Synthesis and Photophysical Properties of [60]Fullerene Adducts Carrying Oligocarbazole Dendrons

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[60]Fullerene adducts carrying oligocarbazole moieties were successfully prepared by the Bingel reactions. Their fluorescence spectra and transient absorption spectra suggested the intramolecular electron transfer from the oligocarbazole moiety to the fullerene moiety mainly via $^1C_{60}{}^*$.

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[60]Fullerene–donor dyads linked by covalent bondings have attracted much interest from the aspects of charge-separated states arising from the intramolecular photoinduced electron transfer.[1] Especially, porphyrins and related compounds have been extensively utilized among a variety of donor moieties.[1] In contrast, there have been only a few examples of carbazole-linked fullerene adducts,[2,3] although carbazole is a good electron donor known as a component of photoconductive poly(*N*-vinylcarbazole) (PVCz).[4] Quite recently, we have successfully prepared [60]fullerene adduct **1** (Chart 1) bearing a carbazole residue by using Bingel reaction.[5] However, the photoinduced electron transfer via the excited states of [60]fullerene was not evidently detected in adduct **1**. Aiming at the construction of further new fullerene–donor dyad systems, which can facilitate the electron transfer, the introduction of two carbazole moieties or oligocarbazole moieties onto the [60]fullerene surface was undertaken. Herein, we have designed three [60]fullerene adducts **2** and **3** bearing two carbazole or oligocarbazole moieties attached to the cyclopropane ring symmetrically. The trimeric carbazole moieties in **3** have larger π-conjugated system and more electron-donating ability than the single carbazole systems in **1** and **2**.[6]

Both **2** and **3** are expected to be accessible by the Bingel reactions using malonate esters **4** and **5**, respectively (Scheme 1). The preparation of **4** and **5** was accomplished by the reaction of malonyl dichloride with the precursor alcohols, which were readily obtained by the $NaBH_4$-reduction of the corresponding aldehydes. Scheme 2 depicts the synthetic sequence of **5** as a representative.

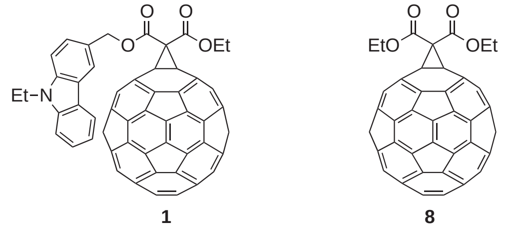
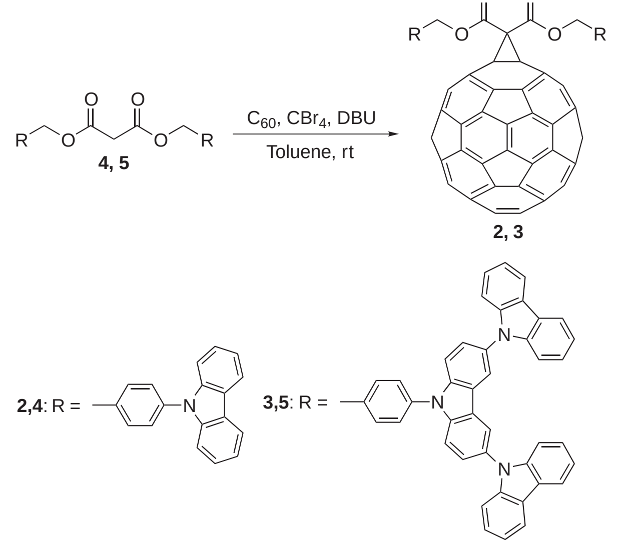
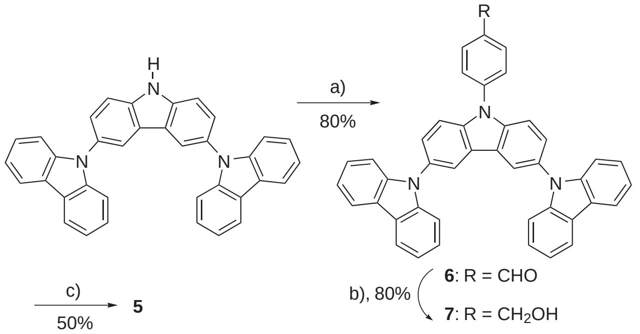


Chart 1.



Scheme 1.



Scheme 2. Reagents and conditions: a) 4-BrC_6H_4CHO, K_2CO_3, (t-Bu)$_3$P, Pd(OAc)$_2$, xylene. b) $NaBH_4$, EtOH. c) Malonyl dichloride, pyridine, CH_2Cl_2.

The Bingel reaction of **4** and **5** with [60]fullerene was carried out under conventional conditions;[7] **4** and **5** were allowed to react with [60]fullerene, CBr_4, and DBU in toluene at room temperature for 6 h to give monoadducts **2** and **3** in 30 and 29% isolated yields, respectively (Scheme 1), along with bisadducts as regioisomeric mixtures. Both **2** and **3** were isolated by column chromatography (silica gel) with toluene as the eluent.

Monoadducts **2** and **3** were definitely characterized by ^1H and ^{13}C NMR, APCI-mass, and UV–vis spectroscopies. The ^1H NMR spectra, composed of carbazole and phenyl proton peaks and benzyl proton peak (singlet), apparently demonstrated their structures.[8] Among these peaks, phenyl and benzyl proton peaks were down-field shifted relative to those of precursors **4**

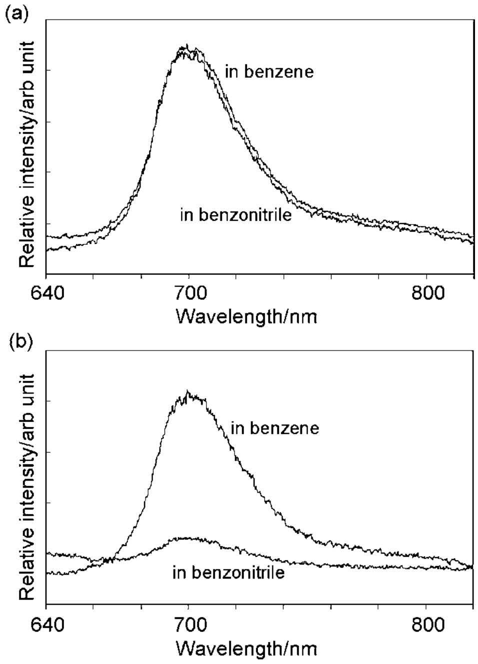


Figure 1. Fluorescence spectra of (a) **2** and (b) **3** in benzene and benzonitrile at room temperature ($\lambda_{ex} = 430\,\text{nm}$).

and **5**, due to the deshielding effect of the fullerene moiety. The APCI-mass spectra of **2** and **3** afforded a molecular ion peak of $m/z = 1332$ and 1992, respectively. The UV–vis spectra of these adducts exhibited a sharp peak around 430 nm and a broad band around 700 nm, which are characteristic of cyclopropanated [60]fullerene monoadducts.[9]

Fluorescence spectra of **2** and **3** were measured at room temperature under several conditions (Figure 1). In 292-nm excitation, which can afford the excited state (^{1}Carbazole*) of carbazole moiety as well as [60]fullerene moiety, the fluorescence of carbazole moieties in **2** and **3** was almost completely quenched in benzene, cyclohexane, or dichloromethane, whereas precursors **4** and **5** afforded intense emission at this excitation wavelength. This quenching in **2** and **3** is probably ascribed to the intramolecular energy (and/or electron) transfer from the carbazole moiety to the fullerene moiety, since the S_1 energy of carbazole is higher than that of C_{60}. In order to produce the excited state ($^1C_{60}{}^*$) of [60]fullerene moiety exclusively, the fluorescence spectra were also measured in 430-nm excitation. In benzene, both **2** and **3** exhibited weak and broad fluorescence around 700 nm, similar to [60]fullerene monoadducts without a carbazole moiety such as **8**. There was no appreciable difference in the fluorescence intensity between **2** and **3**. Thus, it is obvious that the fluorescence of [60]fullerene moiety for **2** and **3** is not quenched in benzene. In benzonitrile, however, the behavior of **2** and **3** remarkably contrasts with each other. While **2** showed almost the same emission as that in benzene, the fluorescence of **3** was extremely quenched. The quenching in **3** indicates that the intramolecular electron transfer from the carbazole moiety to the fullerene moiety via $^1C_{60}{}^*$ takes place, as previously observed in the [60]fullerene adduct bearing an *N*,*N*-dimethylaniline moiety.[10] On the contrary, it is obvious that the intramolecular electron transfer via $^1C_{60}{}^*$ is hardly involved in **2**. Such difference in fluorescence in benzonitrile between **2** and **3** seems quite reasonable, since the trimeric carbazole moiety in **3** has more electron-donating ability than the monomeric carbazole moiety in **2**; the difference in their oxidation potentials is ca. 0.2 V.[6]

Transient absorption spectra of **2** and **3** were also measured by 532-nm laser flash photolysis in benzonitrile at room temperature along with reference monoadduct **8**. All of **2**, **3**, and **8** exhibited transient absorption spectra characteristic of the excited triplet state ($^3C_{60}{}^*$) of [60]fullerene moiety with a maximum around 710–720 nm. However, the initial absorbance in **3** at 720 nm was considerably small compared to that in **2** and **8**. This observation is consistent with the results in fluorescence measurements; for **3** in benzonitrile, $^1C_{60}{}^*$ is significantly quenched by the intramolecular electron transfer via $^1C_{60}{}^*$, leading to the less extent of ISC to $^3C_{60}{}^*$ in **3** than **2** and **8**. Furthermore, the lifetime of $^3C_{60}{}^*$ in **3** (28 μs) determined at 720 nm was shorter than those in **2** and **8** (42 μs), which may suggest the possibility of the intramolecular electron transfer via $^3C_{60}{}^*$ in addition to $^1C_{60}{}^*$ in **3**.

In summary, we have first successfully synthesized oligocarbazole-linked [60]fullerene adduct **3**. The fluorescence spectra and transient absorption spectra of **3** suggested the intramolecular electron transfer from the oligocarbazole moiety to the fullerene moiety mainly via $^1C_{60}{}^*$. More detailed photophysical investigation and synthesis of other oligocarbazole-linked [60]fullerene adducts is now in progress.

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8 Selected spectroscopic data of **2** and **3**. **2**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.67 (s, 4H), 7.26–7.29 (m, 4H), 7.33–7.38 (m, 8H), 7.61 (d, $J = 8.0$ Hz, 4H), 7.74 (d, $J = 8.0$ Hz, 4H), 8.12 (d, $J = 7.5$ Hz, 4H). **3**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.71 (s, 4H), 7.24–7.28 (m, 8H), 7.34–7.37 (m, 16H), 7.54 (d, $J = 9.0$ Hz, 4H), 7.61 (d, $J = 9.0$ Hz, 4H), 7.77 (d, $J = 8.0$ Hz, 4H), 7.85 (d, $J = 8.5$ Hz, 4H), 8.13 (d, $J = 8.0$ Hz, 8H), 8.24 (s, 4H).

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