



## A designed fluorescent anthracene derivative: Theory, calculation, synthesis, and characterization



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### ABSTRACT

5,11-Bis(phenylethynyl)benzo[1,2-f:4,5-f']diisoindole-1,3,7,9(2*H*,8*H*)-tetraone **1H** was designed as an application of the theoretical design principle for fluorescent molecules which is derived from the vibronic coupling density analysis. For solubility reasons, tertiary-butylated **1H**, 2,8-di-*tert*-butyl-5,11-bis(phenylethynyl)benzo[1,2-f:4,5-f']diisoindole-1,3,7,9(2*H*,8*H*)-tetraone **1** was synthesized and its fluorescence properties were measured. It is found that the photoluminescence quantum yield of **1** was 96%. We discuss the rationale for designing **1H** as a highly efficient fluorescent molecule, and compare the theoretical calculations for **1** with the observed absorption and photoluminescence spectra.

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### 1. Introduction

Fluorescent molecules are widely used in organic light-emitting diodes (OLEDs) [1–8] and organic fluorescent probes [9]. In particular, the development of light-emitting materials for OLEDs with high electroluminescence (EL) external quantum yields (QYs) is an important subject. In OLEDs, 25% singlet and 75% triplet excitons are generated, but in fluorescent OLEDs, triplet excitons end up in radiationless transitions. On the other hand, in phosphorescent OLEDs, triplet excitons are mainly used. Recently, thermally activated delayed fluorescence (TADF) was applied in OLEDs, to use both singlet and triplet excitons [10], and high EL external quantum yields (QYs) were observed [11]. In order to design OLEDs with high ELQYs, using any of the fluorescence, phosphorescence, and TADF mechanisms, the radiative processes should be more rapid than the radiationless processes.

In radiationless vibronic processes, vibronic couplings (VCs) or electron–phonon couplings play a crucial role [12]. Vibrational relaxation (VR) leads to energy dissipation. A low QY is caused by internal conversion (IC), which is a radiationless transition.

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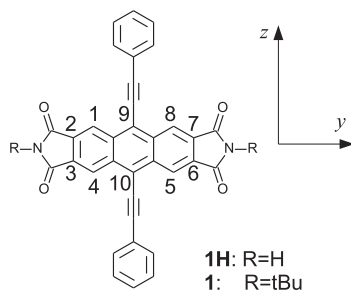
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VRs and ICs are the consequences of diagonal and off-diagonal VCs, respectively. Therefore, the vibronic coupling constants (VCCs)  $V_{ij,\alpha}$  should be small, which are defined by electronic states  $S_i$  and  $S_j$ , and vibrational mode  $\alpha$ . Small diagonal VCCs  $V_{i,\alpha}$  ( $= V_{ii,\alpha}$ ) suppress the reorganization energy  $\Delta E_i$ , or VR, in the Franck–Condon (FC)  $S_i$  state [12]. Small off-diagonal VCCs are required for the suppression of ICs.

The VCC is given by the spatial integration of the vibronic coupling density (VCD) [13], which describes the spatial distribution of VC in a molecule. The VCD is defined by  $\eta_{i,\alpha} := v_\alpha \Delta \rho_i$  for  $i = j$ , and  $\eta_{ij,\alpha} := v_\alpha \rho_{ij}$  for  $i \neq j$ , where  $v_\alpha$  is defined as the potential derivative with respect to normal-mode  $\alpha$ .  $\Delta \rho_i$  ( $:= \rho_i - \rho_0$ ) and  $\rho_{ij}$  are defined as the electron density difference between the  $S_i$  and  $S_0$  states and overlap density between the  $S_i$  and  $S_j$  states, respectively. A delocalized  $\Delta \rho_i$  or  $\rho_{ij}$  does not overlap  $v_\alpha$  largely, so that it gives rise to small VCDs, which result in small VCCs. Therefore, we can control to reduce the VCCs via VCD analysis.

A large transition dipole moment (TDM) is desirable for strong fluorescence. The transition dipole moment density (TDMD) [14] analysis also enables us to enhance TDM.

In our previous study, we showed why the dichlorination of anthracene enhances the QY, using the VCD and TDMD concepts, and proposed a design principle for fluorescent anthracene derivatives with high photoluminescence (PL) quantum yield (PLQY): *introduction of the same long  $\pi$ -conjugated substituents at the C9 and C10 atoms along the C9–C10 axis so that the point group is kept*



**Figure 1.** Structures of **1** and **1H**. The orientations of the molecules are set in the  $yz$ -plane in the calculation. The numbers indicate labels for the anthracene carbon atoms.

at  $D_{2h}$  [15]. We used this principle to design anthracene derivative, 5,11-bis(phenylethynyl)benzo[1,2-f:4,5-f']diisindole-1,3,7,9(2H,8H)-tetraone **1H** (Figure 1), as an application of the design principle. For solubility reasons, we also designed tertiary-butylated **1H**, 2,8-di-*tert*-butyl-5,11-bis(phenylethynyl)benzo[1,2-f:4,5-f']diisindole-1,3,7,9(2H,8H)-tetraone **1** (Figure 1).

In this Letter, we report the fluorescent molecule, **1H**, as an application of the design principle, and report the synthesis, measurement of fluorescence properties of **1**. We also discuss the rationale for designing **1H** as a highly efficient fluorescent molecule, and compare the theoretical calculations for **1** with the observed absorption and PL spectra. The structure of **1H** is similar to that of 9,10-diphenylanthracene (DPA), which is a well-known fluorescent molecule with 90% of PLQY [16]. In this Letter, the vibronic couplings and TDMs of anthracene and DPA are also given for comparison. The present analysis elucidates the effect of the 9,10-substitution in anthracene.

## 2. Methods

First, we designed **1H** and **1** using the VCD and TDMD analyses. Then, **1** was synthesized, and identified using its  $^1\text{H}$  NMR and mass spectra. The absorption and PL spectra, and the absolute PLQY for **1** were measured. The absorption and PL spectra of **1** were also simulated, on the basis of a previous study [17]. Solvent effect is not considered. The solvent effects on vibronic couplings have been discussed in the previous work [17]. The computational and experimental details are described in the Supplementary Data; the synthesis of **1** is shown in Figure S1.

## 3. Results and discussion

The calculated transition energies for absorption and fluorescence, oscillator strengths, and TDMs for **1H**, **1**, anthracene, and

**Table 1**  
Calculated transition energies for absorption and emission  $E$ , wavelengths  $\lambda$ , oscillator strengths  $f$ , and transition dipole moments  $\mu$  between the  $S_1$  and  $S_0$  states for **1H**, **1**, 9,10-diphenylanthracene (DPA) and anthracene.

		$E$ eV	$\lambda$ nm	$f$	$\mu$ a.u.
<b>1H</b>	Abs.	2.3036	538.22	0.6209	3.3149
	Em.	2.0780	596.66	0.6062	3.4496
<b>1</b>	Abs.	2.3096	536.82	0.6092	3.2811
	Em.	2.0827	595.30	0.5957	3.4168
Anthracene <sup>a</sup>	Abs.	3.2138	385.78	0.0524	0.8160
	Em.	2.7677	447.97	0.0542	0.8939
DPA	Abs.	3.1590	392.48	0.1507	1.3954
	Em.	2.6308	471.27	0.2145	1.8243

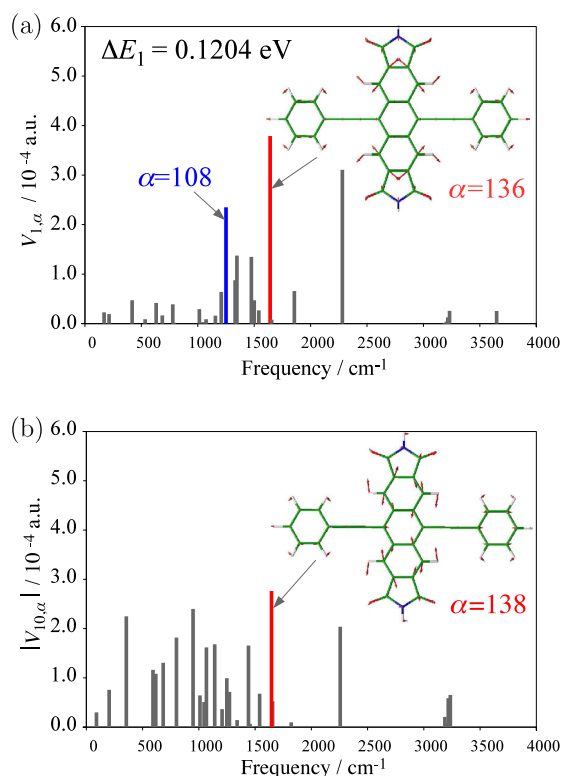
<sup>a</sup> Ref. [15].

DPA are listed in Table 1. In comparison with those for anthracene, the oscillator strengths for **1H** and **1** are large. This is ascribed to the introduction of a phenylethynyl group, on the basis of the results of TDMD analysis, as we will discuss later.

The diagonal VCCs in the FC  $S_1$  states are shown in Figure 2a. The VCCs for **1H** are smaller than those for anthracene, so **1H** has a smaller reorganization energy  $\Delta E_1$ : **1H** (0.1204 eV) < anthracene (0.2332 eV) [15]. The calculated diagonal VCCs for **1** are not very different from those for **1H**, as shown in Figure 2b. This is because the electronic structures are not much affected by the introduction of tertiary butyl groups. Therefore,  $\Delta E_1$  for **1** (=0.1211 eV) is almost the same as that for **1H**. The small  $\Delta E_1$  indicates low energy loss in the  $S_1$  state, and large FC factors; this contributes to enhancement of the fluorescence rate.

The suppression of the VCCs is caused by the introduction of carboximide groups. The diagonal VC of the maximum-coupling mode,  $\omega_{136} = 1640.96 \text{ cm}^{-1}$ , for **1H** was analyzed using the VCD concept.  $v_{136}$  obtained from the maximum-coupling mode is localized on the sides of anthracene carbon atoms (Figure 3a). A previous study showed that  $v_x$  for the maximum-coupling mode  $\alpha$  and  $\Delta\rho_1$  for anthracene are localized on the sides of C2, C3, C6, and C7 carbon atoms, and  $v_x$  couples strongly with  $\Delta\rho_1$  on these carbon atoms [15].  $\Delta\rho_1$  of **1H** is shown in Figure 3b. It is found that the carboximide groups act as electron-withdrawing groups, and  $\Delta\rho_1$  on these side carbon atoms is reduced. The small overlap between  $v_x$  and  $\Delta\rho_1$  around these carbon atoms gives rise to a small  $\eta_{1,\alpha}$  (Figure 3c). For this reason, the VCC for the maximum-coupling mode is suppressed.

The off-diagonal VCCs for **1H**, shown in Figure 2b, are on the same level as those for anthracene [15]. This is because of the delocalized overlap density  $\rho_{10}$  (see the off-diagonal VCD analysis shown in Figure S2). The delocalized  $\rho_{10}$  does not overlap  $v_x$  largely, and hence,  $\eta_{10,\alpha}$  becomes small. In addition, the number of



**Figure 2.** Vibronic coupling constants for the normal modes of **1H**: (a) diagonal elements in the Franck–Condon  $S_1$  state and maximum-coupling mode  $\omega_{136} = 1640.96 \text{ cm}^{-1}$ , and (b) off-diagonal elements between the  $S_1$  and  $S_0$  states and maximum-coupling mode  $\omega_{138} = 1646.09 \text{ cm}^{-1}$ .

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