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# A Superior Synthesis of Longitudinally Twisted Acenes

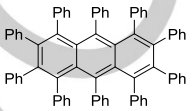
Robert G. Clevenger,[a] Bharat Kumar,[b] Elizabeth M. Menuey,[a] Gene-Hsiang Lee,[c] Dustin Patterson,[b] and Kathleen V. Kilway*[a]

**Abstract:** Seven longitudinally twisted acenes—an anthracene, two tetracenes, three pentacenes, and a hexacene—have been synthesized by the addition of aryllithium reagents to the appropriate quinone precursors, followed by $SnCl_2$-mediated reduction of their diol intermediates, and several of these acenes have been crystallographically characterized. The new syntheses of the three previously reported twisted acenes, decaphenylanthracene (**1**), 9,10,11,20,21,22-hexaphenyltetrabenzo[*a*,*c*,*l*,*n*]pentacene (**2**), and 9,10,11,12,13,14,15,16-octaphenyldibenzo[*a*,*c*]tetracene (**14**), resulted in a reduction of the number of synthetic steps and an improvement of their overall yields were increased by factors of 50-, 24-, and 66-fold, respectively. All of the twisted acene syntheses reported here are suitable for the synthesis of at least gram quantities of these remarkable hydrocarbon.characters.

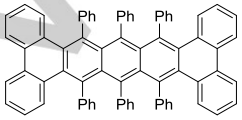
## Introduction

Longitudinally twisted acenes (LTAs) have long been of interest due in part to the remarkable helical shapes many of them have exhibited in their X-ray crystal structures and to their generally pleasing aesthetics.[1] Besides their remarkable twists, several LTAs have exhibited theoretically interesting and potentially useful physical properties.[2–5] Of particular note are decaphenylanthracene[6] (**1**), the longest perphenylacene yet described, with an end-to-end twist of 63°, and 9,10,11,20,21,22-hexaphenyltetrabenzo[*a*,*c*,*l*,*n*]pentacene[7,8] (**2**), arguably the most impressive LTA synthesized to date, with the exceptional end-to-end twist of 144º, the largest yet known. Anthracene **1** was found to display exceptionally stable electrogenerated chemiluminescence (ECL),[9] and pentacene **2** was resolved into its pure enantiomers, which possessed extremely large specific rotations of $[\alpha]_D = \pm 7400°$.

The synthetic methodology used to produce compounds **1** and **2**, and which is predominantly used to synthesize sterically congested acenes in general,[1,10–15] is by what we will refer to as the "benzyne" approach: the design of a benzyne precursor and its subsequent trapping by a diene compatible with the reaction conditions necessary to generate the aryne. Typically, this requires long syntheses resulting in low overall yields. For instance, anthracene **1** has a convergent eight-step synthesis from commercially available tetracyclone (**3**) and gave a reported overall yield of 0.1%.[6]

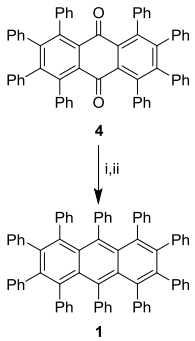



**1**




**2**

However, a classical method for the syntheses of substituted polycyclic aromatic hydrocarbons (PAHs) is by what we will call the "quinone" approach: the addition of an organometallic reagent to a suitable quinone precursor, followed by the reduction of its diol intermediate. Interestingly, it has been applied to the syntheses of several sterically congested anthracenes.[16–19] Intrigued, we added phenyllithium to a refluxing suspension of octaphenylanthraquinone[20] (**4**) in dry benzene. The diol intermediate, which was isolated from the reaction mixture but not purified, was treated with $SnCl_2$ and HCl in refluxing THF to form **1** in 52% yield, a 50-fold improvement over its original synthesis (Scheme 1). As it turns out, this "quinone" approach proves not only to be a superior alternative to the synthesis of compound **1**, but for compound **2** as well, and as a facile means of obtaining several LTAs in general, all of which is presented here in the following paragraphs.




**Scheme 1.** Conditions: i. phenyllithium, benzene, rt 17 h; ii. anhyd. $SnCl_2$, HCl, THF, reflux 1 h, 52% (steps i and ii).

## Results and Discussion

A convenient quinone precursor for pentacene **2** is 9,11,20,22-tetraphenyltetrabenzo[*a*,*c*,*l*,*n*]pentacene-10,21-dione[21,22] (**5**), which is known and typically prepared by the double addition of

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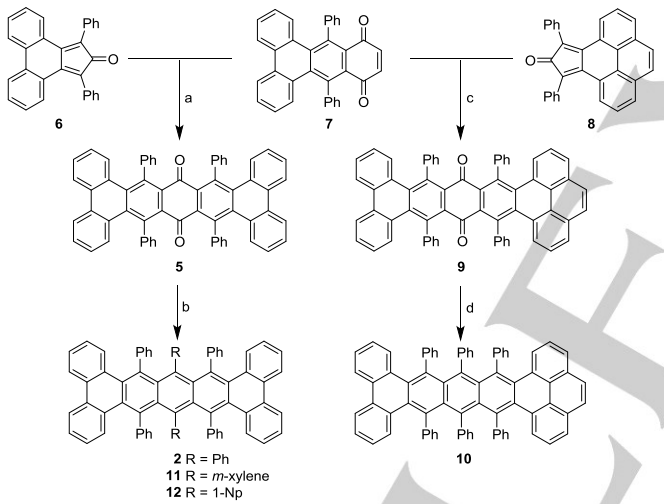
phencyclone[23–25] (**6**) to one-half equivalent of *p*-benzoquinone. But as illustrated in Scheme 2, it may also be prepared by the condensation of the previously reported 9,14-diphenylbenzo[*f*]tetraphene-10,13-dione[26] (**7**) with **6** in 36% yield. Although this route is less efficient than that described above—quinone **5** was previously prepared in 69% yield—compound **7** is a useful precursor from which to build other polycyclic quinones. For instance, heating **7** with pyrenecyclone[27] (**8**) in nitrobenzene gave 9,11,20,22-tetraphenyltetrabenzo[*a*,*c*,*lm*,*qr*]hexacene-10,21-dione (**9**) in 57% yield.

Phenyllithium added smoothly to a refluxing suspension of **5** in dry benzene, followed by treatment of its crude diol intermediate with $SnCl_2$ and HCl in refluxing THF. After recrystallization of the isolated red solid, compound **2** was produced cleanly in 73% yield. This three-step synthesis from phencyclone (**6**) gave **2** in an overall yield of 20%, an estimated 24-fold improvement over its original seven convergent step synthesis. Phenyllithium addition to **9**, followed by $SnCl_2$-mediated reduction produced 9,10,11,20,21,22-hexaphenyltetrabenzo[*a*,*c*,*lm*,*qr*]hexacene (**10**) in 35% yield.




**Scheme 2.** 1-Np represents a 1-naphthyl group. Conditions: (a) nitrobenzene, reflux 24 h, 36%; (b) for **2**: i. phenyllithium, benzene, reflux 1 h, rt 20 h; ii. anhyd. $SnCl_2$, THF, HCl, reflux 1 h, 73% (steps i and ii); for **11**: i. 5-bromo-*m*-xylenes, *n*BuLi, THF, -78 °C, benzene, reflux 1 h, rt 22 h; ii. $SnCl_2$•$2H_2O$, THF, HCl, reflux 1 h, 55% (steps i and ii); for **12**: i. 1-bromonaphthalene, *n*BuLi, THF, -78 °C, benzene, reflux 1 h, rt 24 h; ii. $SnCl_2$•$2H_2O$, THF, HCl, reflux 1 h, 29% (steps i and ii); (c) nitrobenzene, reflux 24 h, 57%; and (d) i. phenyllithium, benzene, reflux 30 min, rt 24 h; ii. $SnCl_2$•$2H_2O$, THF, HCl, reflux 1 h, 35% (steps i and ii).

Compound **10** is a red solid, and crystals suitable for X-ray analysis were obtained from 1,2,4-trimethylbenzene–MeOH. Its molecular structure is shown in Figure 1. Acene **10** crystallizes in a special position in the monoclinic space group *C*2/*c*, with Z = 4, and it possesses crystallographic $C_2$ symmetry. Although the pyrene moiety in compound **10** would appear to offer the same steric congestion as its phenanthrene equivalent, the C6A–C5A–C21–C20 torsion angle measures at 134.6°, almost 10° less than that reported for compound **2**, and less than the AM1-predicted 141°. Crystal structures of previously reported LTAs typically show that the overall twist of the acene is distributed somewhat evenly among the individual benzene rings,[1] and the individual rings of compound **10** showed a similarly even distribution. The twists of five rings measured (from left-to-right) 20°, 30°, 29°, 30°, and 21°, respectively, with the exception being the terminal ring on the pyrene subunit, which possessed a nominal 4° twist. Average distance between ipso carbons and benzo hydrogens [e.g., C22–H1] is 2.33 Å, while the average distance between ipso carbons [e.g., C28–C34] is 2.94 Å. These intramolecular non-bonded contacts are virtually identical to those observed in pentacene **2**.

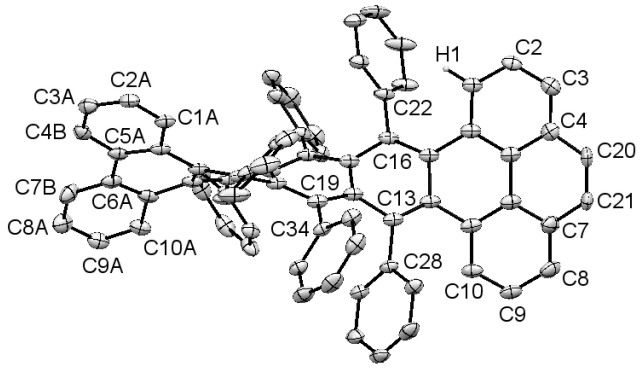



**Figure 1.** Molecular structure of compound **10**. Thermal ellipsoids have been drawn at the 50% probability level, and all hydrogens except H1 have been omitted for clarity.

A seemingly straightforward means of obtaining LTAs with even greater twists than that of pentacene **2** would be by the addition of bulkier aryllithium reagents to quinone **5**. 5-Bromo-*m*-xylene was converted to its corresponding aryllithium reagent by treatment with *n*-butyllithium at -78 °C, and it was added to a refluxing suspension of quinone **5** in dry benzene. $SnCl_2$-mediated reduction of the diol intermediate afforded 10,21-bis(3,5-dimethylphenyl)-9,11,20,22-tetraphenyltetrabenzo[*a*,*c*,*l*,*n*]pentacene (**11**) in 55% yield. Crystals of compound **11** suitable for X-ray analysis were obtained from $CH_2Cl_2$–hexanes, and its molecular structure is shown in Figure 2. Acene **11** crystallizes in a general position in the monoclinic space group $P2_1/c$, with Z = 4. We assumed that derivative **11**, with its sterically demanding xylene substituents, would naturally possess an even greater end-to-end twist than the 144° twist observed in **2**, albeit not necessarily dramatically greater. But AM1 calculations predicted, somewhat to our surprise, that both compounds should possess identical end-to-end twists. We were therefore pleased to find the C28–C27–C3–C19 torsion angle measured at 147.7°, with individual rings twists (from left-to-right) of 27°, 29°, 28°, 30°, and 31°, respectively, thus making acene **11** the most twisted pentacene yet known. Average distance between

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ipso carbons and benzo hydrogens [e.g., C35–H77] for **11** is 2.42 Å, slightly greater than that observed in compound **2**, while the average distance between ipso carbons [e.g., C35–C41] is 2.94 Å. which is identical.

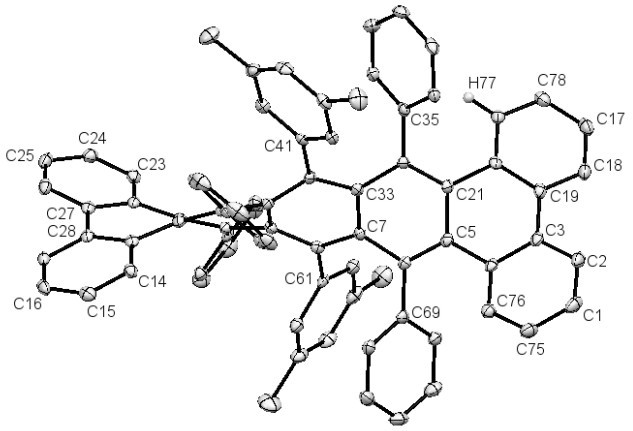


**Figure 2.** Molecular structure of compound **11**. Thermal ellipsoids have been drawn at the 50% probability level, and all hydrogens except H77 have been omitted for clarity.

Surprisingly, the addition of the even bulkier 1-naphthyl (1-Np) substituent proved to be just as facile as the others. Similar to the synthesis of compound **11** described previously, 10,21-di(1-naphthyl)-9,11,20,22-tetraphenyltetrabenzo[*a*,*c*,*l*,*n*]pentacene (**12**) was produced in 29% yield. With the addition of naphthyl substituents, the formation of both *cis*- and *trans*-isomers is a likely possibility. But the $^{1}$H NMR spectrum of **12**—derived from the reduction of the crude diol intermediate—showed the predominance of only one isomer. Which one? The X-ray crystal structure of quinone **5**,[22] which shows the carbonyl groups *trans* to one another and tilted up, with the surrounding phenyl substituents splayed open and situated underneath, would lead one to expect the *trans*-isomer to be the dominant, if not exclusive, product formed. Chromatographic purification of the crude diol was used to obtain a pure diol, as determined by TLC, and after its reduction, we were able to obtain a clean NMR spectrum of a single isomer—what we posit to be the pure *trans*-isomer.

Crystals for X-ray analysis for compound **12** were grown from the product obtained from the reduction of the crude diol, and its molecular structure is shown in Figure 3. Acene **12** crystallizes in a general position in the triclinic space group *P*1, with Z = 2, and shows only the presence of the *trans*-isomer. The C10–C11–C29–C30 torsion angle measures at 140.9°, less than the AM1 calculated 144° end-to-end twist, with individual rings twists (from left-to-right) of 26°, 29°, 29°, 29°, and 27°, respectively. Average distance between ipso carbons and benzo hydrogens [e.g., C71–H25] for **12** is 2.37 Å, while the average distance between ipso carbons [e.g., C71–C61] is 2.94 Å. The C–C distances are virtually identical to those observed in pentacene **2**, while the C–H distances differ only slightly.

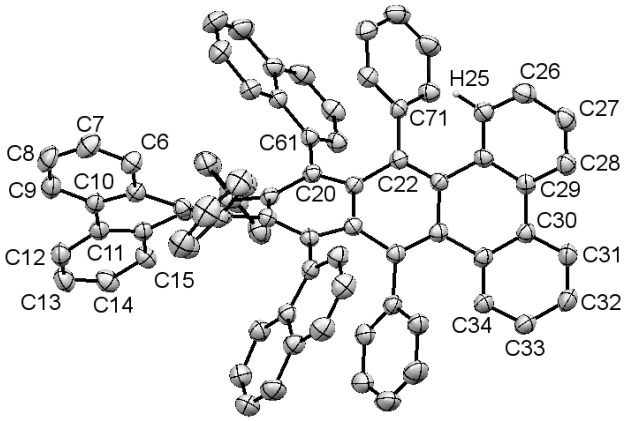


**Figure 3.** Molecular structure of compound **12**. Thermal ellipsoids have been drawn at the 50% probability level, and all hydrogens except H25 have been omitted for clarity.

Refluxing **7** with tetracyclone (**3**) in nitrobenzene formed 9,11,12,13,14,16-hexaphenyldibenzo[*a,c*]tetracene-10,15-dione (**13**) in 22% yield (Scheme 3), a reasonable precursor for the previously reported 9,10,11,12,13,14,15,16-octaphenyldibenzo-[*a,c*]tetracene[28] (**14**). Phenyllithium was added to **13** in dry THF, but unlike with the previous syntheses, isolation of the crude diol was skipped—a solution of $SnCl_2$ and HCl were added directly to the reaction contents, giving **14** in 40% yield. The overall yield of acene **14** from phencyclone (**6**) was 6.6%, an almost 66-fold improvement over its original synthesis. Condensation of dienone **7** with the easily prepared acecyclone[23] (**15**) gave 7,9,18,20-tetraphenylacenaphtho[1,2-*k*]dibenzo[*a*,*c*]tetracene-8,19-dione (**16**) in 54% yield. Addition of phenyllithium followed by reduction produced 7,8,9,18,19,20-hexaphenylacenaphtho-[1,2-*k*]dibenzo[*a*,*c*]tetracene (**17**) in 20% yield.

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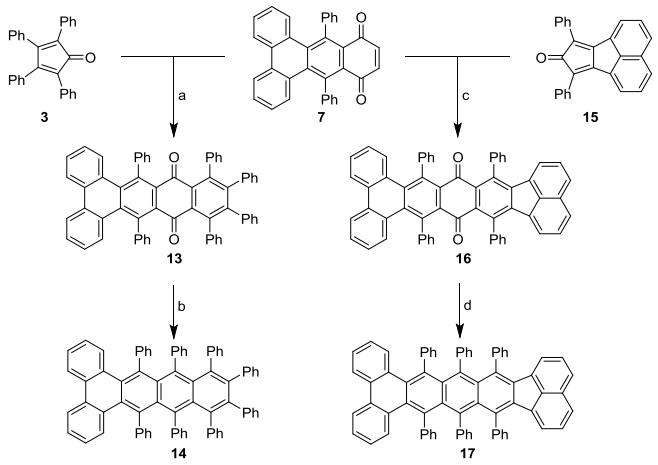

**Scheme 3.** Conditions: (a) nitrobenzene, reflux 48 h, 22%; (b) i. phenyllithium, THF, rt 1.5 h, reflux 1.5 h; ii. $SnCl_2$•$2H_2O$, THF, HCl, reflux 18 h, 40% (steps i and ii); (c) nitrobenzene, reflux 25 h, 54%; (d) i. phenyllithium, THF, rt 24 h; ii. $SnCl_2$•$2H_2O$, THF, HCl, reflux 16 h, 20% (steps i and ii).

Orange crystals of acene **17** suitable for X-ray analysis were grown from EtOAc–$CH_2Cl_2$, and its molecular structure is shown in Figure 4. Acene **17** lies in a general position and crystallizes in the monoclinic space group $P2_1/n$, with Z = 4. The C22–C21–C15–C14 torsion angle measures 102.3°, while the end-to-end twist of the tetracene substructure within is 96.1°—AM1 calculations predict an overall twist of 109° and the tetracene substructure twist to be 104.5°. Compound **17** displays remarkable stability in a chloroform solution exposed to air and ambient light, showing only slight decomposition, as judged by TLC, even after several weeks.

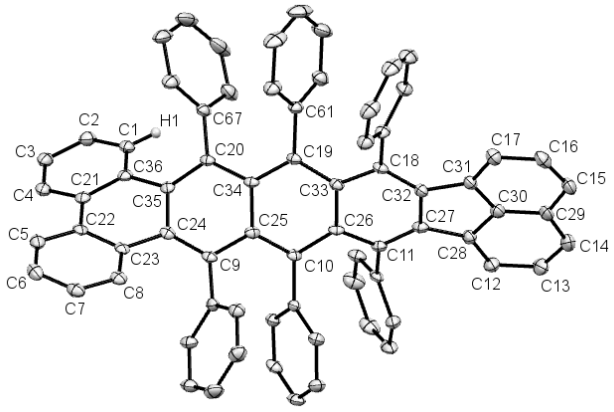


**Figure 4.** Molecular structure of compound **17**. Thermal ellipsoids have been drawn at the 50% probability level, and all hydrogens except H1 have been omitted for clarity.

## Conclusions

We have adapted a classical method for the synthesis of substituted acenes, which we have coined the “quinone” approach, as an alternative to the “benzyne” approach for the synthesis of seven longitudinally twisted acenes. It is quite evident that if a suitable quinone precursor is available, it is a far superior approach, as demonstrated by the relatively facile syntheses of the previously reported compounds **1**, **2**, and **14**, whose overall yields were increased by 50-, 24-, and 66-fold, respectively. Professor Pascal, to whom we have communicated our preliminary synthetic results, reports that a first-year graduate student was able to prepare five grams of pentacene **2** in less than two weeks by using our method, which also speaks its scalability. AM1 calculations provide a good guide for the end-to-end twists of LTAs, but cannot predict how the twists will be impacted by crystal packing forces as compounds **10** (134.6° versus AM1 141.5°), **11** (147.7° versus AM1 144.1°), and **12** demonstrate (140.9° versus AM1 144°). And counter to what one would think, addition of bulkier aryllithium substituents—as compared to the phenyl group—has little to no impact on the end-to-end twist as predicted by AM1 and confirmed by X-ray crystallography, although each differs slightly from calculations in their solid state.

**Table 1.** Theoretical and observed twist dihedral angle.

| Compound | AM1 | X-ray |
|---|---|---|
| **1**[6] | 67° | 63° |
| **2**[7,8] | 144° | 144° |
| **10** | 141.5° | 134.6 |
| **11** | 144.1° | 147.7° |
| **12** | 144° | 140.9° |
| **14**[28] | 109.3° | 105° |
| **17** | 109°, 104.5° | 102.3°, 96.1° |

## Experimental Section

*Materials and Methods*

All commercial reagents obtained were used as purchased unless noted otherwise. THF was distilled from sodium–benzophenone and benzene was distilled from calcium hydride, both under an argon atmosphere. All melting points were recorded on a Mel-Temp apparatus and are uncorrected. TLC was performed on 0.25 mm polyester-backed silica gel plates with $F_{254}$ indicator. Spots were visualized with UV light (254 nm and 365 nm). Column chromatography was performed with silica

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gel 60Å (18–32 μm mesh). $^1$H NMR spectra were recorded on a Varian AC 400 spectrometer operating at 400 MHz. Chemical shifts ($\delta$) are reported in ppm using the residual solvent peak as the internal standard ($CHCl_3$: $\delta$ 7.26). $^1$H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets, m = multiplet, br = broad signal), coupling constant (reported to the nearest 0.5 Hz), and integration. $^{13}$C NMR spectra were recorded on a Varian AC 400 spectrometer operating at 101 MHz. Chemical shifts ($\delta$) are reported in ppm using the residual solvent peak as the internal standard ($CHCl_3$: $\delta$ 77.0). Mass spectra were recorded using either an atmospheric pressure photoionization (APPI) source on a time-of-flight (TOF) instrument in the positive mode with the use of toluene to promote ionization when necessary, an electrospray ionization (ESI) source on a time-of-flight (TOF) instrument in the positive mode, or a matrix assisted laser desorption (MALDI-TOF). UV-Vis spectra were collected on an Ocean Optics USB2000 UV-Vis-NIR spectrophotometer. X-ray data were collected by using graphite monochromated Mo K$\alpha$ radiation (0.71073 Å) on a Nonius KappaCCD diffractometer. No special steps were taken to exclude oxygen or moisture during the growth of X-ray quality crystals. The diffraction data were processed and reduced with DENZO,[29] PLATON,[30] Siemens SHELXTL,[31] and SQUEEZE/BYPASS.[32] All structures were solved by direct methods and were refined by full-matrix least-squares on $F^2$ using SHELXTL. All structures were solved by the charge flipping algorithm or direct methods.

**Synthesis of Octaphenylanthraquinone** (**4**)

It was synthesized by a procedure adapted from the work of Lu et al.[20] Tetracyclone **3** (10.0 g, 26.0 mmol) and *p*-benzoquinone (1.49 g, 13.8 mmol) were heated at reflux in nitrobenzene (20 mL) for 23 h. The reaction contents were poured into ethanol (300 mL), and the precipitate was collected via vacuum filtration. The solid was stirred in acetone (100 mL) and vacuum filtered. The crude quinone was subjected to column chromatography (silica gel; eluent: $CH_2Cl_2$). All the fractions containing quinone **4**, $R_f$ 0.69 TLC (silica gel; eluent: 1:9 EtOAc–toluene) were combined, and the solvent was removed under reduced pressure. The residue was triturated with acetone and vacuum filtered to give **4** as a tannish solid, which was used in the next step without any further purification (1.03 g, 1.26 mmol, 9.69%). An analytical sample was obtained by recrystallizing a small amount of **4** from $CHCl_3$–MeOH: mp 401–402 °C (lit.[20] mp 391–392 °C); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 6.71 (dd, $J$ = 7, 2 Hz, 8 H), 6.80–6.83 (m, 12 H), 6.93–6.99 (m, 20 H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 125.9, 126.1, 126.7, 126.9, 130.3, 130.7, 135.4, 137.8, 138.7, 139.8, 146.3, 188.6 (12 of 12 expected resonances observed); NMR spectra are essentially identical to that reported by Lu et al.[20]; HRMS (ESI-TOF) $m/z$ 839.2905 ([M + Na]$^+$), calcd for $C_{62}H_{40}O_2Na$ 839.2921.

**Synthesis of Decaphenylanthracene** (**1**)

Phenyllithium (1.8 M in dibutyl ether, 0.70 mL, 1.3 mmol) was added to a suspension of quinone **4** (200 mg, 0.24 mmol) in dry benzene (10 mL), and the contents were stirred for 17 h at rt under argon. The reaction was quenched by the addition of water (10 mL) and acidified with acetic acid. The contents were poured into water (20 mL) and steam distilled to remove the organic solvents. The solid was collected via vacuum filtration and rinsed with ethanol. The crude diol was brought to reflux in THF (10 mL) in a screw-capped vial. A solution of anhyd. $SnCl_2$ (920 mg, 4.9 mmol) dissolved into HCl (1 mL) was added in one portion to the refluxing THF suspension. The reaction contents were maintained at reflux for 1 h. The reaction contents were diluted with acetone (15 mL) and filtered. The solid was recrystallized from $CHCl_3$–MeOH to give **1** as a yellow solid (120 mg, 0.13 mmol, 52%): mp >400 °C (lit.[6] mp >400 °C); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 6.27 (d, $J$ = 8 Hz, 8 H), 6.41 (t, $J$ = 7 Hz, 4 H), 6.47–6.60 (m, 22 H), 6.70–6.78 (m, 16 H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 124.1, 124.8, 125.4, 125.9, 126.1, 126.4, 131.1, 131.8, 132.3, 134.8, 135.9, 136.9, 138.5, 140.4, 140.9, 142.0 (16 of 16 expected resonances observed); NMR spectra are essentially identical to that reported by Qiao et al.[6]; HRMS (ESI-TOF) $m/z$ 961.3787 ([M + Na]$^+$), calcd for $C_{74}H_{50}Na$ 961.3805.

**Synthesis of Phencyclone** (**6**)

It was synthesized by a procedure adapted from the work of Pascal et al.[24] Small aliquots of a solution of NaOH (1.09 g, 27.3 mmol) in ethanol (30 mL) were added to a suspension of 9,10-phenanthrenequinone (3.02 g, 14.5 mmol) and 1,3-diphenylacetone (3.28 g, 15.6 mmol) in ethanol (100 mL). Once complete, the reaction contents were stirred at rt for 15 min, then heated to a gentle reflux, at which point the flask was immediately placed into an ice-bath. Once cooled, the precipitate was collected via vacuum filtration and rinsed with ethanol to give **6** as a black solid, which was used in the next step without any further purification (4.90 g, 12.8 mmol, 88.3%): $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 6.95 (t, $J$ = 7 Hz, 2 H), 7.28–7.30 (m, 2 H), 7.36–7.45 (m, 10 H), 7.55 (dd, $J$ = 8, 1 Hz, 2 H), 7.81 (d, $J$ = 7.5 Hz, 2 H); NMR spectrum is essentially identical to that reported by Marchand et al.[25]; HRMS (ESI-TOF) $m/z$ 405.1250 ([M + Na]$^+$), calcd for $C_{29}H_{18}ONa$ 405.1250.

**Synthesis of 9,14-Diphenylbenzo[*f*]tetraphene-10,13-dione** (**7**)

It was was synthesized by a procedure adapted from the work of Mondal et al.[26] Phencyclone **6** (5.08 g, 13.3 mmol) and *p*-benzoquinone (4.82 g, 44.6 mmol) were heated at reflux in nitrobenzene (20 mL) for 2 h. The reaction contents were poured into ethanol (300 mL) and the precipitate was collected via vacuum filtration. The solid was dissolved in a minimal amount of $CH_2Cl_2$, and it was subjected to column chromatography (silica gel; eluent: $CH_2Cl_2$). A red band was collected with $R_f$ 0.54 TLC (silica gel; eluent: 1:9 EtOAc–toluene). The solvent was removed under reduced pressure to give **7** as an orange solid, which was used in the next step without any further purification (4.58 g, 9.95 mmol, 74.9%). An analytical sample was obtained by recrystallizing a small amount of **7** from $CHCl_3$–MeOH: mp 320.5 °C dec (lit.[26] mp 305 °C); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 6.88 (s, 2 H), 7.07 (td, $J$ = 8, 1 Hz, 2 H), 7.33–7.36 (m, 4 H), 7.44–7.52 (m, 10 H), 8.40 (d, $J$ = 7.5 Hz, 2 H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 123.3, 125.7, 127.7, 128.1, 129.0, 129.5, 129.9,

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130.3, 130.7, 132.4, 136.5, 138.9, 139.6, 141.2, 186.9 (15 of 15 expected resonances observed); HRMS (ESI-TOF) *m*/*z* 483.1354 ([M + Na]$^+$), calcd for $C_{34}H_{20}O_2Na$ 483.1356.

**Synthesis of 9,11,20,22-Tetraphenyltetrabenzo[*a,c,l,n*]pentacene-10,21-dione** (**5**)

Quinone **7** (660 mg, 1.4 mmol) and phencyclone **6** (610 mg, 1.6 mmol) were placed into a screw-capped vial and gradually heated to reflux in nitrobenzene (4 mL) over the course of 1 h. The reaction contents were maintained at reflux for 24 h. The reaction mixture was diluted with acetone (20 mL) and the precipitate was collected via vacuum filtration. The solid was boiled briefly in nitrobenzene (20 mL) and diluted with acetone (10 mL). The precipitate was collected via vacuum filtration to give **5** as a yellow solid, which was used in the next step without any further purification (420 mg, 0.52 mmol, 36%): mp >400 °C (lit.[21] mp 460–461 °C); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.02 (td, *J* = 8, 1 Hz, 4 H), 7.22–7.33 (m, 20 H), 7.43 (td, *J* = 8, 1 Hz, 4 H), 7.51 (dd, *J* = 8.5, 1 Hz, 4 H), 8.35 (dd, *J* = 8, 1 Hz, 4 H); NMR spectrum is essentially identical to that reported by Pascal et al.[22]

**Synthesis of Pyrenecyclone** (**8**)

It was synthesized by a procedure adapted from the work of Pascal et al.[24] A solution of KOH (240 mg, 4.3 mmol) in ethanol (5 mL) was added in small aliquots to a stirring suspension of pyrene-4,5-dione[33] (460 mg, 2.0 mmol) and 1,3-diphenylacetone (450 mg, 2.1 mmol) in ethanol (50 mL). Once the addition was complete, the reaction contents were stirred at rt for 15 min. The reaction mixture was heated to reflux and then immediately cooled in an ice-bath. The precipitate was collected via vacuum filtration and rinsed with ethanol. Recrystallization from $CHCl_3$–MeOH gave **8** as a brown solid, which was used in the next step without any further purification (350 mg, 0.86 mmol, 43%): mp 226 °C dec (lit.[27] mp 235–239 °C); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.25 (t, *J* = 8 Hz, 2 H), 7.39–7.50 (m, 10 H), 7.66 (s, 2 H), 7.74 (dd, *J* = 7.5, 1 Hz, 2 H), 7.87 (dd, *J* = 7.5, 1 Hz, 2 H); NMR spectrum is essentially identical to that reported by Pascal et al.[27]; HRMS (ESI-TOF) *m*/*z* 407.1420 ([M + H]$^+$), calcd for $C_{31}H_{19}O$ 407.1430.

**Synthesis of 9,11,20,22-Tetraphenyltetrabenzo[*a,c,lm,qr*]hexacene-10,21-dione** (**9**)

Quinone **7** (510 mg, 1.1 mmol) and pyrenecyclone **8** (510 mg, 1.3 mmol) were placed into a screw-capped vial and heated to reflux over the course of 1.5 h in nitrobenzene (3 mL). The reflux was maintained for 24 h. The reaction contents were diluted with acetone (25 mL). The precipitate was collected via vacuum filtration and rinsed with ethanol and acetone. The solid was briefly boiled in nitrobenzene (10 mL) and then diluted with acetone (10 mL). The precipitate was collected via vacuum filtration to give **9** as a yellow solid, which was used in the next step without any further purification (530 mg, 0.63 mmol, 57%). An analytical sample was obtained by subjecting a small amount of **9** to column chromatography (silica gel; eluent: toluene, followed by 20% $CH_2Cl_2$–toluene): mp >400 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.02 (t, *J* = 8 Hz, 2 H), 7.16–7.26 (m, 8 H), 7.28–7.35 (m, 12 H), 7.38 (t, *J* = 8 Hz, 2 H), 7.43 (t, *J* = 7.5 Hz, 2 H), 7.53 (d, *J* = 8.5 Hz, 2 H), 7.80 (d, *J* = 8 Hz, 2 H), 7.92 (s, 2 H), 7.94 (d, *J* = 7.5 Hz, 2 H), 8.36 (d, *J* = 8 Hz, 2 H); due to poor solubility, a definitive $^{13}$C NMR spectral characterization of **9** could not be obtained; HRMS (ESI-TOF) *m*/*z* 859.2605 ([M + Na]$^+$), calcd for $C_{64}H_{36}O_2Na$ 859.2608.

**Synthesis of 9,10,11,20,21,22-Hexaphenyltetrabenzo[*a,c,l,n*]pentacene** (**2**)

Phenyllithium (1.8 M in dibutyl ether, 0.4 mL, 0.7 mmol) was added to a suspension of quinone **5** (110 mg, 0.14 mmol) in dry benzene (8 mL) under argon at reflux. The reaction contents were maintained at reflux for 1 h and then stirred for 20 h at rt. The reaction was quenched by the addition of water (10 mL) and acidified with acetic acid. The contents were poured into water (10 mL) and steam distilled to remove the organic solvents. The aqueous mixture was extracted with $CH_2Cl_2$, dried over $Na_2SO_4$, and filtered. The solvent was removed under reduced pressure. The crude diol was heated at reflux in THF (6 mL) in a screw-capped vial. A solution of anhyd. $SnCl_2$ (1.09 g, 5.75 mmol) dissolved into HCl (1 mL) was added in one portion to the refluxing THF solution. The reaction contents were maintained at reflux for 1 h. The THF was removed under reduced pressure, and the residue was triturated with water (20 mL). The solid was collected via vacuum filtration and rinsed thoroughly with ethanol. Recrystallization from $CHCl_3$–MeOH gave **2** as a red solid (92 mg, 0.098 mmol, 73%): mp >400 °C (lit.[7,8] mp >470 °C); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 6.41 (t, *J* = 7.5 Hz, 4 H), 6.52 (tt, *J* = 7.5, 1.5 Hz, 2 H), 6.56 (dd, *J* = 8.5, 1 Hz, 4 H), 6.62–6.71 (m, 12 H), 6.73–6.77 (m, 8 H), 6.86 (tt, *J* = 7.5, 1.5 Hz, 4 H), 6.92 (td, *J* = 7.5, 1 Hz, 4 H), 7.23 (td, *J* = 7.5, 1 Hz, 4 H), 8.06 (dd, *J* = 8, 1 Hz, 4 H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 123.4, 125.3, 125.7, 126.2, 126.6, 127.7, 127.8, 128.0, 130.0, 132.1, 132.6, 132.9, 133.0, 133.1, 134.1, 134.2, 135.0, 140.0, 141.1 (19 of 22 expected resonances observed; but the $\delta$ 126.6 resonance may contain two lines); NMR spectra are essentially identical to that reported by Lu et al.[7,8]; MS (MALDI-TOF) *m*/*z* 934.290 ([M]$^+$), calcd for $C_{74}H_{46}$ 934.3600.

**Synthesis of 9,10,11,20,21,22-Hexaphenyltetrabenzo[*a,c,lm,qr*]hexacene** (**10**)

Phenyllithium (2 M in dibutyl ether, 0.80 mL, 1.6 mmol) was added to a suspension of quinone **9** (210 mg, 0.25 mmol) in dry benzene (10 mL) at rt under argon. The reaction was heated at reflux for 30 min and then stirred for 24 h at rt. The reaction was quenched by the addition of water (10 mL) and acidified with acetic acid. The contents were poured into water (20 mL) and steam distilled to remove the organic solvents. The aqueous mixture was extracted with $CH_2Cl_2$. The organic extract was dried over $Na_2SO_4$ and filtered. The solvent was removed under reduced pressure. The crude diol was heated at reflux in THF (8 mL) with $SnCl_2$•$2H_2O$ (1.05 g, 4.65 mmol) and HCl (1 mL) in a screw-capped vial for 1 h. The reaction contents were poured into water (70 mL) and extracted with $CH_2Cl_2$. The organic extract was dried over $Na_2SO_4$ and filtered. The solvent was removed under reduced pressure. The residue was subjected to column chromatography (silica gel; eluent: hexanes, followed by

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20% toluene–hexanes). A red fluorescent band was collected with $R_f$ 0.42 TLC (silica gel; eluent: 3:7 $CH_2Cl_2$–hexanes). Recrystallization from $CHCl_3$–MeOH gave **10** as a red solid (85 mg, 0.089 mmol, 35%): mp >400 ºC; $^1$H NMR (400 MHz, $CDCl_3$, 25 °C) $\delta$ 6.40 (q, $J$ = 8 Hz, 4 H), 6.51 (d, $J$ = 7.5 Hz, 2 H), 6.53–6.68 (m, 13 H), 6.72–6.79 (m, 7 H), 6.84–6.89 (m, 6 H), 6.92–7.01 (m, 4 H), 7.07 (t, $J$ = 8 Hz, 2 H), 7.21–7.25 (m, 2 H), 7.70 (d, $J$ = 7.5 Hz, 2 H), 7.79 (s, 2 H), 8.06 (dd, $J$ = 8, 1 Hz, 2 H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 123.4, 124.3, 125.3, 125.4, 125.7, 126.2, 126.6, 127.7, 127.8, 127.9, 128.0, 128.2, 130.1, 130.6, 130.7, 132.1, 132.6, 132.8, 132.9, 133.1, 133.2, 133.3, 134.2, 134.9, 135.1, 135.3, 140.0, 141.2, 141.5 (29 of 32 expected resonances observed; but the $\delta$ 127.7, 128.0, 133.1, and 134.2 resonances may contain two lines, and the $\delta$ 126.2 and 126.6 resonances may contain three lines); UV ($CHCl_3$) $\lambda_{max}$ (log $\epsilon$) 403 (4.97), 486 (sh, 3.99), 508 (4.04), 543 (3.87); HRMS (ESI-TOF) $m/z$ 958.3537 ([M]$^+$), calcd for $C_{76}H_{46}$ 958.3600; crystals suitable for X-ray analysis were obtained from 1,2,4-trimethylbenzene–MeOH.

**Synthesis of 10,21-Bis(3,5-dimethylphenyl)-9,11,20,22-tetraphenyltetrabenzo[*a,c,l,n*] pentacene** (**11**)

*n*-Butyllithium (2.5 M in hexanes, 1.2 mL, 3.0 mmol) was added in small aliquots to a solution of 5-bromo-*m*-xylenes (0.45 mL, 3.3 mmol) in dry THF (6 mL) which was cooled to -78 °C under argon. Once the addition was complete, the contents were allowed to stir at -78 °C for 20 min, and then stirred at rt until the opaque contents became clear. The resulting lithium reagent was added to a refluxing suspension of quinone **5** (210 mg, 0.26 mmol) in dry benzene (20 mL) under argon. The reaction contents were maintained at reflux for 1 h, and then stirred for 22 h at rt. The reaction was quenched by the addition of water (10 mL) and acidified with acetic acid. The contents were poured into water (20 mL) and steam distilled to remove the organic solvents. The aqueous mixture was extracted with $CH_2Cl_2$, dried over $Na_2SO_4$, filtered, and the solvent removed under reduced pressure. The residue was placed into a screw-capped vial with THF (8 mL) and the contents brought to reflux. A solution of $SnCl_2$•$2H_2O$ (4.06 g, 18.0 mmol) dissolved into HCl (1 mL) was added in one portion to the refluxing THF solution. The reaction contents were maintained at reflux for 1 h. The THF was removed under reduced pressure. An equal volume of a water–ethanol solution (30 mL) was added to the residue and the resulting precipitate was collected via vacuum filtration, and rinsed with ethanol. The solid was subjected to column chromatography (silica gel; eluent: hexanes, followed by 1:3 $CH_2Cl_2$–hexanes). A red fluorescent band was collected with $R_f$ 0.46 TLC (silica gel; eluent: 3:7 $CH_2Cl_2$–hexanes). Recrystallization from *o*-dichlorobenzene–acetone gave **11** as a red solid (140 mg, 0.14 mmol, 55%): mp >400 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 1.77 (s, 12 H), 6.04 (s, 2 H), 6.18 (d, $J$ = 1.5 Hz, 4 H), 6.62–6.65 (m, 4 H), 6.67–6.70 (m, 8 H), 6.73–6.78 (m, 8 H), 6.85 (tt, $J$ = 7.5, 1.5 Hz, 4 H), 6.95 (td, $J$ = 7.5, 1 Hz, 4 H), 7.23 (td, $J$ = 7.5, 1 Hz, 4 H), 8.08 (dd, $J$ = 8, 1 Hz, 4 H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 20.4, 123.4, 125.3, 125.8, 126.5, 127.2, 127.3, 127.4, 130.2, 132.3, 132.6, 132.9, 133.0, 133.2, 134.3, 134.5, 135.1, 139.5, 141.2 (19 of 19 expected resonances observed; but the $\delta$ 127.2 and 132.6 resonances may contain two lines); UV ($CHCl_3$) $\lambda_{max}$ (log $\epsilon$) 376 (sh, 5.04), 393 (5.25), 481 (sh, 3.81), 505 (3.90), 539 (3.79); HRMS (APPI-TOF) $m/z$ 991.4248 ([M + H]$^+$), calcd for $C_{78}H_{55}$ 991.4298; crystals suitable for X-ray analysis were obtained from $CH_2Cl_2$–MeOH.

**Synthesis of 10,21-Di(1-naphthyl)-9,11,20,22-tetraphenyl tetrabenzo[*a,c,l,n*]pentacene** (**12**)

*n*-Butyllithium (2.5 M in hexanes, 1.2 mL, 3.0 mmol) was added in small aliquots to a solution of 1-bromonaphthalene (0.45 mL, 3.2 mmol) in dry THF (6 mL), which was cooled to -78 °C under argon. Once the addition was complete, the contents were allowed to stir at -78 °C for 20 min and then stirred at rt until the opaque contents became clear. The resulting lithium reagent was added to a refluxing suspension of quinone **5** (220 mg, 0.27 mmol) in dry benzene (20 mL) under argon. The reaction contents were maintained at reflux for 1 h and then stirred for 24 h at rt. The reaction was quenched by the addition of water (10 mL) and acidified with acetic acid. The contents were poured into water (20 mL) and steam distilled to remove the organic solvents. The aqueous mixture was extracted with $CH_2Cl_2$, dried over $Na_2SO_4$, and filtered. The solvent was removed under reduced pressure. The residue was placed into a screw-capped vial with THF (8 mL) and the contents brought to reflux. A solution of $SnCl_2$•$2H_2O$ (3.88 g, 17.2 mmol) dissolved into HCl (1 mL) was added in one portion to the refluxing THF solution. The reaction contents were maintained at reflux for 1 h. The solvent was removed under reduced pressure, and the residue was dissolved into $CH_2Cl_2$. The organic solvent was washed with water (75 mL), dried over $Na_2SO_4$, and filtered. The solvent was removed under reduced pressure. The solid was subjected to column chromatography (silica gel; eluent: hexanes, followed by 1:3 and then 1:1 $CH_2Cl_2$–hexanes). A red fluorescent band was collected with $R_f$ 0.69 TLC (silica gel; eluent: 1:1 $CH_2Cl_2$–hexanes). Recrystallization from *o*-dichlorobenzene–acetone gave **12** as a red solid (81 mg, 0.078 mmol, 29%): mp >400 °C; a clean NMR spectra was obtained by subjecting a small amount of the crude diol to column chromatography (silica gel; eluent: toluene). A blue fluorescent band was collected with $R_f$ 0.30 TLC (silica gel; eluent: 3:7 hexanes–toluene). This band was again subjected to column chromatography (silica gel; eluent: hexanes, followed by 2:3 toluene–hexanes). The eluent was removed under reduced pressure and the residue triturated with methanol and then acetone to give presumably the pure *trans*-diol, which was reduced to form **12** under conditions stated above; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 5.71 (dq, $J$ = 8, 1 Hz, 2 H), 6.16–6.24 (m, 4 H), 6.33 (tt, $J$ = 7.5, 1.5 Hz, 2 H), 6.42 (td, 7.5, 1 Hz, 2 H), 6.54–6.58 (m, 6 H), 6.61 (dt, $J$ = 7.5, 1.5 Hz, 2 H), 6.65–6.71 (m, 6 H), 6.73–6.77 (m, 2 H), 6.86 (td, $J$ = 7.5, 1.5 Hz, 2 H), 6.94–6.96 (m, 6 H), 7.02 (d, $J$ = 8.5 Hz, 2 H), 7.06–7.10 (m, 4 H), 7.16 (td, $J$ = 7.5, 1 Hz, 2 H), 7.21 (td, $J$ = 7.5, 1 Hz, 2 H), 7.31 (dd, $J$ = 8.5, 1.5 Hz, 2 H), 7.99 (dd, $J$ = 8, 1 Hz, 2 H), 8.05 (dd, $J$ = 8, 1 Hz, 2 H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 123.1, 123.4, 124.4, 124.6, 124.8, 125.0, 125.2, 125.3, 126.1, 126.5, 126.6, 126.9, 127.1, 127.3, 127.5, 128.0, 130.0, 131.1, 131.8, 131.9, 132.0, 132.1, 132.4, 132.6, 132.8, 133.0, 133.4, 133.7, 134.4, 134.6, 134.7, 134.8, 137.9, 140.3, 140.5 (35 of 37

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expected resonances observed; but the *δ* 126.5, 130.0, and 131.1 resonances may contain two lines); UV ($CHCl_3$) $\lambda_{max}$ (log ε) 391 (5.09), 478 (sh, 3.80), 508 (3.91), 537 (3.82); HRMS (APPI-TOF) *m*/*z* 1035.3928 ([M + H]$^+$), calcd for $C_{82}H_{51}$ 1035.3985; crystals suitable for X-ray analysis were obtained from toluene–MeOH.

**Synthesis of Acecyclone** (**15**)

It was synthesized by a procedure adapted from the work of Pascal et al.[24] Small aliquots of a solution of NaOH (1.57 g, 39.3 mmol) in ethanol (50 mL) were added to a suspension of acequinone (4.00 g, 22.0 mmol) and 1,3-diphenylacetone (5.25 g, 25.0 mmol) in ethanol (100 mL) at rt. Once complete, the reaction contents were stirred at rt for 15 min, then heated to a gentle reflux, at which point the flask was immediately placed into an ice-bath. Once cooled, the precipitate was collected via vacuum filtration and rinsed with ethanol to give **15** as a brown solid, which was used in the next step without any further purification (7.40 g, 20.8 mmol, 94.6%). An analytical sample was obtained by recrystallizing a small amount of **15** from $CHCl_3$–MeOH: mp 286–289 °C gas evolution (lit.[23] mp 289–290 °C); $^1$H NMR (400 MHz, $CDCl_3$) *δ* 7.41 (tt, *J* = 7.5, 1.5 Hz, 2 H), 7.50–7.55 (m, 4 H), 7.59 (t, *J* = 7.5 Hz, 2 H), 7.82–7.84 (m, 4 H), 7.87 (d, *J* = 8 Hz, 2 H), 8.07 (d, *J* = 7 Hz, 2 H); HRMS (ESI-TOF) *m*/*z* 379.1096 ([M + Na]$^+$), calcd for $C_{27}H_{16}ONa$ 379.1093.

**Synthesis of 9,11,12,13,14,16-Hexaphenyldibenzo[*a*,*c*]tetracene-10,15-dione** (**13**)

Quinone **7** (1.56 g, 3.39 mmol) and tetracyclone **3** (1.90 g, 4.94 mmol) were heated at reflux in nitrobenzene (5 mL) for 48 h. Methanol (30 mL) was added, and the reaction contents boiled briefly. The resulting precipitate was collected via vacuum filtration, and it was subjected to column chromatography (silica gel; eluent: toluene). A yellow band was collected with $R_f$ 0.72 TLC (silica gel; eluent: 1:9 EtOAc–toluene). The solvent was removed under reduced pressure, and the residue triturated with acetone to give **13** as a yellow solid, which was used in the next step without any further purification (610 mg, 0.75 mmol, 22%). An analytical sample was obtained by recrystallizing a small amount of **13** from $CHCl_3$–MeOH: mp 365–367 °C; $^1$H NMR (400 MHz, $CDCl_3$) *δ* 6.65–6.70 (m, 4 H), 6.82–6.85 (m, 6 H), 6.94–6.98 (m, 8 H), 7.00–7.05 (m, 4 H), 7.10–7.14 (m, 4 H), 7.21–7.25 (m, 6 H), 7.42 (td, *J* = 7.5, 1 Hz, 2 H), 7.62 (dd, *J* = 8.5, 1 Hz, 2 H), 8.36 (dd, *J* = 8, 1 Hz, 2 H); due to poor solubility, a definitive $^{13}$C NMR spectral characterization of **13** could not be obtained; HRMS (ESI-TOF) *m*/*z* 837.2742 ([M + Na]$^+$), calcd for $C_{62}H_{38}O_2Na$ 837.2764.

**Synthesis of 7,9,18,20-Tetraphenylacenaphtho[1,2-*k*]dibenzo[*a*,*c*]tetracene-8,19-dione** (**16**)

Quinone **7** (600 mg, 1.3 mmol) and acecyclone **15** (480 mg, 1.3 mmol) were placed into a screw-capped vial and heated at reflux in nitrobenzene (2 mL) for 25 h. Acetone (10 mL) was added, and the resulting precipitate was collected via vacuum filtration. Recrystallization from nitrobenzene–acetone gave **16** as a yellow solid, which was used in the next step without any further purification (550 mg, 0.70 mmol, 54%). An analytical sample was obtained by recrystallizing a small amount of **16** from $CHCl_3$–MeOH: mp 396–399 °C dec; $^1$H NMR (400 MHz, $CDCl_3$) *δ* 6.63 (d, *J* = 7 Hz, 2 H), 7.02 (td, *J* = 7.5, 1.5 Hz, 2 H), 7.17–7.21 (m, 4 H), 7.26–7.29 (m, 9 H), 7.33 (t, *J* = 7.5 Hz, 2 H), 7.40–7.47 (m, 9 H), 7.64 (dd, *J* = 8.5, 1 Hz, 2 H), 7.79 (d, *J* = 7.5 Hz, 2 H), 8.35 (dd, *J* = 8, 1 Hz, 2 H); due to poor solubility, a definitive $^{13}$C NMR spectral characterization of **16** could not be obtained; HRMS (ESI-TOF) *m*/*z* 809.2420 ([M + Na]$^+$), calcd for $C_{60}H_{34}O_2Na$ 809.2451.

**Synthesis of 9,10,11,12,13,14,15,16-Octaphenyldibenzo[*a*,*c*]tetracene** (**14**)

Phenyllithium (1.8 M in dibutyl ether, 0.50 mL, 0.90 mmol) was added to a suspension of quinone **13** (110 mg, 0.13 mmol) in dry THF (10 mL) under argon. The reaction contents were stirred for 1.5 h at rt and then heated at reflux for 1.5 h. After the contents were cooled to rt, $SnCl_2$•$2H_2O$ (560 mg, 2.5 mmol) and HCl (2 mL) were added, and the mixture heated at reflux for 18 h. The reaction contents were poured into water (40 mL), and diluted with ethyl acetate (50 mL). The aqueous layer was removed and was washed with sat. NaCl (2 x 40 mL), dried over $Na_2SO_4$, and filtered. The solvent was removed under reduced pressure. The residue was subjected to column chromatography (silica gel; eluent: hexanes, followed by 1:4 toluene–hexanes). An orange fluorescent band was collected with $R_f$ 0.57 TLC (silica gel; eluent: 2:3 $CH_2Cl_2$–hexanes). Recrystallization from $CHCl_3$–MeOH gave **14** as an orange solid (50 mg, 0.053 mmol, 40%): mp >400 °C (lit.[28] mp >400 °C); $^1$H NMR (400 MHz, $CDCl_3$) *δ* 6.20 (d, *J* = 8 Hz, 2 H), 6.26 (t, *J* = 7.5 Hz, 2 H), 6.34–6.38 (m, 4 H), 6.45–6.54 (m, 12 H), 6.60–6.84 (m, 18 H), 6.90–6.95 (m, 4 H), 7.06 (td, *J* = 7.5, 1 Hz, 2 H), 7.20 (td, *J* = 7.5, 1 Hz, 2 H), 8.02 (dd, *J* = 8, 1 Hz, 2 H); $^{13}$C NMR (101 MHz, $CDCl_3$, 35 °C) *δ* 123.4, 124.4, 124.9, 125.4, 125.6, 125.9, 126.1, 126.2, 126.5, 127.6, 127.8, 128.2, 129.9, 130.7 (br), 131.5, 131.9 (br), 132.2, 132.6, 132.7, 132.9, 133.1, 134.1, 134.8, 135.1, 135.2, 137.0, 138.5, 140.4, 140.5, 141.5, 141.6 (29 expected but 31 of a theoretically possible 37 resonances observed; but the *δ* 125.9, 126.5, and 132.6 resonances may contain two lines); NMR spectra are essentially identical to that reported by Qiao et al.[28]; MS (MALDI-TOF) *m*/*z* 936.355 ([M]$^+$), calcd for $C_{74}H_{48}$ 936.3756.

**Synthesis of 7,8,9,18,19,20-Hexaphenylacenaphtho[1,2-*k*]dibenzo[*a*,*c*]tetracene** (**17**)

Phenyllithium (2 M in dibutyl ether, 0.70 mL, 1.4 mmol) was added to a suspension of quinone **16** (200 mg, 0.25 mmol) in dry THF (10 mL), and the contents were stirred for 24 h at rt under argon. The reaction was quenched with the addition of water (10 mL), acidified with acetic acid, poured into water (20 mL), and steam distilled to remove the organic solvents. The solid was collected via vacuum filtration and rinsed with ethanol. The crude diol was heated at reflux in THF (6 mL) with $SnCl_2$•$2H_2O$ (1.82 g, 8.07 mmol) and HCl (0.5 mL) in a screw-capped vial for 16 h. The reaction contents were poured into water (60 mL) and extracted with $CH_2Cl_2$. The organic extract was washed with sat. NaCl (100 mL), dried over $Na_2SO_4$, and filtered. The solvent was removed under reduced pressure. The residue was subjected to column chromatography (silica gel; eluent: hexanes, followed by

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1:4 $CH_2Cl_2$–hexanes). An orange fluorescent band was collected with $R_f$ 0.60 TLC (silica gel; eluent: 2:3 $CH_2Cl_2$–hexanes). This fraction was subjected to column chromatography (silica gel; eluent: hexanes, followed by 3:7 toluene–hexanes). Recrystallization from toluene–MeOH gave **17** as an orange solid (47 mg, 0.052 mmol, 20%): mp >400 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 6.39–6.53 (m, 12 H), 6.57–6.67 (m, 6 H), 6.71 (td, $J$ = 8, 1 Hz, 2 H), 6.78–6.83 (m, 4 H), 6.86–7.10 (m, 12 H), 7.19 (t, $J$ = 7.5 Hz, 4 H), 7.61 (d, $J$ = 8 Hz, 2 H), 8.02 (dd, $J$ = 8, 1 Hz, 2 H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 121.8, 123.4, 125.3, 125.4, 125.7, 125.9, 126.1, 126.4, 126.5, 127.5, 127.6, 127.8 (br), 127.9, 128.4, 129.7, 129.9 (br), 130.2, 132.0, 132.5, 133.1, 133.2, 133.5, 134.0, 134.1, 134.6, 135.6, 135.7, 136.1, 136.6, 140.3, 140.4, 141.7 (31 expected but 32 of a theoretically possible 37 resonances observed; but the $\delta$ 132.0 resonance may contain two lines); UV ($CHCl_3$) $\lambda_{max}$ (log $\epsilon$) 265 (4.42), 370 (4.67), 388 (4.66), 406 (4.62), 486 (3.97), 512 (3.96); HRMS (ESI-TOF) $m/z$ 931.3311 ([M + Na]$^+$), calcd for $C_{72}H_{44}Na$ 931.3335; crystals suitable for X-ray analysis were obtained from EtOAc–$CH_2Cl_2$.

**Computational methodology**

All calculations were performed using AM1 as implemented in Gaussian 09.[34] Geometry optimizations were performed for all compounds followed by frequency calculations to confirm structures obtained correspond to a minima.

**Supplementary data**

$^1$H and $^{13}$C NMR spectra of compounds **7**, **9**, **10**, **11**, **12**, **13**, **16**, and **17** and the AM1 optimized structures of compounds **1**, **10**, **11**, **12**, **14**, and **17** are included in the supplemental material. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 1570789, 1570790, 1570791, and 1570792. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

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**Keywords:** Acenes • Pentacene • Quinones • Reduction • Tetracene

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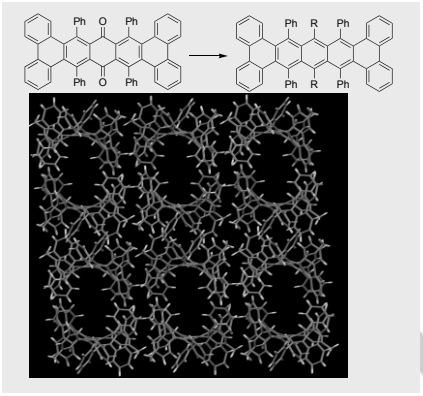
The addition of several aryllithium reagents to a variety of sterically congested polycyclic quinones followed by $SnCl_2$-mediated reduction allowed relatively easy access to a large number of longitudinally twisted acenes. This facile approach also allows one to prepare these remarkable hydrocarbons in gram-scale quantities if desired.

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