

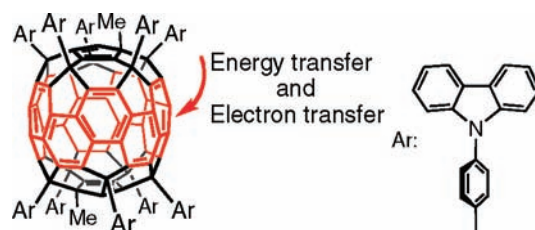
Light Emission of [10]Cyclophenacene through Energy Transfer from Neighboring Carbazolyphenyl Dendrons

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ABSTRACT



A dendritic deca(carbazolyphenyl)[60]fullerene bearing a cyclic benzenoid core was synthesized. The photophysical studies indicated that intramolecular energy transfer and electron transfer took place from the linked carbazolyphenyl moieties to the core—cyclic benzenoid moiety. The fluorescence quantum yield of the deca-adduct was determined to be 0.21 in toluene. Rich photophysical functions and their dendritic structures suggest that the photoactive decaadducts will serve as luminescent scaffolds in materials application.

Dendritic molecules are an interesting class of molecule, consisting of the core part and peripheral side chain units and hence giving us a variety of opportunities for molecular engineering of huge structures.¹ One can build a larger structure more efficiently as we employ the larger core and the more efficient side chain growing method. It is therefore natural that fullerene has been utilized as the dendrimer core because of its nanometer-scale size and moderately high chemical reactivity. For example, a dendritic hexapyrrolidine C_{60} derivative with a T_h -symmetric fullerene core (Figure 1, right)² shows a long phosphorescence lifetime ($\tau = 4$ s).^{3,4} Some other fullerenes bearing six side chains have been prepared by the Bingel–Hirsch reaction,⁵ 1,3-dipolar reaction,³ and platinum complexation.⁶

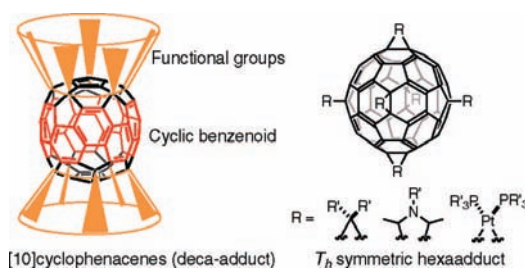


Figure 1. Structures of [10]cyclophenacene and hexaadduct.

We recently proposed that fullerene bearing ten aromatic side chains is an attractive alternative for the efficiency of the synthesis and for the hoop-shaped 40π -electron cyclophenacene system (Figure 1, left; e.g., **2**).⁷ This unique core shows

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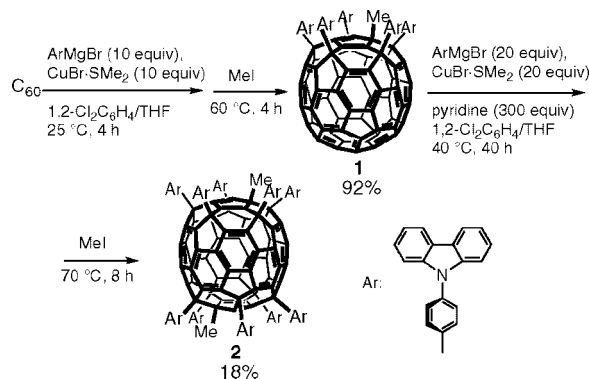
the highest fluorescence quantum yield ($\phi = 0.18$) among fullerene derivatives and a long fluorescence lifetime ($\tau \approx 65\text{--}75$ ns).^{7c} In addition, one can install organic (e.g., the methyl groups in **2** and functionalized alkyl groups⁸) and inorganic groups in the top and the bottom concave cavity of the molecule.⁹ We can also modify the side chains to endow new properties to the molecules, as we have shown that we bestow the pentaadducts an ability to form columnar or lamellar liquid crystalline assemblies.^{10,11} In this communication, we report the installation of ten photoactive units to the fullerene core, in which the side chains catch photons and transmit them to the central cyclophenacene core. We have chosen carbazolyphenyl groups as dendrons because the carbazole unit shows intense luminescence and electron mobility^{12,13} and the phenylene group acts as a linker to connect the carbazole group to the fullerene core by the organocopper methodology we developed earlier.¹⁴ We found that efficient energy transfer¹⁵ and photoinduced charge transfer¹⁶ from the ten carbazolyl antennas to the central π -system occur.

The reaction of [60]fullerene with an arylcopper reagent in the presence of excess pyridine is known to take place ten times to give a decaaddition product such as **2** in a single step. However, application of this reaction to the carbazolyphenyl copper reagent was found to be impractically slow (decaaddition 95 h and methylation 38 h, yield ca. 20%). We found that the ten carbazolyphenyl groups are

better added in two steps, that is, five groups in the first step and five others in the second. The first addition of a copper reagent, which was prepared from a carbazolyphenyl Grignard reagent and $\text{CuBr}\cdot\text{SMe}_2$, afforded the penta(carbazolyphenyl) adduct (**1**) in 92% after MeI trapping of the copper intermediate. The addition of the same reagent to the pentaadduct **1** but now in the presence of pyridine^{7c} afforded the dendritic decaadduct (**2**, yield: 18%).¹⁷ Byproducts of this reaction were a regioisomer of **2** and an octaadduct (details are shown in the Supporting Information).

The electrochemical behavior of **2** was first investigated with cyclic voltammetry (CV, Figure S5, Supporting Information). The CV data showed two-step reversible one-electron reduction at $E_{1/2} = -1.85$ and -2.32 V (vs Fc/Fc^+ , in THF). Notable is the significantly lower reduction potentials of **2** (280 mV difference for the first reduction) compared with those of a prototypal decaaryl adduct, i.e., 4-*n*-butylphenyl adduct (-2.13 and -2.51 V), indicating that the carbazolyl group acts as an electron-withdrawing group rather than a donating group as expected for an ordinary *p*-nitrogen substituent. It is evident that the nonplanar conformation of the carbazolyphenyl group relative to the phenylene group attached to the fullerene core (as indicated in Scheme 1) does not

Scheme 1. Synthesis of the Decaadduct



allow the *p*-nitrogen lone pair to be conjugated to the phenylene π -system.¹⁸

The decaadduct **2** in chloroform showed two intense absorption bands (293 and 341 nm) and one shoulder (329 nm) in the UV region and a weak absorption at 457 nm in the visible region (red line in Figure 2). The strong absorption in the UV region is largely due to the ten carbazolyphenyl moieties (cf. 9-phenylcarbazole that lacks the fullerene group, Figure S6, Supporting Information), as is evident by comparison with the spectrum of a deca-4-*n*-butylphenyl congener that lacks the carbazolyl groups (blue line).^{7c} A weak absorption at 457 nm shared in common by **2** and the deca-4-*n*-butylphenyl fullerene is due to the [10]cyclophenacene.^{7c}

(17) Compound **2** has three isomers owing to the position of the methyl attached to the fullerene relative to the position of the aryl groups (only one isomer is shown in Scheme 1).

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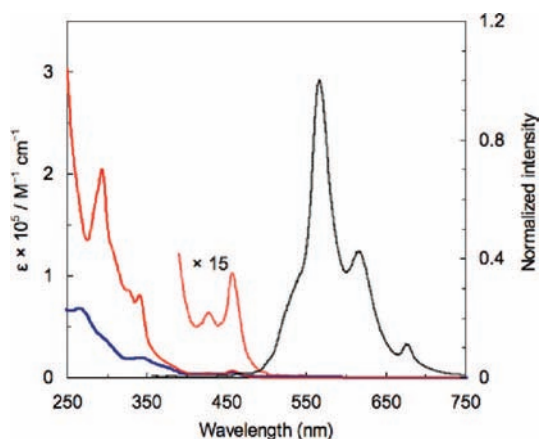


Figure 2. Absorption (red) and fluorescence (black) spectra of **2** (1×10^{-6} M) in chloroform at 25 °C ($\lambda_{\text{ex}} = 334$ nm). The peak at 670 nm is due to the instrument excitation monochromator. The blue line is an absorption spectrum of $\text{C}_{60}(\text{C}_6\text{H}_4\text{-}^n\text{Bu})_{10}\text{H}_2$ in cyclohexane.

The fluorescence spectrum of **2** upon excitation at 334 nm (where the carbazolyl groups absorb the light) in chloroform exhibited an interesting feature (Figure 2, black line). Thus, the molecule emits light only from the [10]cyclophenacene group (480–700 nm) and not from the carbazolylphenyl groups (340–450 nm observed for 9-phenylcarbazole upon excitation at 334 nm, Figure S6, Supporting Information). The profile of the emission at 480–700 nm is the same as those observed for the deca-4-*n*-butylphenyl congener and related [10]cyclophenacenes.^{7c}

The fluorescence quantum yield and lifetime of **2** in toluene were determined to be $\phi = 0.21$ and $\tau = 75$ ns (Figure S7, Supporting Information), respectively. The characteristic feature of the fluorescence spectra of **2** was affected neither by the excitation wavelength nor by the concentration (Figure S8, Supporting Information), indicating that an intramolecular “energy” transfer took place from the excited carbazolylphenyl groups to the cyclophenacene. The compound **2** shows a remarkably large difference (4240 cm^{-1}) between the narrowest gap absorption peak and the maximum emission peak, which suggests a use of **2** as a useful luminescent material (cf. Stokes shift of parent C_{60} is 1500 cm^{-1}).¹⁹

Solvent dependency of the fluorescence intensity was observed upon excitation of the fullerene group at 456 nm (Figure S9, Supporting Information), just as the same tendency was observed upon excitation of the carbazolyl group at 334 nm. As a result, the fluorescence pattern was exactly the same in different solvents, but the fluorescence

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intensity decreased as the solvent polarity increased (Table S1, Supporting Information). The quantum yields 0.21 in toluene ($\epsilon_r = 2.38$), 0.19 in CHCl_3 ($\epsilon_r = 4.81$), and 0.17 in DMF ($\epsilon_r = 36.7$). We consider that this polarity dependence is an indication of intramolecular “electron” transfer from the carbazolylphenyl groups to the excited cyclic benzenoid moiety. We suggest a deactivation pathway of the excited singlet state of **2**, which includes fast and efficient intramolecular energy transfer and electron transfer¹³ from the carbazolylphenyl moiety to the fullerene ($^1\text{C}_{60}^*$) (Figure 3).

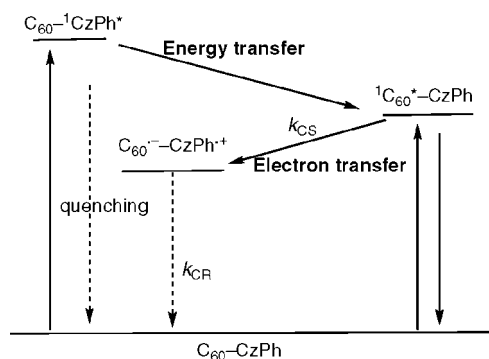


Figure 3. Proposed energy diagram for the deactivation pathway of the excited singlet state of decaadduct **2**. CzPh: the carbazolylphenyl unit.

In summary, we have synthesized a fluorescent dendritic fullerene derivative **2** that bears a [10]cyclophenacene in the core and ten carbazolyl groups as dendrons and observed an efficient energy transfer and electron transfer between the dendrons and the conjugated core. The carbazolyl groups thus show energy and the electron-donating properties in the excited states, while they act as electron-withdrawing groups in the ground state (i.e., CV behavior). Examination of the effects of the second-generation dendritic polycarbazolyl structure (i.e., a 3,6-dicarbazolylcarbazolyl unit in place of the carbazolyl groups in this paper)¹³ will be the next subject of studies.

Acknowledgment. We are grateful to Yutaka Sasaki of Science and Technology Research Center, Mitsubishi Chemical Group, for fluorescence lifetime measurement.

Supporting Information Available: Experimental procedures, absorption and fluorescence spectra of 9-phenylcarbazole, fluorescence decay, solvent-dependent fluorescence spectra, and CV data of **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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