Abstract: Due to the partially reduced π-conjugation of the fullerene cage, multi-functionalized fullerene derivatives exhibit remarkable fluorescent properties compared to pristine fullerenes, which have high potential for application in organic light-emitting diodes (OLEDs). In this study two multi-functionalized C_{70} derivatives, C_{70}(OCH_3)_{10}[C(COOEt)_2] and C_{70}(OCH_3)_{10}[C(COOEt)_2]_2, with excellent fluorescent properties, were designed and synthesized. Compared with C_{70}(OCH_3)_{10} containing a single kind of functional group, both the C_{70}(OCH_3)_{10}[C(COOEt)_2] and C_{70}(OCH_3)_{10}[C(COOEt)_2]_2 exhibited enhanced fluorescence properties with blue fluorescence emission. The fluorescence quantum yields of the C_{70}(OCH_3)_{10}[C(COOEt)_2] and C_{70}(OCH_3)_{10}[C(COOEt)_2]_2 were 1.94% and 2.30%, respectively, which were about ten times higher than that of C_{70}(OCH_3)_{10}. The theoretical calculations revealed that the multi-functionalization of the C_{70} increased the S_1–T_1 energy gap, reducing the intersystem crossing efficiency, resulting in the higher fluorescence quantum yield of the C_{70} derivatives. The results indicate that multi-functionalization is a viable strategy to improve the fluorescence of fullerene derivatives.

Keywords: fullerene; multi-functionalization; fluorescence

1. Introduction

Fluorescence studies on fullerenes and their derivatives have attracted great interest from researchers [1–13], who can not only offer vital information on the excited electronic structures of fullerenes and their derivatives, but can also assess their potential applications in organic electronic devices [14,15]. Due to the renowned electron-accepting ability and small reorganization energy of symmetric fullerenes [16,17], the transition from S_0 to S_1 is forbidden, and the intersystem crossing (ISC) efficiency from S_1 to T_1 is very high (close to 100%) [18]. Pristine fullerenes exhibit poor fluorescence properties, such as low-fluorescence quantum yields (Φ of ca. 0.03% for C_{60} and ca. 0.06% for C_{70} in toluene) and short fluorescence lifetimes (τ of 1.2 ns for C_{60} and 0.67 ns for C_{70}) [19–22]. The functionalization of fullerene is a valid way to increase electronic transition forbiddance and the S_1–T_1 energy gap by lowering the symmetry of the fullerene. However, the fluorescence of mono-, bis-, and tris-adducts of fullerene derivatives is still extremely weak, since these adducts cannot effectively destroy the symmetric structure of fullerenes [23]. Multi-functionalization with higher adducts has been proven to be an effective methodology to fine-tune the fluorescence properties of fullerene derivatives. For instance, Rubin et al. reported a hexa-adduct of C_{60} that exhibited much-improved fluorescence intensity [24]. Multi-functionalized C_{60} derivatives with excellent
fluorescence properties were prepared by Nakamura et al. [25–27]. Compared with the studies on the fluorescence properties of C_{60} derivatives, there are few studies on the fluorescence properties of C_{70} derivatives [28].

Herein, we report the synthesis and fluorescence properties of two multi-functionalized C_{70} derivatives, C_{70}(OCH_{3})_{10}[C(COOEt)_{2}] and C_{70}(OCH_{3})_{10}[C(COOEt)_{2}][1]. By carefully controlling the molar ratio of the reactants, C_{70}(OCH_{3})_{10}[C(COOEt)_{2}] and C_{70}(OCH_{3})_{10}[C(COOEt)_{2}] can be readily synthesized from C_{70}(OCH_{3})_{10} by using the Bingel–Hirsch reaction with high selectivity. Due to the reduced π-conjugated system of C_{70}, the fluorescence quantum yield of C_{70}(OCH_{3})_{10}[C(COOEt)_{2}] and C_{70}(OCH_{3})_{10}[C(COOEt)_{2}] was about ten times higher than that of C_{70}(OCH_{3})_{10}. The results provide a method for synthesizing fullerene derivatives with excellent fluorescence, offering valuable materials for organic light-emitting diodes.

2. Materials and Methods

2.1. Materials and Synthesis

C_{70}, iodine monochloride (ICl), silver perchlorate, diethyl bromomalonate, and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were purchased from commercial suppliers and used as received without further purification. Solvents were distilled and dried by standard procedures.

C_{70}Cl_{10} and C_{70}(OCH_{3})_{10} were prepared according to the procedure in the literature [28,29]. C_{70}(OCH_{3})_{10}[C(COOEt)_{2}]: Diethyl bromomalonate (12 mg, 0.05 mmol) and DBU (16 mg, 0.1 mmol) were added to a solution of C_{70}(OCH_{3})_{10} (58 mg, 0.05 mmol) in anhydrous toluene (50 mL). The mixture was stirred overnight under atmosphere at room temperature. The solvent was removed under reduced pressure and the crude product was purified by column chromatography over silica gel with toluene/acetate (10:1) as the eluents to afford C_{70}(OCH_{3})_{10} as a pale-yellow solid (29 mg, 39%).

\[ \delta \text{H NMR (500 MHz, CDCl}_{3}, \text{ppm): } \delta 4.21 (q, J = 7.0 \text{ Hz}, 4H), 3.98 (s, 6H), 3.93 (s, 12H), 3.86 (s, 6H), 3.75 (s, 6H), \text{and 1.22 (t, } J = 7.0 \text{ Hz, 6H).} \]

\[ \delta \text{C NMR (500 MHz, CDCl}_{3}, \text{ppm): } \delta 163.56, 153.40, 153.07, 151.78, 151.29, 150.78, 150.73, 149.91, 149.40, 148.90, 148.54, 148.42, 148.24, 148.22, 148.11, 147.88, 147.79, 146.61, 146.49, 146.13, 145.41, 145.12, 143.71, 142.96, 139.00, 138.83, 138.58, 137.46, 135.93, 134.20, 129.04, 128.23, 86.18, 81.21, 81.03, 80.81, 80.69, 67.79, 65.89, 63.10, 56.18, 56.11, 55.94, 55.91, 55.85, 43.47, \text{and 14.03.} \]

ESI-FT-ICR-HRMS C_{67}H_{40}O_{14}[M+Na]^+ m/z calculated 1331.2310 found 1331.2311.

The C_{70}(OCH_{3})_{10}[C(COOEt)_{2}]: Diethyl bromomalonate (48 mg, 0.2 mmol) and DBU (60 mg, 0.4 mmol) were added to a solution of C_{70}(OCH_{3})_{10} (58 mg, 0.05 mmol) in anhydrous toluene (50 mL). The mixture was stirred overnight under atmosphere at room temperature. The solvent was removed under reduced pressure and the crude product was purified by column chromatography over silica gel with toluene/acetate (5:1) as the eluents to afford C_{70}(OCH_{3})_{10}[C(COOEt)_{2}] as a yellow-light solid (29 mg, 39%).

\[ \delta \text{H NMR (500 MHz, CDCl}_{3}, \text{ppm): } \delta 4.33 (m, 8H), 4.00-3.77 (m, 30H), \text{and 1.38–1.30 (m, 12H).} \]

\[ \delta \text{C NMR (500 MHz, CDCl}_{3}, \text{ppm): } \delta 163.70, 163.67, 163.64, 163.21, 154.21, 153.22, 151.89, 151.80, 151.39, 151.34, 150.58, 150.33, 150.00, 149.62, 149.02, 148.90, 148.59, 148.31, 147.83, 147.53, 147.24, 146.91, 146.62, 146.52, 146.44, 146.30, 145.85, 145.60, 145.30, 145.26, 144.01, 144.60, 144.47, 143.67, 142.71, 139.95, 139.66, 139.12, 138.89, 138.14, 137.77, 137.52, 136.59, 136.24, 135.58, 134.38, 133.50, 130.01, 85.49, 84.51, 81.06, 80.94, 80.86, 80.80, 80.76, 80.70, 67.89, 67.80, 63.10, 63.07, 62.94, 62.88, 55.97, 55.93, 55.87, 55.79, 55.71, 55.68, 55.20, 43.44, 41.00, \text{and 14.06.} \]

ESI-FT-ICR-HRMS C_{94}H_{50}O_{18}[M+Na]^+ m/z calculated 1490.3847 found 1490.2916.

2.2. Characterization

\[ ^{1}H \text{ NMR, } ^{13}C \text{ NMR, and 2D NMR spectra were recorded using Bruker AVIII500 spectrometers (Bruker, Billerica, MA, USA). High-resolution mass spectra (HRMS) were recorded on Agilent G6545XT mass spectrometers (Agilent, Santa Clara, CA, USA). UV-vis absorption spectra in solution were recorded using an Agilent Cary 5000 spectrophotometer (Agilent, Santa Clara, CA, USA).} \]

\[ \text{The spectra were measured in quartz glass cuvettes using spectroscopic grade solvents. Fluorescence spectroscopy in solution was carried out} \]
with an FLS980 spectrometer (Edinburgh Instruments, Livingston, UK). Time-resolved measurements were performed with a PS laser diode and a TCSPC detection unit. Single-crystal X-ray data were collected on a Rigaku Xtalab Synergy diffractometer (Rigaku, Tokyo, Japan). Using Olex2 [30], the initial structure was solved with the SHELX-XT structure solution program using direct method and refined with the XL refinement package using least-squares minimization.

3. Results and Discussion

As shown in Scheme 1, the C$_{70}$(OCH$_3$)$_{10}$[C(COOEt)$_2$] and C$_{70}$(OCH$_3$)$_{10}$[C(COOEt)$_2$]$_2$ were synthesized from C$_{70}$(OCH$_3$)$_{10}$ by Bingel–Hirsch reaction. The deca-adduct C$_{70}$ derivative C$_{70}$(OCH$_3$)$_{10}$ was readily prepared by treating the C$_{70}$Cl$_{10}$ with anhydrous methanol in the presence of silver perchlorate. C$_{70}$(OCH$_3$)$_{10}$[C(COOEt)$_2$] and C$_{70}$(OCH$_3$)$_{10}$[C(COOEt)$_2$]$_2$ can be readily synthesized with high selectivity by carefully controlling the molar ratio of the reactants. Their molecular structures were confirmed by $^1$H, $^{13}$C NMR spectroscopy and high-resolution mass spectrometry (Figures S1–S10). The two-dimensional correlated spectroscopy (COSY) showed that there was mutual coupling of the protons between the methyl and the methylene in the ethyl malonate of both the C$_{70}$(OCH$_3$)$_{10}$[C(COOEt)$_2$] and the C$_{70}$(OCH$_3$)$_{10}$[C(COOEt)$_2$]$_2$ molecules (Figures S4 and S9).

Scheme 1. Synthesis of C$_{70}$(OCH$_3$)$_{10}$[C(COOEt)$_2$] and C$_{70}$(OCH$_3$)$_{10}$[C(COOEt)$_2$]$_2$.

The structure of the C$_{70}$(OCH$_3$)$_{10}$[C(COOEt)$_2$] was unambiguously determined by X-ray crystallographic analysis (Figure 1 and Table S1). Single crystals were obtained through the slow diffusion of hexane into a toluene solution of C$_{70}$(OCH$_3$)$_{10}$[C(COOEt)$_2$]. As shown in Figure 1, all the methoxy groups were distributed on the equatorial region of the C$_{70}$ cage. The malonate group was added to the pole of the C$_{70}$ cage, and the
ester groups were pointed in different directions to minimize the steric hindrance. In the crystalline state, the C$_{70}$(OCH$_3$)$_{10}$[C(COOEt)$_2$]$_2$ molecules displayed ordered packing in all the directions of the a-, b- and c-axes. Although the single crystal of the C$_{70}$(OCH$_3$)$_{10}$[C(COOEt)$_2$]$_2$ was not obtained, the most favorable structure of C$_{70}$(OCH$_3$)$_{10}$[C(COOEt)$_2$]$_2$ was determined through a series of theoretical calculations (Figures S11–S13). As shown in Figure S14, the two malonate groups were distributed at the two poles of the C$_{70}$ cage. Similarly, all the functionalized groups were oriented in different directions to minimize the steric hindrance.

The UV-vis absorption spectra of the C$_{70}$(OCH$_3$)$_{10}$, C$_{70}$(OCH$_3$)$_{10}$[C(COOEt)$_2$]$_2$, and C$_{70}$(OCH$_3$)$_{10}$[C(COOEt)$_2$]$_2$ were measured at room temperature. As shown in Figure 2, the C$_{70}$(OCH$_3$)$_{10}$ exhibited two absorption peaks at 435 and 480 nm in the visible region, and one absorption peak at 315 nm in the ultraviolet region. By contrast, there was no absorption peak in the visible region, but there was one absorption peak in the ultraviolet region (313 nm) for C$_{70}$(OCH$_3$)$_{10}$[C(COOEt)$_2$]$_2$, which was slightly blue-shifted with respect to the C$_{70}$(OCH$_3$)$_{10}$. Similarly, the C$_{70}$(OCH$_3$)$_{10}$[C(COOEt)$_2$]$_2$ showed an absorption peak at 305 nm, which was further blue-shifted compared with that of the C$_{70}$(OCH$_3$)$_{10}$[C(COOEt)$_2$]$_2$. Moreover, a broad shoulder peak around 370 nm was observed for the C$_{70}$(OCH$_3$)$_{10}$[C(COOEt)$_2$]$_2$. The blue-shifting of the absorption peaks of both C$_{70}$(OCH$_3$)$_{10}$[C(COOEt)$_2$]$_2$ and C$_{70}$(OCH$_3$)$_{10}$[C(COOEt)$_2$]$_2$ was caused by the decrease in the π-conjugated system of the C$_{70}$ cage, indicating that the energy gap between the S$_1$ and S$_0$ became larger.

**Figure 1.** Crystal structure of C$_{70}$(OCH$_3$)$_{10}$[C(COOEt)$_2$]$_2$. (A) ORTEP drawing with 50% ellipsoid probability. The molecular packing along a-axis (B), b-axis (C), and c-axis (D).
To obtain information about the photophysical properties of the C70(OCH3)10, C70(OCH3)10[C(COOEt)2], and C70(OCH3)10[C(COOEt)2]2, we measured the steady-state fluorescence spectra of these C70 derivatives. As shown in Figure 3, the emission peak of the C70(OCH3)10 was 498 nm, with a shoulder peak at 521 nm. The major emission peak at 498 nm was ascribed to the S1 → S0 transition, and the shoulder peak was ascribed to the transition involving the vibronic interactions [4,5]. The fluorescence spectra of the C70(OCH3)10[C(COOEt)2] and C70(OCH3)10[C(COOEt)2]2 were rather similar. The major peaks appeared at 451 and 454 nm for the C70(OCH3)10[C(COOEt)2] and the C70(OCH3)10[C(COOEt)2]2, respectively, while the shoulder peaks were shown at 480, and 481 nm. Obviously, the fluorescence emission peaks of the C70(OCH3)10[C(COOEt)2] and C70(OCH3)10[C(COOEt)2]2 were blue-shifted compared to those of the C70(OCH3)10, indicating that the Bingel–Hirsch reaction can effectively reduce the π-conjugated system of the C70 cage [21]. The fluorescence quantum yields of these fullerene derivatives were obtained with integrating spheres. The fluorescence quantum yields of the C70(OCH3)10[C(COOEt)2] and C70(OCH3)10[C(COOEt)2]2 were 1.94, and 2.30%, respectively, which were about ten times higher than that of the C70(OCH3)10 (0.25%). However, the fluorescence quantum yields of both the C70(OCH3)10[C(COOEt)2] and the C70(OCH3)10[C(COOEt)2]2 were not particularly high, which made them difficult to use as fluorescent labels.

Figure 2. UV-vis absorption spectra of C70(OCH3)10, C70(OCH3)10[C(COOEt)2], and C70(OCH3)10[C(COOEt)2]2 in a 1.0 × 10^{-5} mol/L chloroform solution at room temperature.
Table 1. Normalized steady-state fluorescence spectra of C\textsubscript{70}(OCH\textsubscript{3})\textsubscript{10}, C\textsubscript{70}(OCH\textsubscript{3})\textsubscript{10}[C(COOEt)\textsubscript{2}], and C\textsubscript{70}(OCH\textsubscript{3})\textsubscript{10}[C(COOEt)\textsubscript{2}]\textsubscript{2} at room temperature.

The fluorescent decay profiles of the C\textsubscript{70}(OCH\textsubscript{3})\textsubscript{10}, C\textsubscript{70}(OCH\textsubscript{3})\textsubscript{10}[C(COOEt)\textsubscript{2}], and C\textsubscript{70}(OCH\textsubscript{3})\textsubscript{10}[C(COOEt)\textsubscript{2}]\textsubscript{2} in chloroform were recorded using the time-correlated single-photon counting (TCSPC) method. The fluorescence lifetime of the C\textsubscript{70}(OCH\textsubscript{3})\textsubscript{10} was described by a single-exponential component with \( \tau = 1.16 \) ns. However, the fluorescence lifetime of the C\textsubscript{70}(OCH\textsubscript{3})\textsubscript{10}[C(COOEt)\textsubscript{2}] (\( \tau = 1.99 \) ns) was described by double-exponential components with \( \tau_1 = 1.18 \) ns (70.9\%) and \( \tau_2 = 3.95 \) ns (29.1\%). Similarly, the fluorescence lifetime of the C\textsubscript{70}(OCH\textsubscript{3})\textsubscript{10}[C(COOEt)\textsubscript{2}]\textsubscript{2} (\( \tau = 1.82 \) ns) was also described by bi-exponential components with \( \tau_1 = 1.18 \) ns (72.0\%) and \( \tau_2 = 3.44 \) ns (28.0\%) (Table 1). As shown in Figure 4, the fluorescence lifetimes of the C\textsubscript{70}(OCH\textsubscript{3})\textsubscript{10}[C(COOEt)\textsubscript{2}] and C\textsubscript{70}(OCH\textsubscript{3})\textsubscript{10}[C(COOEt)\textsubscript{2}]\textsubscript{2} were slightly longer than those of the C\textsubscript{70}(OCH\textsubscript{3})\textsubscript{10}, which implies that the number of adducts on fullerene can influence the fluorescence lifetime of fullerene derivatives [27]. Fullerene derivatives with more adducts may have higher fluorescence quantum yields and longer fluorescence lifetimes. Therefore, multi-functionalization is a promising strategy to improve the fluorescence of fullerene derivatives.
were computed through TD-DFT. The excitations of the C70 derivatives resulted in higher fluorescence quantum yields due to reduced intersystem crossing efficiency.

Table 1. Fluorescence lifetimes of C70(OCH3)10, C70(OCH3)10[C(COOEt)2] and C70(OCH3)10[C(COOEt)2]2. The values in parentheses represent the fractions of each kinetic lifetime.

| Compound                  | τ1 (ns) | τ2 (ns) | τ (ns) | QY (%) |
|---------------------------|---------|---------|--------|--------|
| C70(OCH3)10               | 1.16 (100%) |        | 1.16   | 0.25   |
| C70(OCH3)10[C(COOEt)2]    | 1.18 (70.9%) | 3.95 (29.1%) | 1.99   | 1.94   |
| C70(OCH3)10[C(COOEt)2]2   | 1.18 (72.0%) | 3.44 (28.0%) | 1.82   | 2.30   |

Figure 4. Time-resolved fluorescence decay profiles of C70(OCH3)10, C70(OCH3)10[C(COOEt)2], and C70(OCH3)10[C(COOEt)2]2.

To gain insight into the mechanisms of the fluorescence enhancements, we carried out theoretical calculations. Generally, the compounds with high fluorescence quantum yields had large S1–T1 energy gaps. Furthermore, the larger S1–T1 energy gaps appeared when the excitation was more localized. As shown in Figure 5, the difference S1/S0 electronic densities of the C70(OCH3)10, C70(OCH3)10[C(COOEt)2], and C70(OCH3)10[C(COOEt)2]2 were computed through TD-DFT. The excitations of the C70(OCH3)10[C(COOEt)2] and C70(OCH3)10[C(COOEt)2]2 were similar and spatially localized in the same fragment of the molecule, which meant a large S1–T1 energy gap. However, the large spatial extension led to a small S1–T1 energy gap, as with the C70(OCH3)10. Therefore, the further functionalization of the C70(OCH3)10 increased the S1–T1 energy gap, reducing the intersystem crossing efficiency, resulting in the higher fluorescence quantum yield of the C70 derivatives.
were blue-shifted due to the decrease in the π-conjugated system of the C70. Moreover, the C70(OCH3)10[C(COOEt)2] and C70(OCH3)10[C(COOEt)2]2 showed blue fluorescence, and their fluorescence quantum yield was about ten times higher than that of the C70(OCH3)10. The TD-DFT calculations indicated that the multi-functionalization of the C70 increased the S1–T1 energy gap, reducing the intersystem crossing efficiency, resulting in the higher fluorescence quantum yield of the C70 derivatives. The results reveal that multi-functionalization is an effective strategy to improve the fluorescence of fullerene derivatives, providing novel organic electronic materials for organic light-emitting diodes.

4. Conclusions

In summary, two multi-functionalized C70 derivatives, C70(OCH3)10[C(COOEt)2] and C70(OCH3)10[C(COOEt)2]2, were synthesized from C70(OCH3)10 by Bingel–Hirsch reaction with high selectivity. Compared with the C70(OCH3)10, the UV-vis absorption and fluorescence of both the C70(OCH3)10[C(COOEt)2] and the C70(OCH3)10[C(COOEt)2]2 were blue-shifted due to the decrease in the π-conjugated system of the C70. The results reveal that multi-functionalization is an effective strategy to improve the fluorescence of fullerene derivatives, providing novel organic electronic materials for organic light-emitting diodes.
C_{70}(OCH_3)_{10}[C(COOEt)_2]; Figure S3: ESI-FT-ICR-HRMS spectra of C_{70}(OCH_3)_{10}[C(COOEt)_2]; Figure S4: COSY spectra of C_{70}(OCH_3)_{10}[C(COOEt)_2]; Figure S5: HSQC of C_{70}(OCH_3)_{10}[C(COOEt)_2]; Figure S6: $^1$H NMR spectrum (500 MHz, CDCl_3) of C_{70}(OCH_3)_{10}[C(COOEt)_2]; Figure S7: $^{13}$C NMR spectrum (500 MHz, CDCl_3) of C_{70}(OCH_3)_{10}[C(COOEt)_2]; Figure S8: ESI-FT-ICR-HRMS spectra of C_{70}(OCH_3)_{10}[C(COOEt)_2]; Figure S9: COSY spectra of C_{70}(OCH_3)_{10}[C(COOEt)_2]; Figure S10: HSQC spectra of C_{70}(OCH_3)_{10}[C(COOEt)_2]; Table S1: Crystallographic data for C_{70}(OCH_3)_{10}[C(COOEt)_2]; Figure S11: Natural Population Analysis (NPA) charge distribution of C_{70}(OCH_3)_{10}[C(COOEt)_2] (A), C_{70}(OCH_3)_{10}[C(COOEt)_2]-I (B), C_{70}(OCH_3)_{10}[C(COOEt)_2]-II (C), C_{70}(OCH_3)_{10}[C(COOEt)_2]-III (D). And C_{70}(OCH_3)_{10} is shown in three orientations front view, top view and bottom view (E); Figure S12: Electrostatic potentials on the 0.001 a.u. molecular surfaces of C_{70}(OCH_3)_{10} (A), C_{70}(OCH_3)_{10}[C(COOEt)_2] (B) and C_{70}(OCH_3)_{10}[C(COOEt)_2] (C), calculated at B3LYP-D3BJ/6-31G(d, p) level with toluene solvent; Figure S13: Molecular orbitals (HOMO-I, HOMO, LUMO, and LUMO+1) of C_{70}(OCH_3)_{10} (A), C_{70}(OCH_3)_{10}[C(COOEt)_2] (B) and C_{70}(OCH_3)_{10}[C(COOEt)_2] (C) calculated at B3LYP-D3BJ/6-31G(d, p) level, in toluene; Figure S14: The most favorable structure of C_{70}(OCH_3)_{10}[C(COOEt)_2]. References [31–40] are cited in supplementary materials.

Author Contributions: Investigation, writing—original draft, K.L., L.W.; data collection, K.L., L.W., F.-F.X., B.-W.C. and Z.-C.C. Conceptualization, supervision, writing—revision, L.-L.D., S.-Y.X. and L.-S.Z. All authors have read and agreed to the published version of the manuscript.

Funding: This research was supported by the National Nature Science Foundation of China (21721001, 92061122, and 92061204).

Data Availability Statement: The data presented in this study are available in the article and Supplementary Materials.

Conflicts of Interest: The authors declare no conflict of interest.

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