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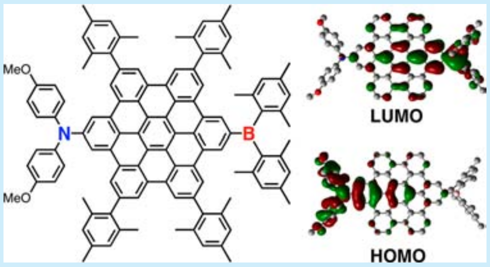
Luminescent Superbenzene with Diarylamino and Diarylboryl Groups

Ryohei Kurata, Kensuke Kaneda, and Akihiro Ito*

Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan

Supporting Information

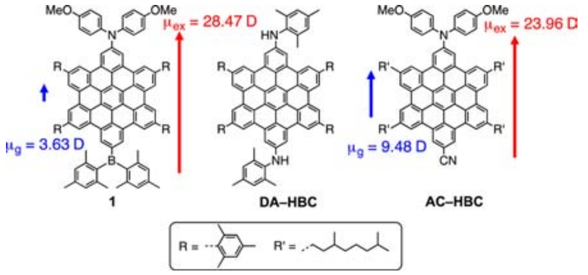
ABSTRACT: Dianisylamino donor and dimesitylboryl acceptor substituents were introduced at the 2,11-positions of hexa-*peri*-hexabonzocoronene (HBC) to demonstrate an effective fluorescent enhancement of HBC as virtually nonfluorescent "superbenzene". The present donor–acceptor substitution replaced the typical weak α-band with an intense intramolecular charge-transfer band in the absorption spectrum, thereby leading to a much larger fluorescence quantum yield (Φ_f = 0.56 in CH_2Cl_2) than any other HBC derivatives.



Polycyclic aromatic hydrocarbons (PAHs) have long been recognized as a pivotal class of compounds in the field of organic chemistry,[1] and after the rise of graphene,[2] the renewed and widespread attention to nanosized graphenes, or extended PAHs, accelerates the precise synthesis and characterization of structurally well-defined graphene fragments.[3] Among a wide variety of PAH molecules, derivatives of hexa-*peri*-hexabenzocoronene (HBC), or so-called "superbenzene", are of great interest because of their similarity to the corresponding benzene derivatives[4] and their application in organic electronics.[5] However, unfortunately, the utilization of HBC core as a chromophore is limited to date, despite the fact that a large number of PAH derivatives such as anthracene, pyrene, and so on are widely used as luminescent materials.[6] This is mainly because (i) HBC itself is not sufficiently soluble in common organic solvents due to the strong aggregation in solution and (ii) the $S_1 \leftarrow S_0$ transition (so-called α-band[1a] in absorption spectroscopy for PAHs) of unsubstituted HBC is symmetrically forbidden.[7]

Recently, Shinokubo and co-workers introduced bulky mesityl group to the HBC core to improve the solubility of the HBC derivatives, and furthermore, additional substitution of electron-donating amino groups at the pseudo-*para*-positions of the HBC core resulted in fluorescence with the highest quantum yield of 0.33 in CH_2Cl_2 (Scheme 1, **DA–HBC**).[8] Although an increase of the intensity in α-band was fulfilled by the lift in degeneracy of HOMOs due to substitution of amino groups, the oscillator strength of the α-band is still relatively low. In this study, we focus on charge-transfer (CT) emission from the HBC derivatives with electron-donating (D) and electron-accepting (A) group, that is, the donor–π–acceptor (D–π–A) system utilizing the HBC core as a π-bridging unit, rather than on enhancement of fluorescence quantum yield by realization of strong intensity of the α-band. Although there are many studies on molecular systems bearing the HBC core as a donor unit,[9] examples of those with the HBC core as a π-bridging unit in the D–π–A system are still rare. Feng, Müllen, and co-workers reported the HBC derivatives with a strong dipole moment due to the push–pull structure in their ground states (Scheme 1, **AC–HBC**).[10] However, the strong aggregation in solution did not allow the elucidation of their optoelectronic properties as a single molecule. In this context, we prepared 2-(dianisylamino)-11-dimesitylboryl-5,8,14,17-tetramesitylhexabenzo[*bc*,*ef*,*hi*,*kl*,*no*,*qr*]coronene (Scheme 1, **1**), where the dianisylamino group and the dimesitylboryl groups as donor and acceptor moieties are introduced at the preudo-*para* positions of the HBC core, and its optoelectronic properties were disclosed. Such B–π–N molecular systems often provide an effective intramolecular CT state.[11]

Scheme 1. Molecular Structures of 1, DA–HBC, and AC–HBC and Schematic Representation of the (TD-)DFT-Computed (B3LYP/6-31G*) Ground (g) and Excited (ex) Dipole Moments of 1′ and AC–HBC′



DFT calculations were carried out at the B3LYP/6-31G* level of theory to understand the electronic state of **1**.[12] Herein, the mesityl (Mes) groups attached to the HBC core were replaced by H atoms (model compound **1′**) because the Mes groups, which were perpendicularly attached to the π-face of the HBC core,[8a] have little influence on the electronic structures of **1**. As shown in Figure 1, the HOMO of **1′** originates from an out-of-phase

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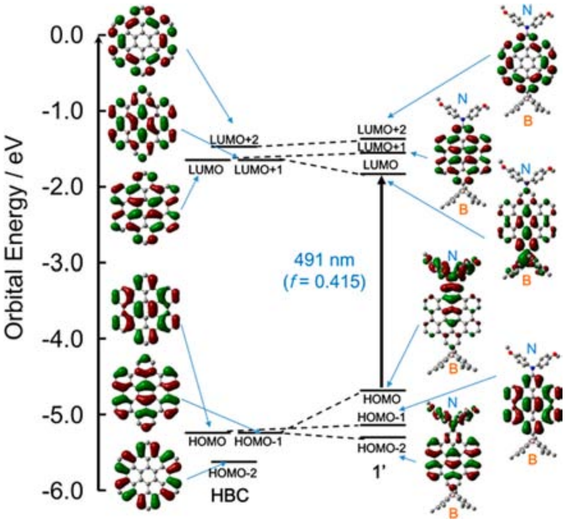
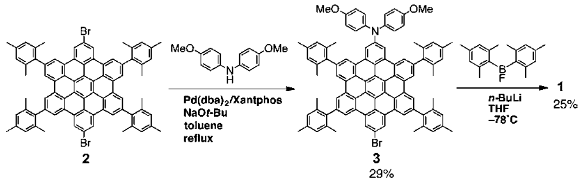


Figure 1. Frontier Kohn−Sham orbital energy levels for the ground state of HBC and **1′** at the B3LYP/6-31G* level of theory. The solid black arrow represents the major transition related to the observed lowest-energy absorption band for **1′**.

orbital interaction between the HOMO−1 of original HBC core and the N 2p orbital, while the LUMO of **1′** originates from an in-phase orbital interaction between the LUMO+1 of the original HBC core and the vacant B 2p orbital. These orbital interactions result in the lift in degeneracy of the frontier MOs of the original HBC core and lower the symmetry of the entire molecule. On the basis of the time-dependent DFT (TD-DFT) method, the unsubstituted HBC can be excited into three characteristic low energy excited states at the Franck−Condon geometry (B3LYP/6-31G*//B3LYP/6-31G*): (i) at 2.84 eV (435.9 nm; α-band (f (oscillator strength) = 0), (ii) 2.98 eV (415.9 nm; p-band (f = 0)), and (iii) 3.42 eV (362.6 nm; β-band (f = 1.43)), and the symmetrically forbidden α-band transition turns out to be allowed due to the introduction of substituents.[8b] Furthermore, in the case of **1′**, one of the allowed α-band transitions can be regarded as a transition of intramolecular CT (ICT) character, as described predominantly by the amine-localized HOMO to the boron-localized LUMO transition, and the usual α- and p-bands are expected to be covered with the more intense ICT band at 2.52 eV (491.2 nm (f = 0.415)) and the β-band at 3.25 eV (381.0 nm (f = 0.513)), thus leading to stronger photoluminescence with higher fluorescence quantum yield (Figure S1). More interestingly, as has already reported on **AC−HBC**, in the ground state, a long-alkyl-chains-omitted model compound of **AC−HBC** (**AC−HBC′**) has a strong dipole moment (9.48 D), whereas **1′** has a moderate one (3.63 D) (Scheme 1). On the other hand, the computed dipole moment (28.47 D) for the S_1 excited state at the Franck−Condon (FC) geometry of **1′** is anticipated to be larger than that of **AC−HBC′** (23.96 D), suggesting the largest change in dipole moment between the ground and excited states (Scheme 1).

Scheme 2. Synthesis of 1



The synthesis of **1** was accomplished through a stepwise substitution of 2,11-dibromo-5,8,14,17-tetramesityl-substituted HBC (**2**), which was newly prepared according to the literature,[13] as illustrated in Scheme 2. Palladium-catalyzed cross-coupling amination reaction[14] of **2** with dianisylamine gave the monoamino-substituted HBC (**3**). The remaining bromo group was then converted into dimesitylboryl group by treatment with dimesitylfluoroborane after lithiation of **3** with *n*-BuLi in THF. The target compound **1** was obtained as a yellow solid and has sufficient solubility in common organic solvents to investigate the optoelectronic properties as a single molecule.

As shown in Figure 2, the UV/vis absorption spectrum of **1** displays a structureless lowest energy band with absorption maximum at 450 nm, together with the β-band with a vibrational progression at 390 nm, in CH_2Cl_2. These observed bands are in good accordance with the aforementioned TD-DFT results, thus indicating that the lowest energy band is assignable to the HOMO−LUMO transition, which is ascribed to the ICT band, rather than typical α- and p-bands (Figure S1). From the numerical integration of the observed ICT band,[11j,15] the oscillator strength is estimated to be 0.27, which is qualitatively in accordance with the TD-DFT result for **1′** (0.415). With increasing solvent polarity from *n*-hexane to CH_2Cl_2, the ICT band shape and maximum of **1** almost remained unchanged, indicating a small ground-state dipole moment, which was calculated to be 3.63 D for **1′** (Scheme 1, Table 1, and Figure S2).

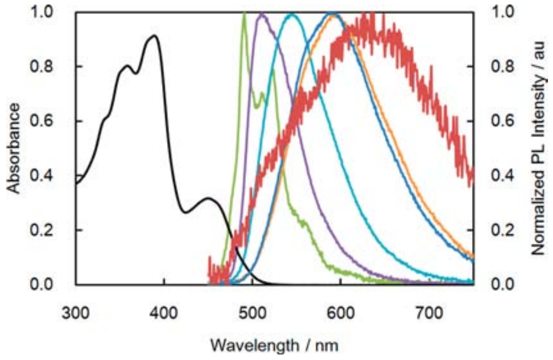


Figure 2. Absorption spectrum of **1** in CH_2Cl_2 (black) and emission spectra of **1** in various solvents; *n*-hexane (green), toluene (purple), chloroform (light blue), THF (yellow), CH_2Cl_2 (blue), and acetone (red).

Table 1. Photophysical Properties of 1 in Various Solvents

solvent	λ_{abs}[a] (nm)	λ_{em}[b] (nm)	Φ_f[c]	Stokes shift (cm^{-1})
n-hexane	453[e]	490	0.08 (0.22)[f]	1667
toluene	461[d]	510	0.29 (0.42)[f]	2048
$CHCl_3$	449[d]	545	0.39 (0.46)[f]	3923
THF	452[d]	591	0.46 (−)[g]	5203
CH_2Cl_2	450[d]	585	0.56 (−)[g]	5128
acetone	445[e]	615	0.05 (−)[g]	6212

[a] Absorption maximum at the lowest energy band. [b] Emission maximum upon photoexcitation at λ = 360 nm measured at 1×10^{-5} M. [c] Absolute fluorescence quantum yield determined with a calibrated integrating sphere system. [d] Measured at 1×10^{-4} M. [e] Measured at 2×10^{-5} M. [f] Absolute fluorescence quantum yield measured in degassed solvent. [g] Significant difference was not observed in degassed solvent.

In contrast, the emission spectra of **1** exhibited a significant bathochromic solvatochromism with increasing solvent polarity, resulting in a bathochromic shift of 125 nm, as expected for previously reported B$-\pi-$N molecular systems[11] (Figure 2 and Table 1). The observation of negligible absorption solvatochromism and pronounced positive emission solvatochromism indicates a large excited-state dipole moment of the fluorescence state, as expected from the DFT-computed dipole moment (28.47 D) for the S_1 excited state at the Franck−Condon (FC) geometry of **1′** (Scheme 1). It should be noted here that the observed spectra remained unchanged in 10^{-5} to 10^{-6} M solution, thus indicating no excimer formation in the range of measured concentrations (Figure S3).

As has been often discussed for D$-\pi-$A molecular systems,[16] the fluorescence state can be determined by a subtle difference in intramolecular D$-\pi-$A conformations, which can be easily affected by the solvent polarity. As is apparent from the observed emission spectra, in *n*-hexane, **1** showed a weak emission with a complicated vibrational fine structure, which is characteristic of HBC itself and unsymmetrically alkyl group substituted HBC derivatives.[7,17] This observation indicates that the emission is from a locally excited (LE) $\pi-\pi^*$ state of the HBC core in a nonpolar environment. In nonpolar media, D−A fluorophores often have a long excited-state lifetime due to the prevention of fast intramolecular electron transfer, leading to quenching of fluorescence by oxygen.[18] As shown in Table 1, an increase of quantum yield in degassed *n*-hexane solution was seen for **1**. Interestingly, such an increase in the degassed solution was gradually diminished on going from *n*-hexane to $CHCl_3$, and no improvement was confirmed in polar solvents like THF, CH_2Cl_2, and acetone, strongly suggesting a shorter fluorescence lifetime of **1** in polar media. To examine the structural relaxation from the FC geometry of **1**, we performed the TD-DFT optimization of the first excited singlet state of **1′** at the B3LYP/6-31* level of theory. As shown in Figure 3, at the $S1$ state of **1′**, the B 2p orbital on the dimesitylboryl group becomes more conjugated with the π−face of the HBC core as a result of (i) decreasing dihedral angle between the BC_3 plane from 25.7° to 17.4° with respect to the HBC plane, and (ii) shortening of the B−C bond by 0.023 Å, while the N 2p orbital on the dianisylamino group becomes less conjugated with the π−face of the HBC core as a result of (i) increasing the dihedral angle between the NC_3 plane from 32.2° to 73.0° with respect to the HBC plane and (ii) elongation of the N−C bond by 0.048 Å. Consequently, the resulting excited state was predicted to be a quasi-twisted intramolecular charge transfer (qTICT) state, which is relaxed from the FC state by 0.28 eV, and thus, the TD-DFT computed emission wavelength of 648 nm ($f = 0.11$) is within the observed emission maxima (Figure 2 and Table 1).

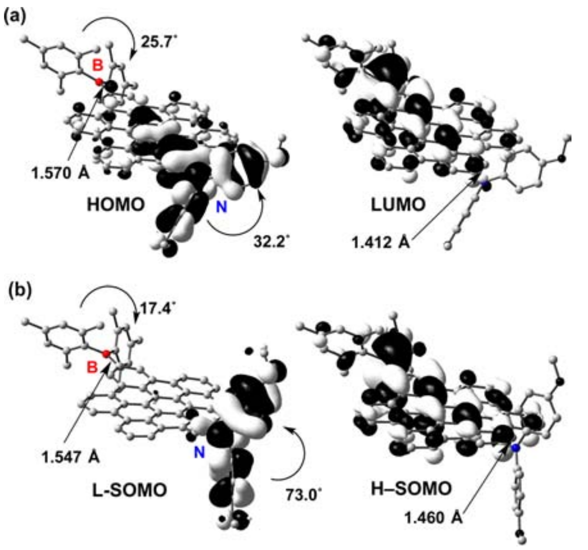


Figure 3. Molecular structures and the frontier orbitals of (a) the DFT-optimized S_0 state and (b) the TD-DFT-optimized S_1 state of **1′** at the B3LYP/6-31G* level of theory; L-SOMO and H-SOMO stand for the lowest and highest singly occupied molecular orbitals at the S_1 state.

Upon increasing the polarity of the solvent, the vibrational structure almost vanished, and bathochromically shifted emission spectra were observed. This is characteristic of an emission from the CT excited state. It has already been reported that the LE state mixes with the CT excited state.[11g,19] In highly polar solvents, the CT excited state is stabilized by the reorganization of the surrounding polar solvents; thus, the emission from the CT excited state becomes dominant. More noteworthy, the intensity of the 0−0 vibrational band relative to the second vibronic band decreases in THF and CH_2Cl_2. This strongly suggests that a conformational change of the CT excited state of **1** is, to some extent, likely to be caused by increasing the polarity of the solvent,[20] thus indicating the structural difference between the ground and excited states.

Consequently, compound **1** exhibited a quite high quantum yield of 0.56 in CH_2Cl_2, as compared with 0.33 of **DA-HBC** in in CH_2Cl_2.[8b,21] Taking account of the fact that 5,8,14,17-tetramesityl-substituted HBC has a very low quantum yield (0.028[8b] in CH_2Cl_2), the present derivative achieved 20-fold enhanced quantum yield without introducing any other fluorophores.[22] In more polar solvents, however, the quantum yield decreased sharply ($\Phi_f = 0.05$ in acetone),[23] probably due to the energy-gap law.[24] It should be noted that the abrupt decrease of the quantum yield of **1** in acetone solution can also be ascribed to the TICT-like excited state often observed in polar environments, resulting in a low radiative rate constant.[11n,16] The dual emission, which is often seen in D$-\pi-$A molecules,[19] was not observed in all of the solvents, probably because of the very weak emission from the LE state. Finally, it is worth noting that **1** showed a photoluminescence in the solid state ($\Phi_f = 0.13$), indicating that the steric hindrance by introducing Mes groups into the HBC core effectively prevents the concentration quenching in the sold state.

In summary, we have prepared a luminescent HBC derivative **1** that has donor and acceptor moieties in the molecule. In comparison to the symmetrically substituted HBC derivatives like **DA-HBC**, the present D$-\pi-$A system proved a significant enhancement of fluorescence quantum yield (Φ_f = 0.56 in CH_2Cl_2). A remarkable solvatochromic emission was found to be derived from the ICT excited state with large dipole moment through the distance of 14.4 Å (estimated by the DFT calculation) between the N and B centers, and the observed emission spectra demonstrated that the fluorescence state can be determined by a subtle difference in intramolecular D$-\pi-$A conformations, which can be easily affected by the solvent polarity. These findings show the potential ability of HBC derivatives to optoelectronic applications.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b03596.

> Experimental procedures, compound data, spectroscopic data, additional data for DFT computations, and full ref 12 (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: aito@scl.kyoto-u.ac.jp.

ORCID

Akihiro Ito: 0000-0002-8698-0032

Notes

The authors declare no competing financial interest.

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(23) The observed PL spectrum of **1** in acetone seems to be noisy as compared to that in *n*-hexane, although the quantum yield in acetone is comparable to that in *n*-hexane (Figure 2). This is probably because the fluorescence signal at each wavelength becomes seemingly weak and noisy, owing to the broadened spectrum observed in acetone solution.

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