

Regiochemically Controlled Synthesis of a β -4- β' [70]Fullerene Bis-Adduct

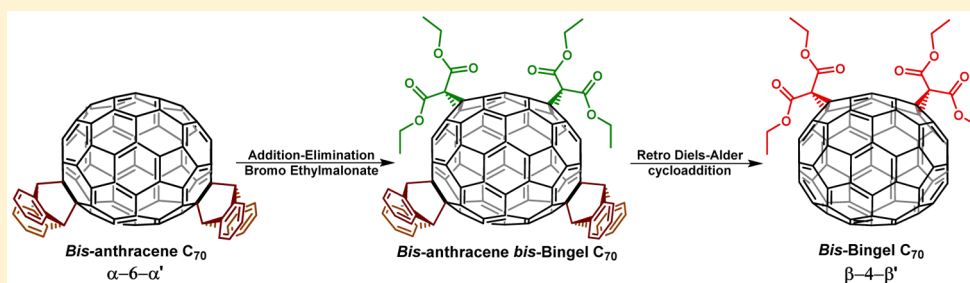
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Supporting Information



ABSTRACT: A β -4- β' C_{70} bis-adduct regioisomer and an uncommon mono-adduct β -malonate C_{70} derivative were synthesized by using a Diels–Alder cycloaddition followed by an addition–elimination of bromo-ethylmalonate and a retro-Diels–Alder cycloaddition reaction. We also report the regioselective synthesis and spectroscopic characterization of C_5 -symmetric tris- and C_{2v} -symmetric tetra-adducts of C_{70} , which are the precursors of the mono- and bis-adduct final products.

INTRODUCTION

Chemical functionalization of fullerenes has been extensively studied,^{1–3} mainly to increase their solubilities and to tune their electronic properties to expand their applications.² Recently, bis-functionalization of fullerenes such as C_{60} and C_{70} has attracted considerable attention due to the higher power conversion efficiencies (PCEs) that they exhibit in organic photovoltaic (OPV) solar cells compared with their respective mono-adduct counterparts.^{4–9} It has also been shown that by replacing C_{60} with C_{70} , higher short circuit currents and an increase in the absorption coefficient in the visible region can be obtained.⁴

The effects of bis-adduct isomerism on device performances of OPV solar cells has been reported; in most cases, it was observed that regioisomerically pure bis-adducts perform better than the corresponding regioisomeric mixtures.^{4,10–15} Consequently, regiochemically controlled multifunctionalization of fullerenes has become critical to obtain pure isomers and to avoid challenging chromatographic separations.¹⁶ There are two well-known methods to reduce the number of isomers: the tether-directed remote multifunctionalization introduced by Diederich et al.,¹⁷ and the topologically controlled method introduced by Kräutler et al.^{18,19} Both methods have been widely used to synthesize bis-, tris-, tetra-, penta-, and hexa-derivatives of C_{60} . However, multifunctionalization of C_{70} has not been extensively investigated, primarily as a result of the

lower symmetry of the D_{5h} - C_{70} compared to that of the I_h - C_{60} , which increases the number of isomers. Thus, when identical addends are used and additions exclusively to [6,6]-bonds are considered, the number of statistically possible bis-regioisomers are 8 for C_{60} and 64 for C_{70} . There are very few examples of tris- and tetra-adducts of C_{70} : the first one was reported in 1995 by Diederich et al.²⁰ They started from the 5 o'clock or the 12 o'clock bis-adduct α -9- α' or α -6- α' , respectively, using a recently introduced nomenclature²¹ and added an excess of bromo-ethylmalonate to obtain one tris-adduct and one C_{2v} - or C_{2v} -symmetric tetra-adduct isomer, respectively.^{22,23}

The synthesis of all possible C_{70} bis-adduct isomers in a selective manner has not been reported. Here, we report the synthesis of a bis-regioisomer using a Diels–Alder cycloaddition followed by an addition–elimination of bromo-ethylmalonate and finally a retro-Diels–Alder cycloaddition reaction to obtain the β -4- β' bis-regioisomer.

RESULTS AND DISCUSSION

We synthesized regioselectively the C_{70} α -6- α' bis-anthracene (BA- C_{70}) using the previously reported Diels–Alder cycloaddition reaction of C_{70} with molten anthracene.²⁴ α -6- α' BA- C_{70} was used as a directing group to decrease the number of

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possible tris- and tetra-adducts. Starting from BA-C₇₀, a total of 11 tris-adduct isomers, including one C_s- and one C_{2v}-symmetric and 16 tetra-adducts and one C_{2v}-symmetric, can be obtained (Figure 1).

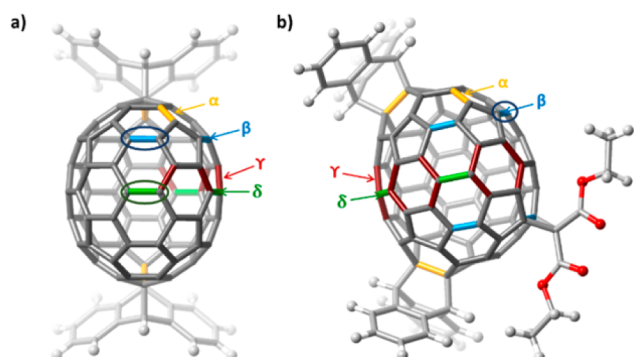
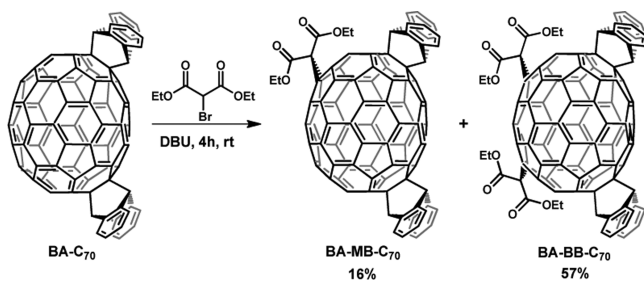


Figure 1. (a) Eleven possible tris-adducts starting from α -6- α' BA-C₇₀. (b) Sixteen possible tetra-adducts starting from the shown tris-adduct. Circled bonds are the C_s- and C_{2v}-symmetric tris- and tetra-adducts. The α -bonds are depicted in yellow; β -bonds are depicted in blue, and γ - and δ -bonds are depicted in red and green, respectively.

Bis-anthracene mono-Bingel C₇₀ tris-adduct (BA-MB-C₇₀) and bis-anthracene bis-Bingel C₇₀ tetra-adduct (BA-BB-C₇₀) were synthesized via a Bingel cycloaddition reaction of α -6- α' BA-C₇₀ with bromo-ethylmalonate in the presence of DBU in the dark (Scheme 1). BA-MB-C₇₀ and BA-BB-C₇₀ were purified

Scheme 1. Mono- and Bis-Additions of Ethylmalonate to α -6- α' Bis-Anthracene C₇₀



using silica gel column chromatography and characterized by UV-vis, 1D and 2D NMR spectroscopy, mass spectrometry, thermal gravimetric analysis (TGA), and CV. Using MALDI-TOF, we confirmed the addition of one and two ethylmalonate groups to the [70]fullerene cage (m/z 998.0551 and 1156.1184), respectively. As reported,²⁴ we were not able to observe the molecular ion peak of the C₇₀ mono-anthracene nor that of the BA-C₇₀ under these conditions. Therefore, ¹H NMR spectroscopy was used to verify the presence of the anthracenes.

The ¹H NMR spectrum of BA-MB-C₇₀ exhibits half of the possible number of signals for the anthracenes (two sets of signals). Two quartets and two triplets corresponding to the ethylmalonate addends were also observed (Figure 2a). These results indicate that BA-MB-C₇₀ is the only C_s-symmetric regioisomer out of the 11 possible tris-adducts (Figure 1a). 34 signals for the sp² carbons were observed in the ¹³C NMR spectrum (Figure S6), in agreement with the C_s-symmetry observed in the ¹H NMR. The preferential formation of a single C_s-symmetric tris-adduct starting from the α -6- α' bis-adduct

was supported by MO calculations, which showed that the calculated α -6- α' bis-adduct has enhanced LUMO coefficients at the C_s-symmetric β -bonds.²² Addition to any of the other α - or β -bonds will result with a sterically congested product.

To unambiguously determine the addition pattern of BA-MB-C₇₀ and to synthesize a new Bingel C₇₀ mono-adduct, a retro-Diels–Alder cycloaddition reaction of this compound was performed by heat treatment of BA-MB-C₇₀ at 240 °C under vacuum. After the product was washed with MeOH, a change in color (from dark green to red brown) and in polarity was observed, indicating the loss of the anthracene groups (14.20 mg, >99% yield, Scheme 2a). The absence of the anthracene groups on mono-Bingel-C₇₀ (MB-C₇₀) was verified by ¹H NMR, where only two quartets and two triplets corresponding to the ethylmalonate addend were observed (Figure 2b). The ¹³C NMR spectrum of MB-C₇₀ showed 34 signals for the sp² carbons (Figure S15), in agreement with the C_s-symmetry observed by ¹H NMR. Additionally, we confirmed that MB-C₇₀ corresponds to the β -isomer by comparison of the UV-vis absorption spectrum with those of previously reported β -pyrrolidine C₇₀ derivatives (Figure S13).^{4,25} As far as we know, this synthetic approach becomes the only methodology to selectively synthesize the uncommon β -Bingel mono-adduct.^{22,26,27}

The number of possible tetra-adduct isomers that can be obtained starting from the BA-MB-C₇₀ tris-adduct^{20,22} is 16, and only one is C_{2v}-symmetric (Figure 1b).^{20,21}

The ¹H NMR spectrum of BA-BB-C₇₀ exhibited half of the possible number of signals for the two anthracenes and for the two ethylmalonate groups (Figure 3a). Therefore, BA-BB-C₇₀ can be unambiguously assigned to the only possible C_{2v}-symmetric regioisomer (Figure 1b).^{20,21} The ¹³C NMR spectrum showed 18 signals for the sp² carbons, in agreement with the presence of two planes of symmetry and a C₂-rotation (Figure S10). The NOESY-NMR spectrum of BA-BB-C₇₀ exhibited a weak correlation between the methyl (–CH₃) protons of the ethyl malonates and the methylene protons of the anthracene addends (Figure S8).²² This correlation shows that the third and fourth additions occurred at the C_{2v}-symmetric β -bonds close to the anthracene groups and not to the other possible α - or β -bonds, for which no correlation would be observed.²²

To synthesize a totally unique bis-adduct regioisomer of C₇₀, a thermal retro-Diels–Alder reaction of BA-BB-C₇₀ was performed (Scheme 2b). As before we also observed a change of the color and polarity of the sample, indicating the successful retro-Diels–Alder removal of the anthracene groups (37.17 mg, > 99% yield). The absence of the anthracene groups of the bis-Bingel C₇₀ (BB-C₇₀) compound was confirmed by ¹H NMR (Figure 3b). The UV-vis absorption spectrum of BB-C₇₀ (Figure S13) was compared with all of the known spectra of pure C₇₀ bis-adducts, and no matches were observed.^{4,20,21,24,25,27,28} Both the ¹H NMR and UV-vis characterization indicated that this compound corresponds to the previously unreported β -4- β' bis-adduct regio-isomer BB-C₇₀. This approach can be used to synthesize other potentially high-performing bis-adduct C₇₀ fullerene acceptors for photovoltaic applications.

The TGA traces of BA-MB-C₇₀ and BA-BB-C₇₀ were recorded upon increasing the temperature at a rate of 3 °C min^{–1} under a flow of 15 psi of ultrahigh purity N₂ (Figure 4). For BA-MB-C₇₀, a 13% weight loss was calculated starting at 161 °C followed by a 13% weight loss starting at 200 °C,

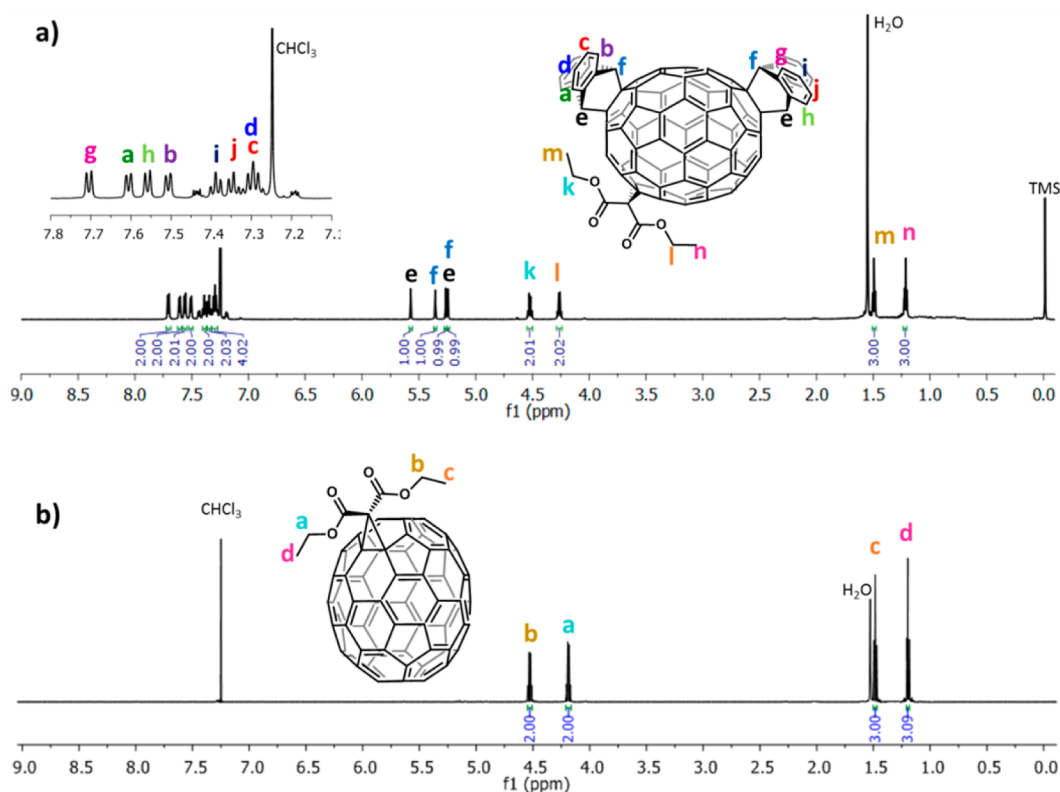
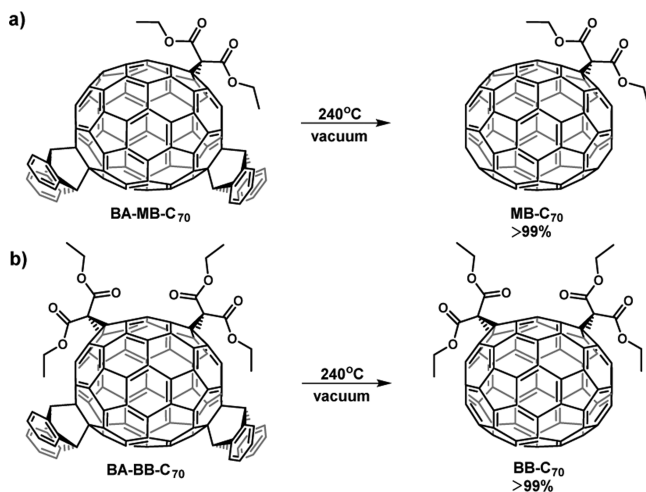


Figure 2. ¹H NMR spectrum (600 MHz; CDCl₃, 298 K) of (a) BA-MB-C₇₀ and (b) MB-C₇₀.

Scheme 2. Retro-Diels–Alder Cycloaddition Reaction Yielding MB-C₇₀ and BB-C₇₀



corresponding to two distinct steps due to the consecutive loss of the two anthracenes. We also observed a 12% weight loss starting at 340 °C corresponding to the loss of the ethylmalonate addend. These results confirm the presence of the tris-adduct. For BA-BB-C₇₀, we observed two distinct steps each of 12% weight loss at 149 and 196 °C, respectively, which correspond to the consecutive loss of the two anthracenes followed by two indistinct steps of 20% weight loss at 340 °C, corresponding to the loss of the two ethylmalonate addends.

The redox properties of BA-MB-C₇₀, BA-BB-C₇₀, MB-C₇₀, and BB-C₇₀ were measured by CV in dichloromethane solutions using 0.1 M *n*-Bu₄NPF₆ as supporting electrolyte (Figure 5). The results are summarized in Table 1. As expected,

with more addends on the C₇₀ cage, we observed a higher cathodic shift with respect to the values for the pristine fullerene C₇₀.⁸ The CV of bis-, tris-, and tetra-adducts showed irreversible cathodic electrochemical behavior, in agreement with previous reports in which potentials more negative than −1.2 V lead to irreversible retro-Bingel cycloadditions.^{29,30} In the case of the mono-adduct, the first and second reduction waves were chemically and electrochemically reversible, similar to the Bingel-C₇₀ α-isomer.^{29–31} To achieve retro-cycloaddition of the Bingel-C₇₀ β-isomer, a more negative potential was required, close to −2 V, unlike its α-isomer, for which the retro-cycloaddition is observed at −1.4 V.^{28,31,32} We also observed one quasi-reversible oxidation due to the presence of the anthracene addends for the bis- and tetra-adduct and one reversible oxidation ($E_{1/2} = 0.76$ V) for the tris-adduct.

CONCLUSION

We successfully synthesized a β-4-β' C₇₀ bis-regioisomer and an uncommon β-Bingel C₇₀ mono-isomer using an addition–retro-addition Diels–Alder reaction and an addition–elimination of bromo-ethylmalonate. This reaction sequence could be useful to synthesize previously unobserved C₇₀ bis-regioisomers. We also report the regioselective synthesis and spectroscopic characterization of the C_s-symmetric tris- and C_{2v}-symmetric tetra-adducts of C₇₀.

EXPERIMENTAL SECTION

Synthesis of BA-MB-C₇₀ and BA-BB-C₇₀. Bis-anthracene-C₇₀ (BA-C₇₀) was synthesized as previously reported and purified immediately before the next reaction.²⁴ BA-C₇₀ (20.0 mg, 0.015 mmol, 1 equiv) was dissolved in 8 mL of anhydrous *o*-DCB and protected from light. Bromo-ethyl malonate (3.6 mg, 0.124 mmol, 8 equiv) and 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) (47.1 mg, 0.309 mmol, 20 equiv) were added, and the mixture was stirred under

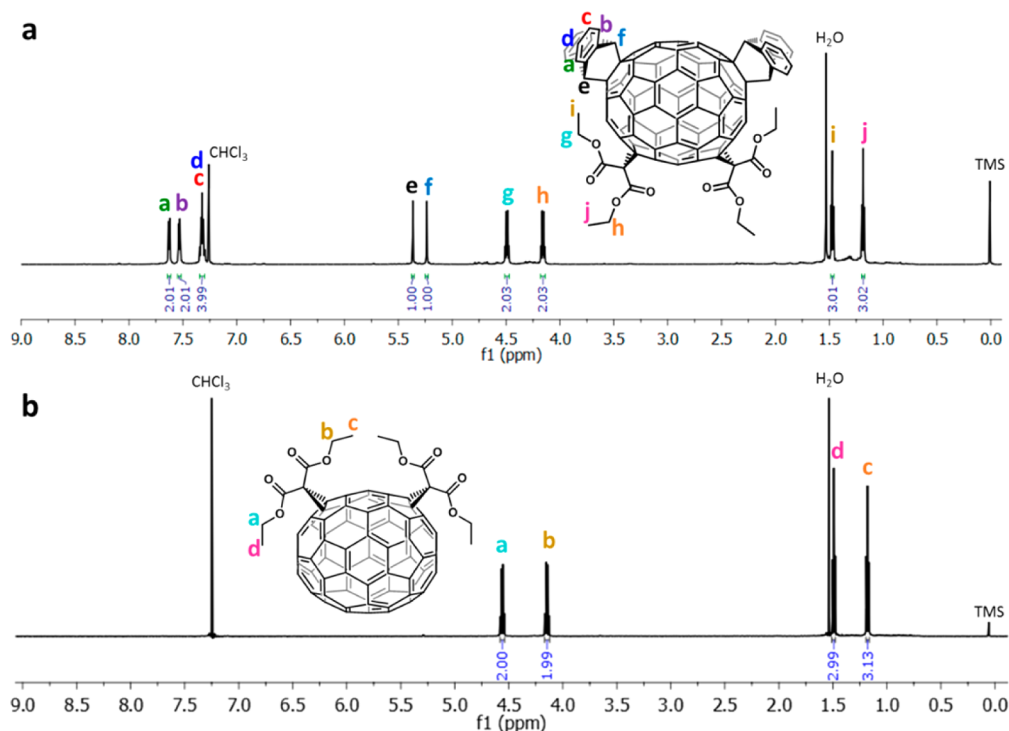


Figure 3. ^1H NMR spectrum (600 MHz; CDCl_3 , 298 K) of (a) BA-BB- C_{70} and (b) BB- C_{70} .

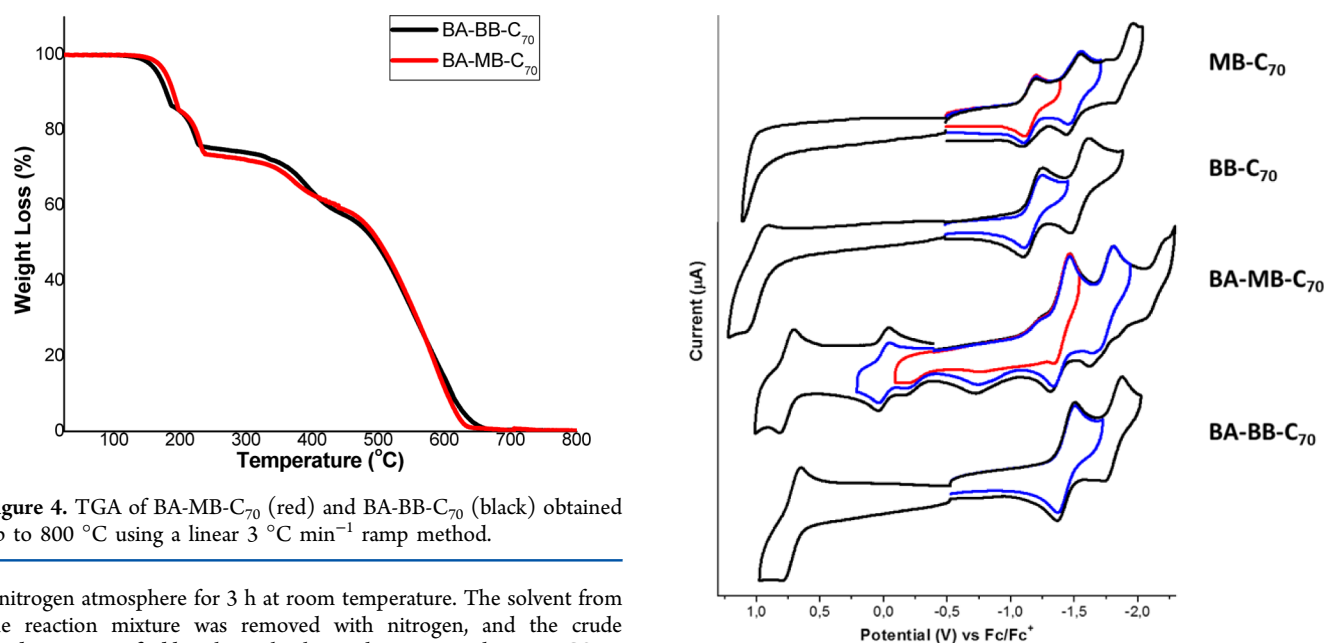


Figure 4. TGA of BA-MB- C_{70} (red) and BA-BB- C_{70} (black) obtained up to 800 $^{\circ}\text{C}$ using a linear 3 $^{\circ}\text{C min}^{-1}$ ramp method.

a nitrogen atmosphere for 3 h at room temperature. The solvent from the reaction mixture was removed with nitrogen, and the crude product was purified by silica gel column chromatography using CS_2 as eluent to separate the unreacted BA- C_{70} , followed by $\text{CS}_2/\text{CHCl}_3$ (4/1 ratio) to collect BA-MB- C_{70} (3.67 mg, 16% yield). Finally, $\text{CS}_2/\text{CHCl}_3$ (1/1 ratio) was used to collect BA-BB- C_{70} (14.10 mg, 57% yield). HPLC chromatograms for the crude and pure compounds are shown in the Supporting Information.

Characterization of BA-MB- C_{70} . MALDI-TOF: $[\text{M}-(356.1565)]^+$ calcd for $[\text{C}_{105}\text{H}_{30}\text{O}_4-(\text{C}_{14}\text{H}_{10})_2]^+$ 998.0579; found 998.0551. ^1H NMR ($\text{CDCl}_3/\text{CS}_2$ (7/3), 600 MHz, 298 K): δ 7.70 (d, 2H_{Ar} , $J = 7.17$), 7.61 (d, 2H_{Ar} , $J = 6.90$), 7.56 (d, 2H_{Ar} , $J = 7.17$), 7.51 (d, 2H_{Ar} , $J = 6.90$), 7.39 (t, 2H_{Ar} , $J = 7.17$), 7.34 (t, 2H_{Ar} , $J = 7.17$), 7.30 (m, 4H_{Ar}), 5.57 (s, 1H), 5.36 (s, 1H), 5.26 (s, 1H), 5.24 (s, 1H), 4.52 (q, 2H , $J = 7.12$), 4.26 (q, 2H , $J = 7.12$), 1.49 (t, 3H , $J = 7.11$), 1.21 (t, 3H , $J = 7.11$) ppm. ^{13}C NMR ($\text{CDCl}_3/\text{CS}_2$ (7/3), 150 MHz, 298 K): δ 159.45, 159.08, 155.94, 155.52, 153.32, 153.04, 152.57, 152.15, 151.90, 151.16, 150.79, 150.32, 150.00, 148.80, 148.64, 143.67, 143.09, 141.69,

Figure 5. Cyclic voltammetry in dichloromethane solutions of BA-MB- C_{70} , BA-BB- C_{70} , MB- C_{70} , and BB- C_{70} .

141.47, 141.36, 141.31, 141.18, 141.15, 140.94, 140.80, 140.34, 139.71, 138.66, 137.81, 136.63, 136.59, 133.81, 132.67, 128.43, 127.15, 127.00, 125.86, 125.74, 125.54, 125.47, 66.40, 65.76, 65.70, 65.64, 63.73, 63.13, 62.83, 59.85, 58.47, 57.47, 55.84, 14.34, 14.10 ppm.

Characterization of BA-BB- C_{70} . MALDI-TOF: $[\text{M}-(356.1565)]^+$ calcd for $[\text{C}_{112}\text{H}_{40}\text{O}_8-(\text{C}_{14}\text{H}_{10})_2]^+$ 1156.1158; found 1156.1184. ^1H NMR ($\text{CDCl}_3/\text{CS}_2$ (7/3), 600 MHz, 298 K): δ 7.63 (d, 2H_{Ar} , $J = 6.52$), 7.53 (d, 2H_{Ar} , $J = 6.52$), 7.32 (m, 4H_{Ar}), 5.36 (s, 1H), 5.24 (s, 1H), 4.49 (q, 2H , $J = 7.13$), 4.16 (q, 2H , $J = 7.13$), 1.47 (t, 3H , $J = 7.13$), 1.19 (t, 3H , $J = 7.13$) ppm. ^{13}C NMR ($\text{CDCl}_3/\text{CS}_2$ (7/3), 150 MHz, 298 K): δ 164.63, 163.94, 160.35, 155.90, 154.20, 149.88,

Table 1. Redox Potentials^a of BA-MB-C₇₀, BA-BB-C₇₀, MB-C₇₀, and BB-C₇₀

	BA-MB-C ₇₀	BA-BB-C ₇₀	MB-C ₇₀	BB-C ₇₀
$E_{\text{ox}}^{0/+}$	0.81	0.80		1.07
$E_{\text{pc}}^{0/-}$	-1.46	-1.50	-1.20	-1.25
$E_{\text{pc}}^{-/-2}$	-1.81	1.88	-1.55	-1.61
$E_{\text{pc}}^{-2/-3}$	-2.22		-1.96	
LUMO ^b	-3.9	-3.8	-4.0	-4.1

^aValues obtained by CV in V vs Fc/Fc⁺. ^bValues obtained using the following formula $E_{\text{LUMO}} = -(E_{\text{(onset,red vs Fc}^+/F_c)} + 5.1) \text{ eV}$.³⁰

149.82, 148.96, 148.59, 141.79, 141.66, 141.41, 141.38, 141.30, 140.50, 140.02, 139.88, 136.24, 134.26, 133.34, 127.01, 126.98, 125.72, 125.47, 124.92, 66.42, 66.07, 63.34, 63.07, 62.53, 57.80, 55.71, 41.13, 14.30, 13.88 ppm.

Retro-Diels–Alder Reaction and Synthesis of MB-C₇₀ and BB-C₇₀. Characterization of MB-C₇₀. Laser desorption Fourier transform ion cyclotron resonance mass spectrometry (LD FT-ICR MS): [M⁻] calcd for C₇₀(C₇H₁₀O₄)⁻ m/z 998.0584; found 998.0589. ¹H NMR (CDCl₃, 600 MHz, 298 K): δ 4.53 (q, 4H, J = 7.20), 4.19 (q, 4H, J = 7.10), 1.48 (t, 6H, J = 7.20) 1.20 (t, 6H, J = 7.10) ppm. ¹³C NMR (CDCl₃, 150 MHz, 298 K): δ 163.86, 163.34, 153.15, 151.44, 149.89, 149.57, 149.53, 149.46, 149.14, 148.94, 148.71, 148.70, 148.27, 147.59, 147.45, 147.19, 147.09, 147.06, 146.54, 146.06, 145.37, 145.24, 145.08, 144.93, 144.62, 144.45, 143.64, 143.39, 141.41, 139.75, 138.39, 132.07, 131.93, 131.90, 131.38, 127.89, 63.52, 63.10, 61.41, 38.49, 14.34, 14.06 ppm.

Characterization of BB-C₇₀. LD FT-ICR MS: [M⁻] calcd for C₇₀(C₇H₁₀O₄)₂⁻ m/z 1156.1163; found 1156.1175. ¹H NMR (CDCl₃, 600 MHz, 298 K): δ 4.57 (q, 2H, J = 7.14), 4.16 (q, 2H, J = 7.14), 1.50 (t, 3H, J = 7.14), 1.19 (t, 3H, J = 7.14) ppm. ¹³C NMR (CDCl₃, 150 MHz, 298 K): δ 164.50, 163.17, 152.44, 149.62, 149.59, 149.20, 147.25, 147.16, 146.85, 146.56, 146.07, 145.80, 144.03, 143.52, 142.59, 140.43, 135.27, 133.22, 133.12, 132.93, 131.77, 124.50, 67.57, 62.92, 61.72, 14.38, 13.92 ppm.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b02301.

General synthetic procedure, mass spectra, UV–vis spectra, 1D and 2D NMR spectra, and HPLC chromatograms (PDF)

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Notes

The authors declare no competing financial interest.

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