[60]Fullerene cycloaddition across hindered acenes†

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The Diels–Alder cycloadditions of [60]fullerene across sterically hindered 6,13-bis(2′,6′-dialkylphenyl)pentacenes, **1** and **2**, produce fullerene–acene monoadducts **3** and **4**. In both cases, further [60]fullerene cycloaddition to form *cis*-bis[60]fullerene adducts is retarded by steric resistance between the [60]fullerene moieties and the *o*-dialkyl substituents. Instead, the fullerene moieties of monoadducts **3** and **4** sensitize the formation of $^1O_2$ which subsequently cycloadds across the acene backbone to produce novel *syn* and *anti* [60]fullerene–dioxo bisadducts, **8–11**.

Introduction

The chemistry between fullerenes and acenes is of interest because the corresponding fullerene–acene adducts represent new molecular architectures that are considered precursors to cyclacenes and single-walled nanotubular compounds (SWNCs).[1] To date, [60]fullerene has been successfully cycloadded across several phenyl substituted acenes.[2] The phenyl substituents direct the regiochemistries of these additions and provide for enhanced solubilities of the acenes and the corresponding fullerene–acene adducts. An interesting feature of this chemistry is that [60]fullerenes add in a diastereoselective *syn* fashion across the acenes due to favorable [60]fullerene–[60]fullerene π–π stacking interactions in both the ground states and the transition states that precede them. To date, there are no reported cases of [60]fullerene cycloaddition across a phenyl substituted acene in which the reaction stops at the monoadduct stage. In all known examples, the addition of the first [60]fullerene addend is followed by a second, more facile *syn* addition. In one case, a third *syn* addition was also reported.[3]

Here, we report two unusual [60]fullerene cycloadditions across sterically hindered 6,13-disubstituted pentacenes. We have prepared and studied pentacenes with both 6,13-bis(2′,6′-dimethylphenyl) and 6,13-bis(2′,6′-diethylphenyl) substituents (Fig. 1). For both pentacenes, [60]fullerene cycloaddition stops at the monoadduct stage due to steric resistance associated with the second addition. Upon standing in solution under ambient conditions, the [60]fullerene monoadducts add singlet oxygen in facile fashion. Both *syn* and *anti* $^1O_2$ adducts form.

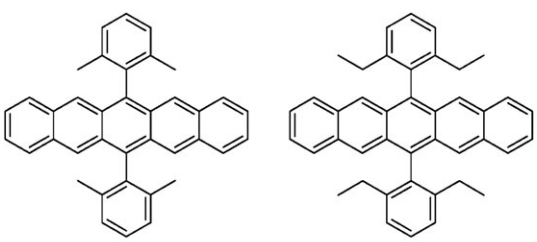
Results and discussion

Acene syntheses

For this study, we synthesized two sterically hindered 6,13-disubstituted pentacenes—the known 6,13-bis(2′,6′-dimethylphenyl)pentacene, **1**, and the previously unknown 6,13-bis(2′,6′-diethylphenyl)pentacene, **2**, using modified Kafafi[4] procedures (Scheme 1). Thus, readily available pentacene-6,13-dione is treated with an appropriate phenyllithium to produce an aromatic diol in 77–78% yield. The diols are reductively aromatized in 88–93% yield using sodium iodide, sodium hypophosphite[5] and acetic acid to produce the corresponding 6,13-disubstituted pentacenes in a relatively clean state. Once prepared, **1** and **2** can be stored for months in the solid state (dark) without significant decomposition. In solution phase, however, they degrade unless protected from light and oxygen. There was no attempt to purify **1** and **2** using chromatographic methods since all such operations would require dissolving and maintaining these compounds in solution phase for unacceptably long durations.

Fullerene–acene chemistries

Compounds **1** and **2** were separately reacted with 5 equivalents of [60]fullerene in boiling carbon disulfide solvent (46 °C) in the dark under nitrogen for 8–16 h. The only observed [60]fullerene–acene products were the corresponding monoadducts, **3** and **4** (Fig. 2) formed in 86 and 84% yield, respectively. Reactions were also successfully performed in boiling toluene (111 °C) giving **3** and **4** in 83 and 81% yield, respectively. No traces of unreacted acene were observed in any of the reactions. Washing the crude product mixtures with chloroform effectively removes the chloroform soluble [60]fullerene–acene monoadducts from unreacted [60]fullerene. Attempts to remove trace impurities *via* chromatographic methods were complicated by the photo-oxidative instabilities of **3** and **4** (*vide infra*). They were nonetheless characterized by



1 **2**

Fig. 1 Structural drawings of 6,13-bis(2′,6′-dimethylphenyl)pentacene, **1**, and 6,13-bis(2′,6′-diethylphenyl)pentacene, **2**.

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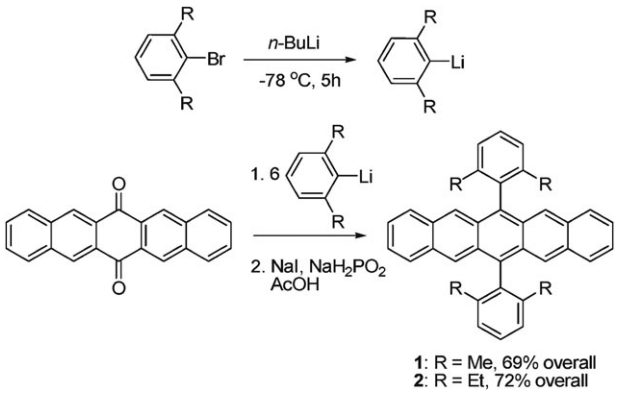
† Electronic supplementary information (ESI) available: ^1H and ^{13}C NMR spectra, LDI mass spectra. See DOI: 10.1039/b710300j



Scheme 1 Synthesis of hindered acenes **1** and **2**.

a combination of ^{1}H NMR spectroscopy, ^{13}C NMR spectroscopy and MALDI mass spectrometry. Both **3** and **4** exhibit two sets of alkyl signals in their ^{1}H and ^{13}C NMR spectra due to slow rotation of the hindered phenyl substituents. In each case, one *o*-alkyl substituent is *syn* with respect to the fullerene addend while the other is *anti*. Two additional aliphatic ^{13}C NMR signals are observed for both **3** and **4** at approximately 56 and 72 ppm[6] corresponding to the sp^3 carbons on the pentacene backbone and the [60]fullerene moiety, respectively. A total of 47 and 44 $^{13}C_{sp^2}$ signals is observed for **3** and **4**, respectively, in the congested C_{sp^2} region where 47 signals are expected in each case. The 3 missing signals for **4** are attributed to coincidental overlap. MALDI mass spectra of **3** and **4** reveal base peaks corresponding to the parent acenes ($M^+ - C_{60}$) as well as signals corresponding to [60]fullerene (M^+ – acene) and in the case of **3**, a molecular ion at m/z 1206.

Although the reactions producing **3** and **4** utilized 5-fold excesses of [60]fullerene, they did not produce the corresponding *cis*-bis[60]fullerene adducts, **5** and **6**, as has been observed in other [60]fullerene–6,13-disubstituted pentacene examples.[2]

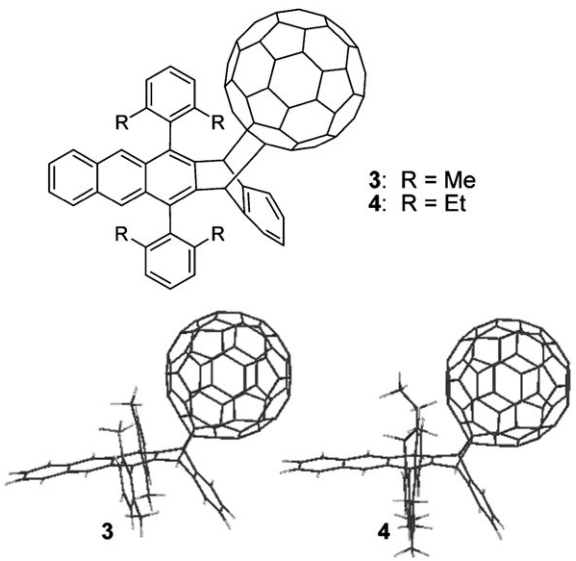


Fig. 2 ChemDraw representation (top) and MM2 minimized (bottom) [60]fullerene–6,13-bis(2′,6′-dimethylphenyl)pentacene monoadduct **3** and [60]fullerene–6,13-bis(2′,6′-diethylphenyl)pentacene monoadduct **4**.

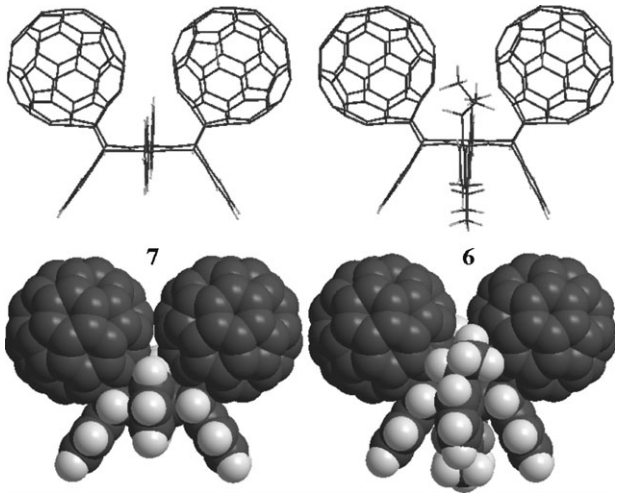


Fig. 3 MM2 minimized structures for the hypothetical bis[60]fullerene adduct of 6,13-bis(2′,6′-diethylphenyl)pentacene, **6**, and the known bis[60]fullerene adduct of 6,13-diphenylpentacene, **7**. The carbons of closest contact on adjacent [60]fullerene moieties are 3.6 and 3.1 Å apart on **6** and **7**, respectively.

Subsequent reactions of **3** and **4** with excess [60]fullerene also failed to produce **5** and **6**. Clearly, the *o*-alkyl groups on **3** and **4** retard the approach of a second [60]fullerene to either face of the acene. But while the kinetics of a second [60]fullerene cycloaddition are not ideal, an examination of MM2 calculated structures for hypothetical **5** and **6** (Fig. 3) also indicates a thermodynamic problem. For comparison, **7** is a known, thermally stable *cis*-bis[60]fullerene adduct of 6,13-diphenylpentacene[7] in which the carbons of closest contact on adjacent [60]fullerene moieties are 3.07 Å apart as determined by X-ray crystal structure analysis.[8] MM2 calculations nearly reproduce the X-ray crystal structure for **7** by placing nearest neighbor [60]fullerene carbon atoms 3.08 Å apart. The same method indicates that steric interactions between [60]fullerene moieties and *o*-alkyl groups prevent an optimal separation between [60]fullerenes on hypothetical **5** and **6**. For **5** and **6**, the carbons of closest contact on adjacent [60]fullerene moieties are calculated to be 3.6 Å apart. Space filling models for **6** and **7** reveal that this extra 0.5 Å of separation significantly reduces [60]fullerene–[60]fullerene π–π stacking interactions (Fig. 3). The π–π stacking interactions are key to bis[60]fullerene adduct stability. In this regard, we note the absence of formation of all C_{2h} *trans*-bis[60]fullerene adducts originating from 6,13-disubstituted pentacenes.[2] The *trans*-bis[60]fullerene adducts are devoid of [60]fullerene–[60]fullerene π–π stacking interactions.

Singlet oxygen addition

Compounds **3** and **4** are stable when stored in the solid state. However, upon standing in solution under ambient conditions, both **3** and **4** readily add singlet oxygen. In this way, [60]fullerene–dioxo adducts of the corresponding 6,13-disubstituted pentacenes are formed in quantitative yield. Thus, compound **3** forms a 4 : 1 mixture of *syn*-**8** to *anti*-**9** [60]fullerene–dioxo adducts while compound **4** forms a 4 : 1 mixture of *syn*-**10** to *anti*-**11** [60]fullerene–dioxo adducts.

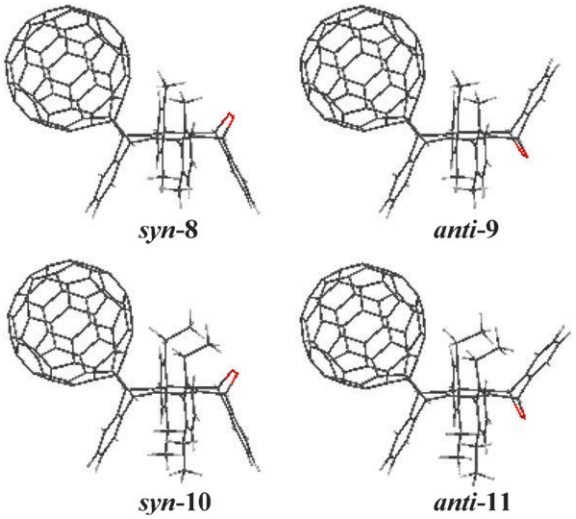
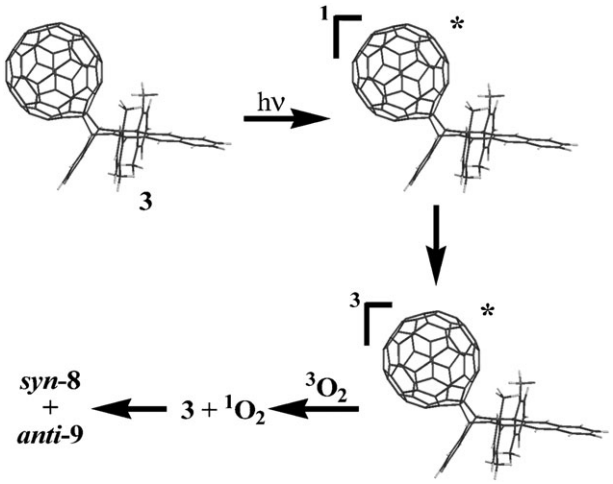


Fig. 4 MM2 structures for the $^1O_2$ adducts of **3** and **4**: *syn*-**8**, *anti*-**9**, *syn*-**10** and *anti*-**11**. Oxygen atoms are shown in red.



Scheme 2 Proposed mechanism for the facile oxidations of **3** and **4** with $^1O_2$. The oxidation of **3** to produce [60]fullerene–dioxo bisadducts **8** and **9** is illustrated.

Compounds **8–11** (Fig. 4) have been isolated *via* flash silica column chromatography and characterized by a combination of ^{1}H NMR spectroscopy, ^{13}C NMR spectroscopy, MALDI mass spectrometry and UV–Vis spectrophotometry. The MALDI mass spectra of **8** and **9** are especially revealing. Each shows a molecular ion at *m*/*z* 1238 as well as fragment ions at *m*/*z* 1222 ($M^+ - O$), 1206 ($M^+ - O_2$), 518 ($M^+ - C_{60}$), 502 ($M^+ - C_{60} - O$), 486 ($M^+ - C_{60} - O_2$) and 720 (C_{60}^+). ^{1}H and ^{13}C NMR spectra for compounds **8–11** include signals due to new methine protons (~5.5–5.7 ppm) and carbons (~77 ppm) on the acene backbone confirming that each possesses a bridged dioxo rather than a quinone structure. Each ^{1}H NMR spectrum contains two sets of AA′XX′ multiplets indicating that the dioxygen bridge is connected at C7 and C12 of the acene backbone (a penultimate ring). The ^{13}C NMR spectra for **8** and **9** both contain a total of 46 C_{sp^2} signals, as expected. Those for compounds **10** and **11** contain 42 and 43 C_{sp^2} signals, respectively. The 4 missing signals for **10** and the 3 missing signals for **11** are attributed to coincidental overlap in the highly congested C_{sp^2} region of the ^{13}C NMR spectra.

Compounds **8** and **10** are assigned *syn* structures whereas **9** and **11** are assigned *anti* structures based upon their respective orders of elution on polar silica columns with CH_2Cl_2 as eluant. Thus, the less polar **9** elutes faster than **8** and the less polar **11** elutes faster than **10**.

Singlet oxygen addition to **3** and **4** occurs across the center rings of the anthracene moieties that remain after [60]fullerene addition. Compared to larger acenes, anthracene is relatively stable to air oxidation, even though it is known to sensitize $^1O_2$ formation.[9] Typically, when $^1O_2$ adducts of anthracenes are sought, a separate dye-sensitizer is added.[10] The facile oxidation of **3** and **4** suggests the mechanism illustrated in Scheme 2 in which the photoexcited [60]fullerene moiety sensitizes formation of highly reactive $^1O_2$ which predominantly adds to the proximate *syn* face of the acene backbone. [60]Fullerene is known to sensitize $^1O_2$ formation[11] as are numerous functionalized fullerenes.[12] The reactions reported here are interesting in that the $^1O_2$ is formed in the presence of [60]fullerene and then immediately trapped in an intramolecular reaction. This behavior suggests that functionalized fullerenes bearing oxidatively sensitive addends may possess limited lifetimes, especially in solution. On the other hand, the facile formation of $^1O_2$ suggests potential applications for functionalized fullerenes in photodynamic therapies.[13]

Conclusion

In conclusion, [60]fullerene cycloadds across sterically hindered 6,13-bis(2′,6′-dialkylphenyl)pentacenes to produce fullerene–acene monoadducts, **3** and **4**. Further [60]fullerene cycloadditions to form *cis*-bis[60]fullerene adducts are not observed. Instead, $^1O_2$ cycloadds across the acene backbone to produce novel [60]fullerene–dioxo bisadducts **8–11**. The addition of highly reactive $^1O_2$ occurs preferentially (4 : 1) across the *syn* face of the acene, strongly suggesting that the fullerene moieties on **3** and **4** sensitize its formation.

Experimental

General procedures

Compounds 1-bromo-2,6-dimethylbenzene and 1-bromo-2,6-diethylbenzene and reagent *n*-butyllithium (1.6 M solution in hexanes) were purchased from Aldrich Chemical Co. and used without further purification. All reactions, unless otherwise noted, were carried out under a slow stream of N_2. All reaction containers were flame dried under vacuum before use. Solvents were purified by standard methods and dried as required. NMR spectra were recorded on a Varian AC 500 spectrometer. ^{1}H and ^{13}C NMR samples were internally referenced to TMS (0.00 ppm). MALDI-TOF mass spectra were acquired on a Shimadzu-Biotech mass spectrometer. Fast atom bombardment high resolution mass spectra were obtained at the Notre Dame University mass spectrometry facility.

Syntheses

6,13-Bis(2′,6′-dimethylphenyl)-6,13-dihydropentacene-6,13-diol. A solution of 1-bromo-2,6-dimethylbenzene (2.17 g,

11.8 mmol) was stirred in dry THF (75 mL) and cooled to −78 °C in a dry ice–acetone bath. Upon cooling, *n*-butyllithium (3.35 mL, 9.8 mmol) was added and the solution was stirred for 5 h at −78 °C. Pentacene-6,13-dione (0.5 g, 2 mmol) was then added to the pale yellow solution and the mixture was allowed to gradually warm to RT with stirring overnight. To the reaction mixture was added 1 M HCl (50 mL). Following extraction with CH_2Cl_2 (100 mL), the organic layer was washed with water and dried over $CaCl_2$. The solvent was removed under vacuum until only ~10 mL remained, at which point hexanes (100 mL) were added, resulting in the formation of a white precipitate. The desired diol was isolated by vacuum filtration (0.66 g, 78%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.73 (s, 4H), 7.7 (m, 4H), 7.4 (m, 4H), 7.22 (t, 2H, J = 7.56 Hz), 7.12 (m, 4H), 2.4 (bs, 12H), 2.20 (s, 2H). ^{13}C NMR (125.68 MHz, $CDCl_3$): δ 143.5, 139.1, 137.7, 133.4, 131.1, 127.9, 127.2, 126.9, 126.3, 79.8, 25.3. LDI-MS m/z: 520 [M^+], 503 [M^+ − OH], 486 [M^+ − 2(OH)].

6,13-Bis(2′,6′-diethylphenyl)-6,13-dihydropentacene-6,13-diol. A procedure similar to that utilized for the synthesis of 6,13-bis(2′,6′-dimethylphenyl)-6,13-dihydropentacene-6,13-diol was followed using 1-bromo-2,6-diethylbenzene (2.0 g, 9.4 mmol), *n*-BuLi (2.66 mL, 7.8 mmol) and pentacene-6,13-dione (0.4 g, 1 mmol). In this way, the desired diol was produced in 77% yield (0.57 g). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.73 (s, 4H), 7.7 (m, 4H), 7.38 (m, 4H), 7.35 (t, 2H, J = 7.57 Hz), 7.2 (m, 4H), 3.4 (bm, 8H), 2.4 (bm, 12H), 2.2 (s, 2H). ^{13}C NMR (125.68 MHz, $CDCl_3$): δ 142.4, 139.5, 133.2, 129.8, 128.8, 127.9, 127.6, 127.5, 126.2, 79.9, 31.6, 14.1. LDI-MS m/z: 576 [M^+], 559 [M^+ − OH], 542 [M^+ − 2(OH)].

6,13-Bis(2′,6′-dimethylphenyl)pentacene (1). A suspension of 6,13-bis(2′,6′-dimethylphenyl)-6,13-dihydropentacene-6,13-diol (0.5 g, 1 mmol), sodium iodide (0.99 g, 6.7 mmol) and sodium hypophosphite (1.09 g, 9.08 mmol) was prepared in glacial acetic acid (25 mL) and heated at reflux for 1.5 h in a round-bottomed flask that was equipped with a reflux condenser. The flask was wrapped in foil to block ambient light throughout the reaction. After cooling, the reaction mixture was filtered and washed with water (50 mL) and methanol (25 mL). After drying at reduced pressure, 6,13-bis(2′,6′-dimethylphenyl)pentacene (**1**) was obtained in 88% yield (0.41 g). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.14 (s, 4H), 7.74 (m, 4H), 7.5 (t, 2H, J = 7.56 Hz), 7.4 (d, 4H, J = 7.56 Hz), 7.22 (m, 4H), 1.8 (s, 12H). ^{13}C NMR (125.68 MHz, $CDCl_3$): δ 138.4, 138.2, 135.5, 131.5, 128.6, 128.0, 127.9, 127.7, 125.0, 124.7, 20.1. LDI-MS m/z: 486 [M^+]. HRMS (FAB+) m/z = 486.2341 (M^+), calcd m/z 486.2348. UV–Vis λ_{max}(nm): 604, 557, 518.

6,13-Bis(2′,6′-diethylphenyl)pentacene (2). A procedure similar to that utilized for the synthesis of pentacene **1** was utilized to produce pentacene **2** in 93% yield (0.35 g). The procedure utilized 6,13-bis(2′,6′-diethylphenyl)-6,13-dihydropentacene-6,13-diol (0.4 g, 0.7 mmol), sodium iodide (0.71 g, 4.8 mmol) and sodium hypophosphite (0.8 g, 7 mmol). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.15 (s, 4H), 7.72 (m, 4H), 7.65 (t, 2H, J = 7.57 Hz), 7.48 (d, 4H, J = 7.57 Hz), 7.21 (m, 4H), 2.11 (q, 8H, J = 7.56 Hz), 0.81 (t, 12H, J = 7.56 Hz). ^{13}C NMR (125.68 MHz, $CDCl_3$): δ 144.1, 137.5, 135.3, 131.4, 128.9, 128.8, 128.4, 126.0, 125.4, 125.2, 26.7, 14.9. LDI-MS m/z: 542 [M^+]. HRMS (FAB+) m/z = 542.2971 (M^+), calcd m/z 542.2974. UV–Vis λ_{max}(nm): 605, 558, 520.

[60]Fullerene–6,13-bis(2′,6′-dimethylphenyl)pentacene monoadduct (3). To a flame dried, N_2-charged round-bottomed flask fitted with a reflux condenser was added [60]fullerene (0.19 g, 0.26 mmol) dissolved in carbon disulfide (25 mL). Pentacene **1** (0.025 g, 0.052 mmol) was then added and the resulting purple solution was allowed to boil for a period of 8 h. The resulting brown solution was concentrated under vacuum, extracted with $CHCl_3$, and the solvent evaporated to yield the crude monoadduct **3** in 86% yield (53.5 mg). ^{1}H NMR (500 MHz, CD_2Cl_2): δ 8.02 (s, 2H), 7.83 (m, 2H), 7.64 (m, 2H), 7.48 (m, 2H), 7.39 (m, 6H), 7.26 (d, 2H, J = 6.58 Hz), 5.6 (s, 2H), 2.05 (s, 6H), 1.81 (s, 6H). ^{13}C NMR (125.68 MHz, CD_2Cl_2): δ 156.5, 156.1, 148.1, 147.0, 146.9, 146.74, 146.69, 146.11 (2), 146.09, 146.06 (2), 146.00, 145.95, 145.92, 145.8, 145.2, 145.1, 143.63, 143.5, 143.1, 142.62, 142.57, 142.52, 142.49, 142.36, 142.18, 142.16, 140.6, 140.3, 138.6, 138.3, 137.9, 137.25, 137.21, 137.1, 134.9, 132.5, 130.7, 128.72, 128.66, 128.42, 128.37, 128.0, 127.1, 126.2, 125.9, 72.3, 56.5, 21.0, 20.6. MALDI-MS m/z: 1206 [M^+], 720 [C_{60}], 486 [M^+ − C_{60}]. UV–Vis λ_{max}(nm): 435.

[60]Fullerene–6,13-bis(2′,6′-diethylphenyl)pentacene monoadduct (4). A procedure similar to that utilized for the synthesis of crude monoadduct **3** was utilized to produce crude monoadduct **4** in 84% yield (48.9 mg). For this reaction, [60]fullerene (0.17 g, 0.24 mmol) and pentacene **2** (0.025 g, 0.046 mmol) were dissolved in carbon disulfide (25 mL) and heated to boiling for 8 h. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.10 (s, 2H), 7.86 (m, 2H), 7.56 (m, 4H), 7.45 (m, 4H), 7.40 (m, 4H), 5.51 (s, 2H), 2.59 (m, 2H), 2.33 (m, 4H), 1.91 (m, 2H), 1.08 (t, 6H, J = 7.56 Hz), 0.69 (t, 6H, J = 7.56 Hz). ^{13}C NMR (125.68 MHz, $CDCl_3$): δ 156.3, 155.8, 147.9, 146.78, 146.71, 146.52, 146.50, 146.01, 145.95, 145.80 (2), 145.75, 145.71, 145.5, 145.0, 144.9, 144.1, 143.52, 143.45, 143.42, 143.3, 142.9 (2), 142.5, 142.2, 142.03, 141.95, 141.90, 140.4, 140.1, 137.6, 136.9, 136.1, 134.4, 131.9, 131.1, 128.9, 128.6, 127.6, 126.7, 126.29, 126.26, 125.9, 125.5, 72.0, 56.2, 27.4, 26.7, 15.2, 15.0. MALDI-MS m/z: 720 [C_{60}], 542 [M^+ − C_{60}]. UV–Vis λ_{max}(nm): 434.

[60]Fullerene–6,13-bis(2′,6′-dimethylphenyl)pentacene–dioxo adducts (8 and 9). Upon standing in chloroform solution exposed to air in ambient light, monoadduct **3** is oxidized to a 4 : 1 mixture of *syn*-**8** : *anti*-**9**. The [60]fullerene–dioxo adducts were isolated using flash column chromatography (silica gel) with CH_2Cl_2 as eluent. *syn* [60]fullerene–dioxo adduct (**8**): ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.63 (m, 2H), 7.47 (m, 2H), 7.34 (d, 4H, J = 4.42 Hz), 7.32 (s, 4H), 7.2 (t, 2H, J = 4.40 Hz), 5.63 (s, 2H), 5.52 (s, 2H), 2.00 (s, 6H), 1.86 (s, 6H). ^{13}C NMR (125.68 MHz, CD_2Cl_2): δ 156.2 (2), 148.1, 146.98, 146.95, 146.8, 146.7, 145.98, 145.94, 145.90, 145.88, 145.86, 145.84, 145.81, 145.1, 143.5, 143.4, 143.1, 143.0, 142.61, 142.57, 142.55, 142.51 (2), 142.15, 142.10, 141.1, 140.5, 140.1, 138.7, 138.6, 137.7, 137.6, 137.2, 135.9, 135.3, 133.5, 129.3, 129.1, 128.6, 128.4, 128.3, 127.8, 127.6, 126.8, 124.3, 77.8 (C_{sp^3}–O), 72.7, 56.3, 21.4, 20.6. MALDI-MS m/z: 1238 [M^+], 1222 [M^+ − 16], 1206 [M^+ − 32], 720 [C_{60}], 518

[$M^+ - C_{60}$], 502 [$M^+ - C_{60} - 16$], 486 [$M^+ - C_{60} - 32$]. UV–Vis λ_{max}(nm): 436. *anti* [60]fullerene–dioxo adduct (**9**): ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.54 (m, 2H), 7.37 (m, 2H), 7.35 (d, 2H, J = 7.56 Hz), 7.31 (m, 2H), 7.22 (d, 2H, J = 7.54 Hz), 7.16 (m, 2H), 7.07 (m, 2H), 5.63 (s, 2H), 5.49 (s, 2H), 2.20 (s, 6H), 1.65 (s, 6H). ^{13}C NMR (125.68 MHz, CD_2Cl_2): δ 155.74, 155.66, 147.6, 146.6, 146.5, 146.3, 146.2, 145.68, 145.66, 145.51, 145.49, 145.43, 145.39, 145.37, 145.34, 144.8, 144.7, 143.2, 143.0, 142.62, 142.57, 142.24, 142.17, 142.10 (2), 142.0, 141.70, 141.65, 140.12, 140.10, 139.7, 138.8, 137.8, 137.5, 137.2, 136.7, 136.4, 134.5, 132.8, 128.6, 128.0, 127.8, 127.7, 127.2, 126.2, 123.1, 77.2 (C_{sp^3}–O), 72.2, 55.7, 20.7, 20.4. MALDI-MS m/z: 1238 [M^+], 1222 [$M^+ - 16$], 1206 [$M^+ - 32$], 720 [C_{60}], 518 [$M^+ - C_{60}$], 502 [$M^+ - C_{60} - 16$], 486 [$M^+ - C_{60} - 32$]. UV-Vis λ_{max}(nm): 435.

[60]Fullerene–6,13-bis(2′,6′-diethylphenyl)pentacene–dioxo adducts (10 and 11). Upon standing in chloroform solution exposed to air in ambient light, monoadduct **4** is oxidized to a 4 : 1 mixture of *syn*-**10** : *anti*-**11**. The dioxo bisadducts were isolated using flash column chromatography (silica gel) with CH_2Cl_2 as eluent. *syn* [60]fullerene–dioxo adduct (**10**): ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.53 (m, 2H), 7.49 (t, 2H, J = 7.56 Hz), 7.45 (m, 2H), 7.39 (d, 2H, J = 7.56 Hz), 7.33 (m, 6H), 5.60 (s, 2H), 5.48 (s, 2H), 2.34 (m, 4H), 2.19 (m, 2H), 2.08 (m, 2H), 1.02 (t, 12H, J = 7.56 Hz). ^{13}C NMR (125.68 MHz, CD_2Cl_2): δ 156.22, 156.18, 148.1, 147.0, 146.79, 146.73, 146.2, 146.06, 146.03, 145.94, 145.93, 145.8, 145.2, 144.3, 143.7, 143.55, 143.51, 143.2, 143.1, 142.7, 142.58, 142.55, 142.48, 142.2, 142.1, 141.1, 140.6, 140.3, 138.7, 137.8, 137.2, 136.5, 134.2, 133.1, 129.8, 128.7, 128.4, 127.8, 126.9, 126.8, 125.2, 124.5, 77.7 (C_{sp^3}–O), 72.7, 56.3, 27.9, 27.3, 15.0, 14.3. MALDI-MS m/z: 720 [C_{60}], 574 [$M^+ - C_{60}$], 558 [$M^+ - C_{60} - 16$], 542 [$M^+ - C_{60} - 32$]. UV-Vis λ_{max}(nm): 436. *anti* [60]fullerene–dioxo adduct (**11**): ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.50 (m, 4H), 7.36 (m, 6H), 7.15 (m, 2H), 7.09 (m, 2H), 5.70 (s, 2H), 5.46 (s, 2H), 2.76 (m, 2H), 2.44 (m, 2H), 2.21 (m, 2H), 1.79 (m, 2H), 1.15 (t, 6H, J = 7.56 Hz), 0.64 (t, 6H, J = 7.56 Hz). ^{13}C NMR (125.68 MHz, $CDCl_3$): δ 156.3, 156.1, 148.1, 147.1, 146.9, 146.73, 146.69, 146.18, 146.14, 146.00, 145.97, 145.94, 145.82, 145.78, 145.2, 145.1, 144.1, 143.7, 143.4, 143.1, 143.03, 143.00, 142.8, 142.56, 142.51, 142.14, 142.07, 140.64, 140.56, 140.1, 138.6, 138.1, 137.0, 136.7, 133.8, 132.8, 129.5, 128.2, 127.5, 126.8, 126.5, 125.6, 124.1, 77.6 (C_{sp^3}–O), 72.8, 56.3, 27.2, 27.0, 15.0, 14.5. MALDI-MS m/z: 720 [C_{60}], 574 [$M^+ - C_{60}$], 558 [$M^+ - C_{60} - 16$], 542 [$M^+ - C_{60} - 32$]. UV–Vis λ_{max}(nm): 436.

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References

1 G. P. Miller, S. Okana and D. Tománek, *J. Chem. Phys*., 2006, **124**, 121102-1–121102-5.
2 For a review, see: J. Briggs and G. P. Miller, *C. R. Chim*., 2006, **9**, 916–927.
3 G. P. Miller and J. Briggs, *Org. Lett*., 2003, **5**, 4203–4206.
4 M. A. Wolak, B.-B. Jang, L. C. Palilis and Z. H. Kafafi, *J. Phys. Chem. B*, 2004, **108**, 5492–5499.
5 N. Vets, M. Smet and W. Dehaen, *Synlett*, 2005, 217–222.
6 See Experimental for precise chemical shift values.
7 G. P. Miller and J. Mack, *Org. Lett*., 2000, **2**, 3979–3982.
8 G. P. Miller, J. Briggs, J. Mack, P. A. Lord, M. M. Olmstead and A. L. Balch, *Org. Lett*., 2003, **5**, 4199–4202.
9 See for example: M. Nowakowska, *Makromol. Chem*., 1978, **179**, 2953–2958.
10 See for example: (*a*) W. Fudickar and T. Linker, *Chem.–Eur. J*., 2006, **12**, 9276–9283; (*b*) E. P. Niu, A. W. H. Mau and K. P. Ghiggino, *Aust. J. Chem*., 1991, **44**, 695–704; (*c*) A. Guarini and P. Tundo, *J. Org. Chem*., 1987, **52**, 3501–3508.
11 J. W. Arbogast, A. P. Darmanyan, C. S. Foote, F. N. Diederich, R. L. Whetten, Y. Rubin, M. M. Alvarez and S. J. Anz, *J. Phys. Chem*., 1991, **95**, 11–12.
12 (*a*) K. K. Chin, S.-C. Chuang, B. Hernandez, M. Selke, C. S. Foote and M. A. Garcia-Garibay, *J. Phys. Chem. A*, 2006, **110**, 13662–13666; (*b*) M. E. Milanesio, M. G. Alvarez, V. Rivarola, J. J. Silber and E. N. Durantini, *Photochem. Photobiol*., 2005, **81**, 891–897; (*c*) C. Yu, T. Canteenwala, M. E. El-Khouly, Y. Araki, K. Pritzker, O. Ito, B. C. Wilson and L. Y. Chiang, *J. Mater. Chem*., 2005, **15**, 1857–1864; (*d*) B. Vileno, A. Sienkiewicz, M. Lekka, A. J. Kulik and L. Forro, *Carbon*, 2004, **42**, 1195–1198; (*e*) S. R. Wilson, M. E. Yurchenko, D. I. Schuster, E. N. Yurchenko, O. Sokolova, S. E. Braslavsky and G. Klihm, *J. Am. Chem. Soc*., 2002, **124**, 1977–1981; (*f*) D. Latassa, O. Enger, C. Thilgen, T. Habicher, H. Offermanns and F. Diederich, *J. Mater. Chem*., 2002, **12**, 1993–1995; (*g*) J. L. Bourdelande, J. Font and R. Gonzalez-Moreno, *Helv. Chim. Acta*, 2001, **84**, 3488–3494; (*h*) F. Prat, C. Marti, S. Nonell, X. Zhang, C. S. Foote, M. R. Gonzalez, J. L. Bourdelande and J. Font, *Phys. Chem. Chem. Phys*., 2001, **3**, 1638–1643; (*i*) R. Stackow, G. Schick, T. Jarrosson, Y. Rubin and C. S. Foote, *J. Phys. Chem. B*, 2000, **104**, 7914–7918; (*j*) F. Prat, R. Stackow, R. Bernstein, W. Qian, Y. Rubin and C. S. Foote, *J. Phys. Chem. A*, 1999, **103**, 7230–7235; (*k*) J. L. Bourdelande, J. Font, R. Gonzalez-Moreno and S. Nonell, *J. Photochem. Photobiol., A*, 1998, **115**, 69–71; (*l*) C. S. Foote, *ACS Symp. Ser*., 1995, **616**, 17–23; (*m*) J. L. Anderson, Y.-Z. An, Y. Rubin and C. S. Foote, *J. Am. Chem. Soc*., 1994, **116**, 9763–9764.
13 See for example: (*a*) O. Stoilova, C. Jerome, C. Detrembleur, A. Mouithys-Mickalad, N. Manolova, I. Rashkov and R. Jerome, *Polymer*, 2007, **48**, 1835–1843; (*b*) C. Detrembleur, O. Stoilova, R. Bryaskova, A. Debuigne, A. Mouithys-Mickalad and R. Jerome, *Macromol. Rapid Commun*., 2006, **27**, 498–504; (*c*) S. Wang, R. Gao, F. Zhou and M. Selke, *J. Mater. Chem*., 2004, **14**, 487–493.