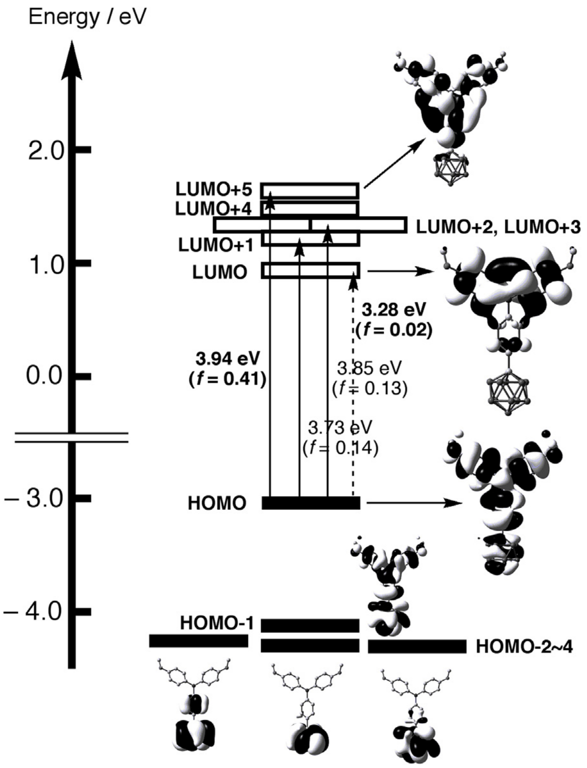

Figure 2. Frontier Kohn–Sham orbital energy levels for carborane-substituted triarylamine **1** at the B3LYP/6-31+G* level of theory (in C_1 symmetry). The broken and solid arrows represent the major contribution to the lowest and next-lowest energy transitions, respectively, on the basis of TD-DFT calculations.

extends over the carborane substituent, while the LUMO is mostly localized on the triarylamine moiety. More importantly, it was confirmed that the vibrational modes originating from carborane substituents do not participate in the maximum-coupling modes, on the basis of VCC analysis [10]. Overall, these remarkable features of **1** meet the requirements for the above-mentioned guiding principle: the overlap density between HOMO and LUMO in **1** is reduced effectively by the extension of the distribution of HOMO into the carborane substituent, as compared to that in TAA [10]. The DFT calculations for doubly and triply carborane-substituted triphenylamines (**2** and **3**) have also the same trend as **1** (Figures S1 and S2).

With these points in mind, we decided to investigate singly, doubly, and triply carborane-substituted triphenylamines **1**–**3** (Scheme 1). The target molecules **1**–**3** were successfully prepared from $[Me_3NH]^+[closo\text{-}CHB_{11}H_{11}]^-$ and the corresponding iodo-substituted triarylamine [*N*,*N*-bis(4-methoxyphenyl)-*N*-(4-iodophenyl)amine for **1**, *N*,*N*-bis(4-iodophenyl)-*N*-(4-methoxyphenyl)amine for **2**, and tris(4-iodophenyl)amine for **3**] by using palladium-catalyzed copper-mediated C—C cross-coupling reaction which has been recently developed by Uchiyama and co-workers [12]. We have finally obtained **1**–**3** as PPh_4^+ salts in 42%, 22%, and 61% yield, respectively, after successive counter ion exchange. These compounds were insoluble in non-polar solvents due to their ionic character.

For the carborane-substituted triphenylamines **1**–**3**, single reversible oxidation waves were observed at $E_{1/2} = +0.19\,V$ (**1**), +0.30 V (**2**), and +0.35 V (**3**) vs $Fc^{0/+}$ by cyclic voltammetry in CH_2Cl_2 (Figure S3), indicating that the electron removal basically takes place from the triphenylamine core, although the oxidation potential increases with the number of carborane-substituents [$E_{1/2} = +0.13\,V$ vs $Fc^{0/+}$ for TAA in CH_2Cl_2]. In addition, the absorption spectrum of **1**–**3** in CH_2Cl_2 (Figure S1) displayed a weak shoulder band similar to that of TAA (Figure 1(a)). Moreover, the absorption spectrum of oxidized species for **1**–**3** was also similar to that for the radical cation of TAA (Figure S4). These data provide evidence that the carborane-substitution does not influence on the electronic structure of triphenylamine core, in accordance with the aforementioned DFT results.

In contrast with TAA, compounds **1**–**3** exhibited fluorescence in the blue to green visible region with good efficiency in CH_2Cl_2 solution (Figure 3(a)). The fluorescence data are summarized in Table 1 and the spectra of **1**–**3** are shown in Figure 3(b). The emission maxima were blue-shifted with increasing number of carborane-substituents. To elucidate the origin of the blue-shift in the emission spectra in connection with the number of carborane-substituents, the geometries for the adiabatic S_1 excited states of