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Stereoselective Tandem Cascade Furan Cycloadditions

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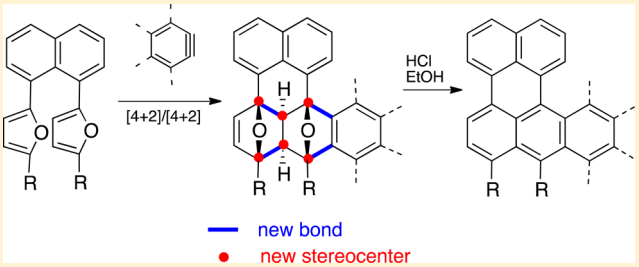
Supporting Information

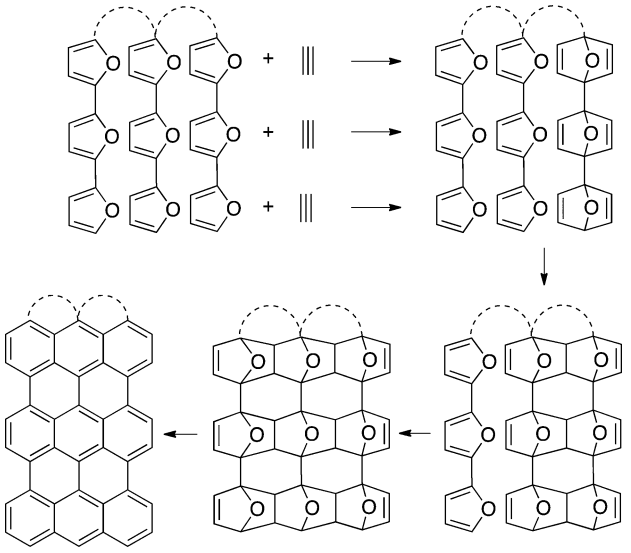
ABSTRACT: Oligofurans linked by a rigid tether undergo tandem cycloaddition reactions with high stereoselectivity. The reaction of bisfurans with dimethyl acetylenedicarboxylate (DMAD) involves tandem [4 + 2]/[4 + 2] cycloadditions in a pincer mode. The reaction of oligofurans with arynes involves stereoselective tandem [4 + 2]/[4 + 2] cycloaddition reactions in a domino mode. The corresponding aryne adducts have been transformed into extended perylene derivatives by deoxygenation and aromatization with HCl/EtOH.



INTRODUCTION

Tandem cycloadditions, in which several processes take place without the isolation of intermediary products, play a very important role in organic synthesis.[1,2] Tandem cascade cycloadditions, defined as those in which two or more cycloadditions take place without additional components or reagents,[2] are particularly efficient from the point of view of atom and step economy. Tandem cascade cycloadditions have been extensively used in organic synthesis, but they have been scarcely employed for the synthesis of molecules of interest in materials science. We have devised a new strategy for the controlled synthesis of nanographenes,[3] two-dimensional (2D) sheets of benzenoid rings, based on tandem cascade oligofuran cycloadditions, as depicted in Scheme 1.[4] The key feature of this strategy is the use of tethered oligofuran chains, to favor the reaction cascades. One dimension of the graphene would be determined by the length of the oligofuran chain, and the second, by the number of chains.[5] The parallel series of [4 + 2] cycloadditions would afford a graphene oxide, which could be transformed into the final graphene by reduction.

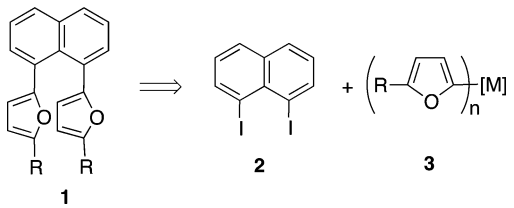
Scheme 1. Proposed Strategy for the Synthesis of Nanographenes



RESULTS AND DISCUSSION

As a proof of concept of this approach we decided to start the study with simple bisfurans, such as **1** (Scheme 2), in which the furan rings are linked through a rigid naphthalene tether. These bisfurans should be available by cross-coupling reactions between 1,8-diiodonaphthalene (**2**) and furan derivatives **3**, as shown in Scheme 2. Furan-derivatives **3** in turn should be obtained by metalation of the corresponding furans. We thought that substituents R, such as tolyl or mesityl, placed at the edge of the "nanographene" might enhance its kinetic stability, particularly against photooxidation, improve its solubility, and modify its solid-phase packing.

Scheme 2. Retrosynthetic Disconnection of Tethered Bisfurans 1



Synthesis of Tethered Oligofurans 1a−c and 7. First of all, substituted furans **4b** and **4c** were prepared. To this aim, we screened different cross-coupling conditions between 2-furyl

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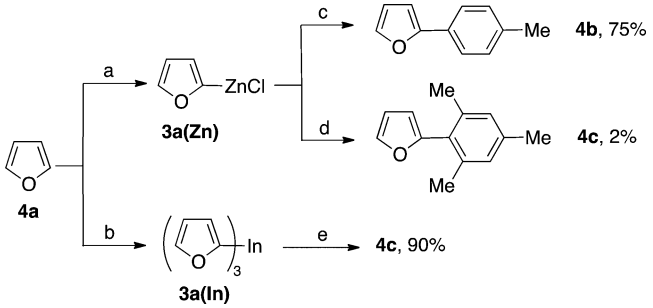
metal derivatives and appropriate aryl halides (Scheme 3). Metalation of furan (**4a**) with BuLi, transmetalation with $ZnCl_2$

Scheme 3. Synthesis of Substituted Furans 4b,c

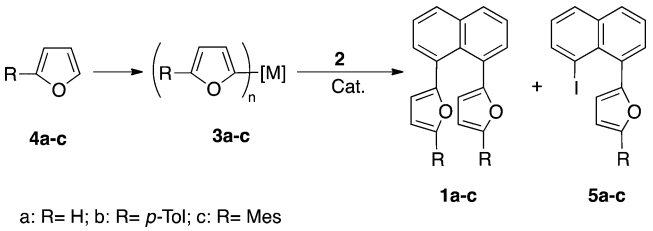


to (2-furyl)ZnCl [**3a**(Zn)], and palladium-catalyzed coupling with *p*-iododotoluene afforded the desired 2-(*p*-tolyl)furan **4b** in 75% yield. However, the attempted coupling of **3a**(Zn) with 2-bromomesitylene in a similar reaction condition afforded **4c** in only 2% yield. This result could be attributed to the high steric hindrance provided by the methyl groups of bromomesitylene (MesBr). To overcome this problem we decided to test the coupling method developed by Sarandeses and Sestelo,[6] based on the use of indium organometallics.

The desired coupling was performed using $(2\text{-furyl})_3In$ [**3a**(In)] and a catalyst generated in situ from $Pd_2(dba)_3$ and an adequate ligand. While ligands such as 1,1′-bis(diphenylphosphino)ferrocene (dppf), tricyclohexylphosphine, triisopropylphosphine, and tri-*o*-tolylphosphine failed to provide reasonable yields of **4c**, the use of dicyclohexylphosphino-(2′,4′,6′-triisopropyl)biphenyl (X-Phos)[7] proved to be crucial, leading to the coupling product **4c** in 90% yield. This is a remarkable result for a cross-coupling reaction involving two highly hindered reagents.

With furans **4a**–**c** in hand we studied the synthesis of tethered bisfurans **1a**–**c** as shown in Scheme 4 and Table 1.

Scheme 4. Synthesis of Furylnaphthalenes



Bisfuran **1a** was obtained in moderate yield by Negishi coupling of (2-furyl)ZnCl [**3a**(Zn)] and 1,7-diiodonaphthalene (**2**) using $NiCl_2$(dppp) or $PdCl_2$(dppf) as catalyst (entries 1 and 2). Better yields were obtained by Suzuki coupling of $(2\text{-furyl})B(OH)_2$ [**3a**(B)], 92% yield] or Stille coupling of $(2\text{-furyl})SnBu_3$ [**3a**(Sn), 99% yield], but in the last case lower yields were obtained when scaling up the reaction (entries 3 and 4). For the preparation of the bisfuran **1b** we planned to use the Suzuki reaction, but the preparation of the 2-[5-(*p*-tolyl)furyl)]boronic acid [**3b**(B)] was not fully reproducible.

To overcome these problems we decided to switch again to the use of indium organometallics. For the optimization of the coupling reaction, we started with unsubstituted furan **4a**. First, we coupled 100 mol % of **2** with 40 mol % of the organoindium

Table 1. Optimization of Coupling Reactions[a]

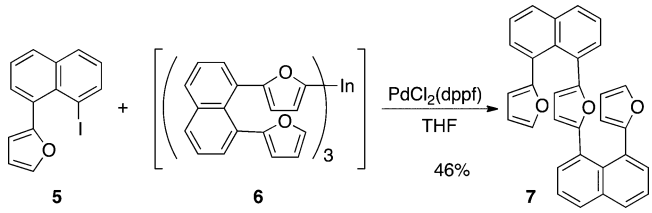
Entry	R–(O)–[M] (n) **3**	Ratio[b] **3**/**2**	Catalyst	**1**, %	**5**, %
1	**3a**(Zn) (2-furyl)ZnCl	3.4	$NiCl_2$(dppp)[c]	**1a**, 63	---
2	" "	10.2	$PdCl_2$(dppf)[d]	**1a**, 60	---
3	**3a**(B) $(2\text{-furyl})B(OH)_2$	4.0	"	**1a**, 92	---
4	**3a**(Sn) $(2\text{-furyl})SnBu_3$	2.2	"	**1a**, 99	---
5	**3a**(In) $(2\text{-furyl})_3In$	0.4	"	**1a**, 2	**5a**, 19
6	" "	1.0	"	**1a**, 33	**5a**, 32
7	" "	3.4	"	**1a**, 92	---
8	**3b**(In) "	3.4	"	**1b**, 75	---
9	**3c**(In) "	3.4	"	**1c**, 99	---

[a]See Scheme 4. [b]Molar ratio assuming the quantitative formation of **3**. [c]dppp: 1,3-bis-(diphenylphosphino)propane. [d]dppf; 1,1′-bis-(diphenylphosphino)ferrocene.

intermediate $(2\text{-furyl})_3In$ [**3a**(In)], the amount corresponding to a 12% excess if all three furyl groups at indium were transferred, and $PdCl_2$(dppf) as catalyst (entry 5). The major product, **5a**, was obtained in 19% yield, resulting from the coupling of only one equivalent of furan. When 100 mol % of indium derivative was used, a mixture of **1a** (33% yield) and **5a** (32% yield) was obtained (entry 6). A higher excess of organomeallic reagent led to 92% of bisfuran **1a** (entry 7). Under similar conditions bisfurans **1b** and **c** were obtained in 75 and 99% yield, respectively (entries 8 and 9).

We realized that monocoupled product **5a** could be a valuable intermediate for the synthesis of new oligofurans. For example, it could be coupled with an indium derivative of **1a**, such as **6**, to afford a trisfuran **7** (Scheme 5). To this aim, we

Scheme 5. Synthesis of Trisfuran 7



treated **1a** with butyl lithium and $InCl_3$ as above, and coupled the resulting indium derivative **6** with iodide **5**, using $PdCl_2$(dppf) as catalyst. After the usual workup, trisfuran **7** was obtained in 46% yield.

Tandem [4 + 2]/[4 + 2] cycloaddition with DMAD.[8−10] First, to trigger the tandem cyclodditions we choose dimethyl acetylenedicarboxylate (DMAD), because it is a very reactive, easy-to-handle dienophile. However, previous reports on tandem furan cycloadditions showed that the initial [4 + 2] adduct can undergo two modes of cycloaddition, leading to adducts termed *domino* and *pincer* (Scheme 6).[2]

When we carried out the reaction of bisfuran **4a** and DMAD in ether at 20 °C for 9 days, an adduct with a molecular mass of 402 was isolated in 33% yield. The same product was obtained in 57% yield, by heating bisfuran **4a** and DMAD in toluene at 111 °C for 6 days.[11] This adduct was identified by NMR spectroscopy and X-ray diffraction studies as *exo,exo*-**8**,[12] which results from the tandem cascade cycloaddition in a *pincer* mode (Scheme 7).

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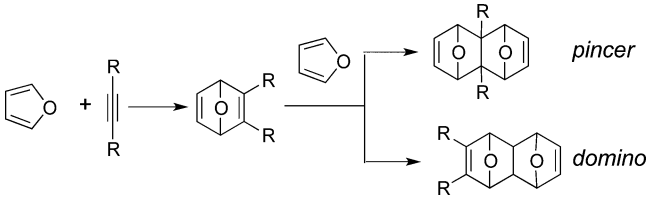
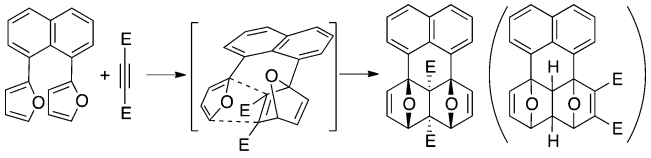
Scheme 6. Tandem [4 + 2] Cycloadditions of Furan and Alkynes

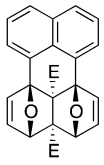
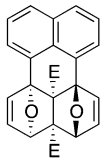
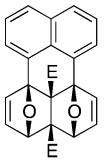
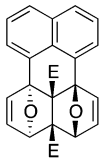
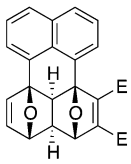
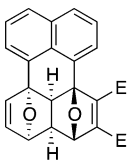
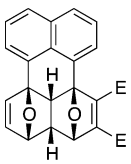
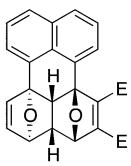


Scheme 7. Tandem [4 + 2]/[4 + 2] Cycloadditions of 1a and DMAD



To understand the reasons for this behavior we carried out a computational study on the formation of the seven isomers that could result from a tandem [4 + 2]/[4 + 2] cycloaddition in *pincer* or in *domino* modes. Single-point calculations were done at the M062x/6-31++G(d,p) level on the corresponding B3LYP/6-31G(d) geometries (see Table 2).[13]

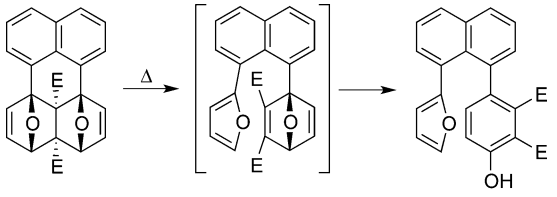
Table 2. Structures and Enthalpies for Possible Adducts 8 and 9

Pincer				
	exo,exo-**8**	*exo,endo*-**8**[a]	*endo,endo*-**8**	*endo,exo*-**8**[a]
ΔH	-26.5	-11.4	16.6	-11.4
ΔH‡	7.1	14.5	32.1	19.6
Domino				
	exo,exo-**9**	*exo,endo*-**9**	*endo,endo*-**9**	*endo,exo*-**9**
ΔH	-29.7	-15.1	3.8	-15.7
ΔH‡	12.8	18.0	31.8	25.9

[a] *exo,endo*-**8** = *endo,exo*-**8**

The formation of *exo,exo*-**8** (*pincer* mode) under kinetic control was predicted by the calculation, a situation in good agreement with the experimental result. According to the calculations, *exo,exo*-**9** (*domino* mode) should be the thermodynamic product. However, we believe that, under our experimental conditions, the process is irreversible and therefore proceeds under kinetic control.[14] In fact, calculations show that the activation barrier for the retro-Diels–Alder reaction from *exo,exo*-**8** (33.6 kcal/mol) to **10** is high enough to make the process irreversible under the reaction conditions. However, we found that if the *exo,exo*-**8** adduct is heated under argon at 180 °C for 1 h, phenol **11** was obtained, presumably formed by the mechanism outlined in Scheme 8.

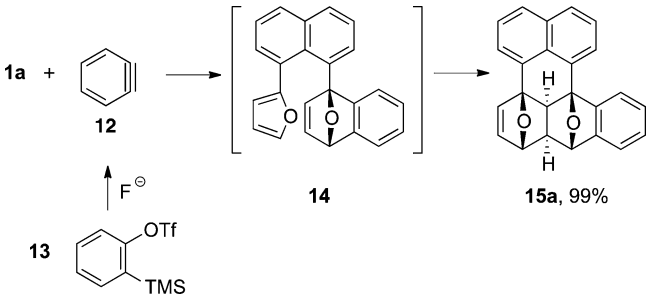
Scheme 8. Thermal Rearrangement of *exo,exo*-8



Tandem [4 + 2]/[4 + 2] Cycloadditions[15,16] Triggered by Arynes. To drive the tandem cycloadditions toward the formation of "nanographene oxides" we chose arynes as dienophiles for several reasons: they are very reactive species, they should react in tandem processes in a *domino* mode (*pincer* modes are not possible), and they contain aromatic rings that will be incorporated in the final adducts, affording after deoxygenation and aromatization, large aromatic structures, namely "nanographenes". These arynes would be generated from the corresponding *o*-(trimethylsilyl)aryl triflates as reported in the literature.[17]

When benzyne (**12**) was generated by treatment of *o*-(trimethylsilyl)phenyl triflate (**13**) with cesium fluoride, in the presence of bisfuran **1a**, an adduct *exo,exo*-**15a** was isolated in 99% yield (Scheme 9). Presumably, *exo,exo*-**15a** was formed

Scheme 9. Tandem [4 + 2]/[4 + 2] Cycloaddition of 1a with Benzyne (12)



through intermediate **14**, by *exo* approximation of the diene to the *exo* face of the dienophile. Remarkably, this is a highly stereoselective tandem cascade *domino* [4 + 2]/[4 + 2] cycloaddition, in which six adjacent stereocenters are formed with total stereocontrol.[18] The stereochemistry of adduct **15a** was established by NMR (NOESY experiments and analysis of the coupling constants in the ^{1}H NMR spectrum).[13] We carried out MO52x/6-31++(d,p) calculations, which showed that the *exo,exo* adduct is favored under kinetic or thermodynamic control.[4,13]

Similar cycloadditions between **1a** and arynes **25**–**33**, generated from the corresponding *o*-(trimethylsilyl)aryl triflates **16**–**24**,[13] yielded the corresponding adducts in moderate to good yields (Table 3, entries 1–10). NMR analysis of these adducts shows the same stereochemical outcome as for **15a**. Substituted benzynes **25**–**27** react with bisfuran **1a** to afford the corresponding adducts **34a**, **35**, and **36**, respectively, in moderate to good yields (entries 1–3). Asymmetrically

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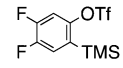
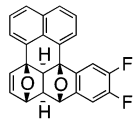
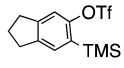
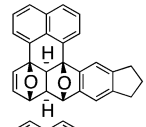
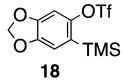
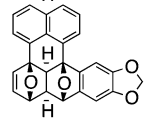
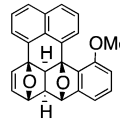
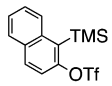
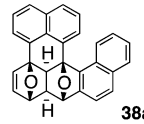
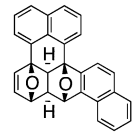
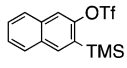
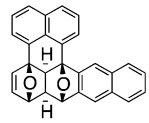
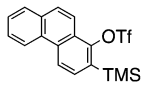
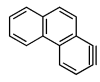
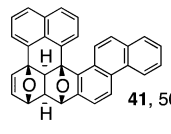
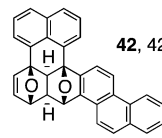
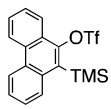
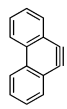
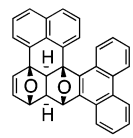
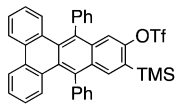
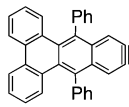
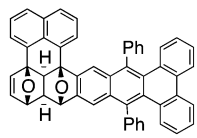
Table 3. [4 + 2]/[4 + 2] Cascade Cycloadditions of Bisfuran 1a and Arynes 25−33

Entry	Aryne precursor	Aryne	Adduct, yield
1	 **16**	 **25**	 **34a**, 53%
2	 **17**	 **26**	 **35**, 82%
3	 **18**	 **27**	 **36**, 88%
4	 **19**	 **28**	 **37**, 95%
5	 **20**	 **29**	 **38a**, 55% +  **39a**, 34%
6	 **21**	 **30**	 **40a**, 51%
7	 **22**	 **31**	 **41**, 50% +  **42**, 42%
8	 **23**	 **32**	 **43**, 76%
9	 **24**	 **33**	 **44**, 38%

substituted benzyne **28** reacts with complete regioselectivity to afford adduct **37** in 88% yield (entry 4).

On the contrary, asymmetric 1-naphthyne (**29**) reacts with bisfuran **1a** to give a mixture of regioisomers **38a** and **39a** in 55 and 34% yield, respectively (entry 5). 2-Naphthyne (**30**) reacts with **1a**, leading to adduct **40a** in 51% yield (entry 6). 1-Phenanthryne (**31**) reacts with **1a** to afford a mixture of regioisomers **41** and **42**, in 42% and 50% yield, respectively (entry 7). Symmetric arynes **32** and **33** led to adducts **43** and **44**, respectively (entries 8 and 9). Cycloadducts **34**−**44** showed the same relative stereochemistry, which was confirmed by X-ray diffraction analysis of compound **43**.[4]

We have also studied the reactivity of substituted bisfurans **1b**,**c** against some arynes. Substituted bisfuran **1b** (R = *p*-Tol) reacts with arynes **12**, **25**, **29**, and **30** in a way similar to that of **1a**, as shown in Table 4 (entries 1−4). NMR analysis of these adducts shows the same stereochemical outcome as for **15a**. However, an unusually low yield was obtained from the reaction of benzyne (**12**) and bisfuran **1c** (R= Mes), probably due to the bulky mesityl groups, which hinder both cycloadditions in the tandem process leading to **15c** (entry 5).

Trisfuran **7** reacts with benzyne (**12**) in a tandem cascade [4 + 2]/[4 + 2]/[4 + 2] cycloaddition to afford *exo,exo,exo,exo*-**45** in an excellent 56% yield (Scheme 10). Remarkably, this transformation involves the stereoselective formation of 6 new bonds and 10 adjacent stereocenters! Again, we were able to univocally confirm the stereochemical outcome of adduct **45** by X-ray diffraction studies.

Deoxygenation/Aromatization of Aryne Cycloadducts. Finally, to convert the obtained "nanographene oxides" into the corresponding PAHs, deoxygenation/aromatization processes are required. These reactions were optimized with adduct **15a**. All initial attempts to reduce adduct **15a** to benzo[*a*]perylene (**46a**) failed, due to the instability of this

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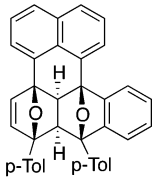
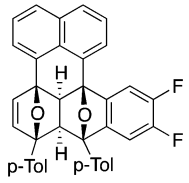
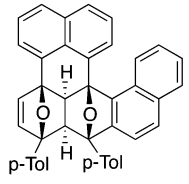
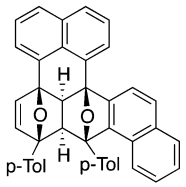
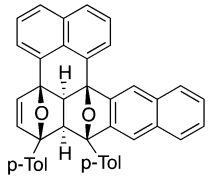
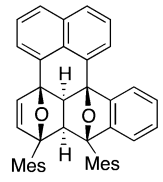
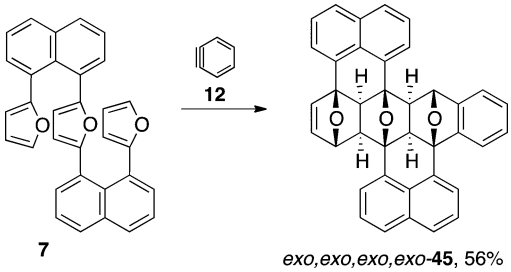
Table 4. [4 + 2]/[4 + 2] Cascade Cycloadditions of Bisfuran 1b/1c and Arynes 12, 25, 29, and 30

Entry	Bisfuran	Aryne	Adduct, yield
1	**1b**	**12**	 **15b**, 83%
2	**1b**	**25**	 **34b**, 56%
3	**1b**	**29**	 +  **38b**, 35%[a] **39b**, 17%[a]
4	**1b**	**30**	 **40b**, 59%
5	**1c**	**12**	 **15c**, 15%

[a]**38b** and **39b** were obtained as an inseparable mixture. Yields determined by NMR.

Scheme 10. Tandem [4 + 2]/[4 + 2]/[4 + 2] Cycloaddition of 7 with Benzyne (12)



compound in the presence of oxygen and light. After some experimentation, we found that benzo[*a*]perylene (**46a**) can be obtained in 72% yield by treatment of **15a** with HCl in refluxing EtOH in the absence of light.[19] Under the same conditions, adducts shown in Table 3 were transformed into the corresponding benzenoid hydrocarbons (Figure 1).

The deoxygenation of substituted derivatives **15b**, **15c**, **36b**, **40b**, **41b**, and **42b** proved to be more difficult under these conditions, leading to complex mixtures. To facilitate the formal elimination of water from these adducts we planned to perform the aromatization in two synthetic operations: the reduction of the olefinic double bond by a catalytic hydrogenation followed by the deoxygenation by double endoxide opening and dehydration in acidic conditions.[20] These alternative procedures were tested with substituted adducts **15b**, **34b**, and **40b**. Reduction of **15b**, **34b**, and **40b** with H_2 (5 atm) and Ni Raney afforded intermediates **58**, **59**, and **60**, which were transformed into benzoperylenes **46b** (42% yield), **47b** (27% yield), and **53b** (19% yield), respectively, by treatment with HCl/EtOH (Scheme 11).

Electronic Properties of PAHs 46−57. All the prepared PAHs contain both perylene and acene units.[21] Acenes are the subject of a huge amount of work due to their interesting electronic properties and their potential use as organic semiconductors in electronic/photonic devices.[22] The fundamental parameters for the evaluation of acenes as potential candidates as semiconductors are the energies of frontier orbitals (E_{HOMO}, E_{LUMO}), the HOMO−LUMO gap, and the kinetic stability against atmospheric conditions (O_2/light). For

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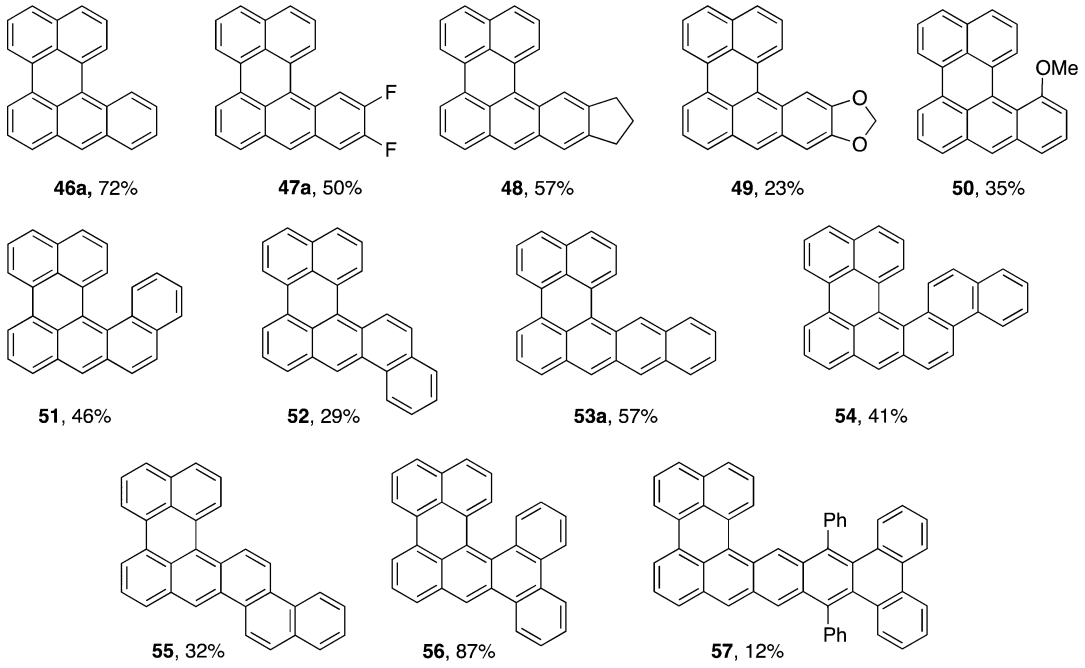


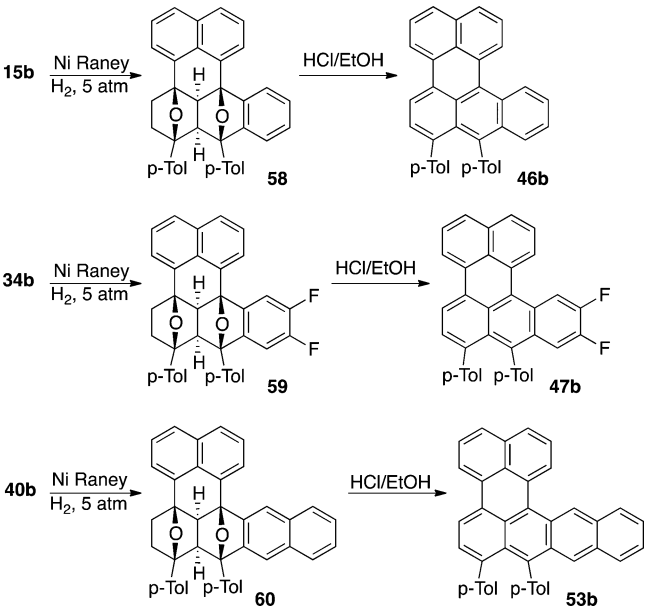
46a, 72% **47a**, 50% **48**, 57% **49**, 23% **50**, 35%

51, 46% **52**, 29% **53a**, 57% **54**, 41%

55, 32% **56**, 87% **57**, 12%

Figure 1. PAHs obtained by deoxygenation/aromatization.

Scheme 11. Stepwise Reduction of Adducts 15b, 34b, and 40b



example, pentacene owns very interesting electronic properties (gap: 2.1 eV, high mobility, etc.), but is very unstable in the presence of oxygen and light.

We have studied the basic parameters of our acenes computationally as well as experimentally (Table 5). Most compounds in Table 4 show optical gaps close to that of pentacene (2.1 eV), with remarkable optical gaps of 2.01, 1.90, and 1.85 eV for **53a**, **53b**, and **57**, respectively. All compounds in Figure 2 in solution, with the exception of **56**, are sensitive to photooxidation in the presence of oxygen and sunlight, while as expected, substituted derivatives **46b**, **47b**, and **53b** are much more stable.

While photooxidation of these compounds in the presence of air and light gives complex mixtures of products, under these conditions, compound **56** underwent a clean cyclo-dehydrogenation to quantitatively afford **61** (Scheme 12). Even the photon flux used to record its UV spectrum causes the cyclo-dehydrogenation.

Dibenzo[*cd*,*n*]naphtho[3,2,1,8-*pqra*]perylene (**61**) is very insoluble in all solvents tested, preventing the recording of its ^{13}C NMR spectrum. Remarkably, its structure has been recently confirmed by means of atomic force microscopy (AFM).[23,24]

■ CONCLUSIONS

In summary, the tandem cascade cycloadditions reported here allow a rapid increase in the molecular connectivity with complete control of the relative stereochemistry. Bisfuran **1a** reacts with DMAD in a tandem [4 + 2]/[4 + 2] cycloaddition in a pincer mode with the stereoselective formation of four bonds and six adjacent stereocenters. Bisfurans **1** react with arynes in tandem [4 + 2]/[4 + 2] cycloadditions in a *domino* mode with the stereoselective formation of four bonds and six adjacent stereocenters. Trisfuran **7** reacts with benzyne in a tandem [4 + 2]/[4 + 2]/[4 + 2] cycloaddition in a *domino* mode with the stereoselective formation of six bonds and ten adjacent stereocenters. Extended PAHs combining *cata*- and *peri*-ring fusion are easily obtained by treatment of the cycloadducts with HCl in EtOH. Extension of this methodology to other oligofuran topologies for the synthesis of larger PAHs and nanographenes is in progress.

■ EXPERIMENTAL SECTION

General. All reactions were carried out under argon using oven-dried glassware. TLC was performed on silica gel 60 F254; chromatograms were visualized with UV light (254 and 360 nm). Flash column chromatography was performed on silica gel 60 (ASTM 230−400 mesh). High-resolution mass spectra were obtained using a quadrupole mass analyzer.

Aryne precursors **13**,[17b] **16**,[17b,24] **17**,[25] **18**,[26] **19**,[17b] **20**,[17b,27] **21**,[28] **22**,[17b,29] **23**,[17b,27] and **24**,[30] $Pd(PPh_3)_4$, 1,8-diiodonaphthalene (**2**),[31]

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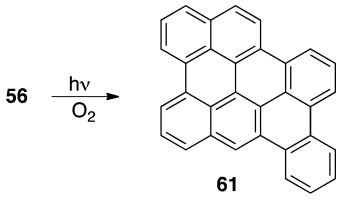
Table 5. Photophysical and Electrochemical Data for Compounds 46−57

	λ_{onset} [a]	λ_{em} [a]	E_{ox} [b]	E_{HOMO} [c]	E_{red} [b]	E_{LUMO} [d]	Gap_{opt} [e]	Gap_{elc} [f]
46a	507	518	0.28	−5.08	−1.97	−2.83	2.34	2.25
46b	527	557	0.19	−4.99	–	−2.80[g]	2.19	–
47a	501	573	0.32	−5.12	−2.03[g]	−2.77	2.35	2.35
47b	520	599	0.36	−5.16	−1.90	−2.89	2.22	2.27
48	510	524	0.17	−4.97	−2.08	−2.72	2.30	2.25
49	500	528	0.29	−5.09	−2.05	−2.75	2.35	2.34
50	537	531	0.20	−5.00	−1.94	−2.86	2.31	2.14
51	550	537	0.38	−5.17	−1.93	−2.87	2.25	2.30
52	540	506	0.45	−5.25	−1.97	−2.83	2.30	2.42
53a	560	604	0.03	−4.83	−1.76	−3.04	2.01	1.79
53b	610	643	0.12	−4.92	−1.78	−3.02	1.90	1.90
54	560	541	0.33	−5.14	−1.90	−2.90	2.21	2.24
55	550	521	0.36	−5.16	−1.85	−2.95	2.25	2.25
56	548	544	0.45	−5.25	−1.92	−2.88	2.26	2.37
57	643	661	0.06	−4.86	−1.68	−3.12	1.85	1.74

[a]nm, in $CHCl_3$. [b]V, determined by cyclic voltammetry (CV) in solution (CH_2Cl_2/0.1 M Bu_4NPF_6), working electrode: Pt, reference electrode: AgCl/Ag, counter electrode: platinum wire, internal standard: ferrocene. [c]eV, calculated from E_{HOMO}= −(4.8 + Eox). [d]eV, calculated from E_{LUMO}= −(4.8 + E_{red}). [e]eV, calculated from the UV onset. [f]eV, calculated from CV data. [g]There is an irreversible reduction at −1.63 V.

Scheme 12. Photochemical Cyclodehydrogenation of 56



furyl derivative **3a**(Sn),[32] and tolylfuran **4b**[33] were prepared following published procedures. Furyl derivative **7a** (THF solution) was prepared *in situ* by reaction of furan with *n*-BuLi and $ZnCl_2$. *n*-BuLi and Bu_4NF (TBAF) were used in solution in hexane (2.4 M) and THF (1.0 M), respectively.

Synthesis of ***2*****-mesitylfuran (*****4c*****).*** [34] *n*-BuLi (6.20 mL, 2.43 M in hexane, 15.1 mmol) was added dropwise to a stirred solution of furan (**4a**, 1.10 mL, 15.1 mmol) in THF (25 mL) at 0 °C, and the solution was stirred further for 30 min. The resulting solution was slowly added to a suspension of $InCl_3$ (1.10 g, 5.02 mmol) in THF (25 mL) at −78 °C, and the mixture was stirred for 30 min. The cooling bath was removed; when the solution reached 25 °C, it was added to a refluxing solution of bromomesitylene (380 μL, 5.02 mmol), $Pd_2(dba)_3$ (135 mg, 0.12 mmol) and dicyclohexylphosphino-(2′,4′,6′-triisopropyl)-biphenyl (X-Phos, 114 mg, 0.24 mmol) in THF (50 mL), and the mixture was refluxed for 15 h. MeOH (1 mL) was added, the solution was evaporated in vacuo, and the residue solved in Et_2O. The ethereal solution was successively washed with hydrochloric acid (5%), with a saturated solution of $NaHCO_3$ and with brine, dried over anhydrous Na_2SO_4, and evaporated in vacuo. The residue was purified by column chromatography (SiO_2, hexane) to yield **4c** (840 mg, 99%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 1.7, 0.6 Hz, 1H), 6.97 (s, 2H), 6.52 (dd, *J* = 3.2, 1.8 Hz, 1H), 6.30 (dd, *J* = 3.1, 0.5 Hz, 1H), 2.36 (s, 3H), 2.22 (s, 6H); LRMS (EI) *m*/*z* (%): 186 (100, M^+), 171 (15), 157 (54), 142 (49).

General Procedure for the Coupling of Diiodonaphthalene (2) and Furans (4a−c) via Indium Derivatives. *n*-BuLi 0.6 M in hexane (10.2 equiv) was added dropwise to a stirred solution of furan **4** (10.2 equiv) in THF (0.6 M) at 0 °C. After 30 min the mixture was carefully added over a suspension of $InCl_3$ (3.4 equiv) in THF (0.2M) at −78 °C. The mixture was stirred for 30 min and the temperature was slowly raised until 25 °C. This was added to a refluxing solution of 1,8-difurylnaphthalene (**9**, 1 equiv) and $PdCl_2$(dppf) (0.10−0.05 equiv) in THF (0.03 M), and the mixture was refluxed for 18 h. MeOH (1 mL) was added, and the mixture was evaporated in vacuo and solved in ether. The solution was washed with hydrochloric acid (5%) and with an aqueous saturated solution of $NaHCO_3$ and brine. The organic phase was dried over Na_2SO_4, filtered, and evaporated in vacuo. The residue was chromatographed in a column (Al_2O_3 or SiO_2).

*1,8-Difurylnaphthalene (****1a****):* 647 mg, 95% yield, oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 8.1, 1.4 Hz, 2H), 7.66 (dd, *J* = 7.1, 1.4 Hz, 2H), 7.54 (dd, *J* = 8.1, 7.1 Hz, 2H), 7.17 (dd, *J* = 1.8, 0.7 Hz, 2H), 6.22 (dd, *J* = 3.3, 0.7 Hz, 2H), 6.13 (dd, *J* = 3.3, 0.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.4 (2C), 141.5 (2CH), 135.0 (C), 130.2 (2CH), 129.3 (2CH), 128.8 (2C), 128.7 (C), 125.1 (2CH), 110.9 (2CH), 107.3 (2CH); LRMS (EI), *m*/*z* (%): 260 (M^+, 82), 231 (50) 203 (100). HRMS (EI) calcd for $C_{18}H_{12}O_2$: 260.0837, found: 260.0830.

*1,8-Bis(5-(p-tolyl)furan-2-yl)naphthalene (****1b****):* 647 mg, 75% yield, orange solid; mp 124−125 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 8.2, 1.2 Hz, 2H), 7.77 (dd, *J* = 7.1, 1.3 Hz, 2H), 7.58 (dd, *J* = 8.0, 7.2 Hz, 2H), 7.26 (d, *J* = 8.2 Hz, 4H), 6.97 (d, *J* = 7.9 Hz, 4H), 6.28 (d, *J* = 3.4 Hz, 2H), 6.26 (d, *J* = 3.4 Hz, 2H), 2.27 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.7 (2C), 153.2 (2C), 136.1 (2C), 135.2 (C), 130.2 (2CH), 129.3 (2CH), 129.1 (2C), 128.7 (4CH), 128.5 (C), 128.0 (2C), 125.2 (2CH), 123.5 (4CH), 109.5 (2CH), 105.51 (2CH), 21.2 ($2CH_3$). LRMS (EI) *m*/*z* (%): 440 (75, M^+), 321 (38), 119 (100); HRMS (EI) calcd for $C_{32}H_{24}O_2$: 440.1776, found: 440.1788.

*1,8-Bis(5-mesitylfuran-2-yl)naphthalene (****1c****):* 196 mg, 99% yield, orange solid, mp 173−175 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 8.2, 1.2 Hz, 2H), 7.79 (dd, *J* = 7.2, 1.2 Hz, 2H), 7.65−7.55 (dd, *J* = 8.0, 7.3 Hz, 2H), 7.01 (s, 4H), 6.16 (d, *J* = 3.3 Hz, 2H), 6.06 (d, *J* = 3.2 Hz, 2H), 2.38 (s, 6H), 2.36 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.5 (3C), 150.1 (3C), 138.1 (6C), 135.2 (2C), 129.2 (2CH), 128.4 (6CH), 128.2 (C), 128.0 (C), 125.2 (2CH), 111.3 (2CH), 110.2 (2CH), 21.1 ($2CH_3$), 21.0 ($4CH_3$); LRMS (EI) *m*/*z* (%): 496 (79, M^+), 349 (11), 147 (100); HRMS (EI) calcd for $C_{36}H_{32}O_2$: 496.2402, found: 496.2399.

*Synthesis of 1-Iodo-8-furylnaphthalene (****5****).* Using the general procedure for the indium-promoted couplings, but with a 1:1 molar ratio of furan (**4a**) and diiodonaphthalene (**2**) a mixture of **1a** (33% yield) and **5** (yellow oil, 103 mg, 32% yield) was obtained. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.26 (dd, *J* = 7.3, 1.1 Hz, 1H), 7.90 (dd, *J* = 8.2, 1.6 Hz, 2H), 7.63 (dd, *J* = 5.7, 1.5 Hz, 2H), 7.49 (dd, *J* = 8.0, 7.3 Hz, 1H), 7.16−7.08 (m, 1H), 6.58 (dd, *J* = 3.2, 1.8 Hz, 1H), 6.49 (dd, *J* = 3.2, 0.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.5 (C), 142.0 (CH), 141.8 (CH), 135.4 (C), 132.8 (C), 132.4 (CH), 131.0 (CH), 130.4 (C), 129.6 (CH), 126.8 (CH), 125.1 (CH), 112.1 (CH), 111.2 (CH), 91.4 (C); LRMS (EI) *m*/*z* (%): 320 (69, M^+), 193 (29), 165 (100); HRMS (EI) calcd for $C_{14}H_9IO$: 319.9698, found: 319.9699.

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*Synthesis of 2,5-Bis(8-(furan-2-yl)naphthalen-1-yl)furan (**7**).* *n*-BuLi (840 μL, 2.43 M in hexane, 2.04 mmol) was added dropwise to a stirred solution of 1,8-difurylnaphthalene (**1a**, 530 mg, 2.04 mmol) in THF (10 mL) at 0 °C, and the solution was stirred for further 30 min. The resulting solution was slowly added to a suspension of $InCl_3$ (149 mg, 2.04 mmol) in THF (5 mL) at −78 °C, and the mixture was stirred for 30 min. The cooling bath was removed, and when the solution reached 25 °C, it was added to a refluxing solution of 1-iodo-8-furylnaphthalene (**5**, 128 mg, 0.40 mmol) and $PdCl_2$(dppf) (16 mg, 0.02 mmol) in THF (15 mL), and the mixture was refluxed for 15 h. Then MeOH (1 mL) was added, the solution was evaporated in vacuo, and the residue solved in Et_2O. The ethereal solution was successively washed with hydrochloric acid (5%), with a saturated solution of $NaHCO_3$, and with brine, then was dried over anhydrous Na_2SO_4, and evaporated in vacuo. The residue was purified by column chromatography (Al_2O_3, hexano/CH_2Cl_2 9:1 a 1:1) to yield **7** (83 mg, 46%) as a white solid, mp 53−55 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91−7.86 (m, 4H), 7.62−7.54 (m, 6H), 7.49 (dd, *J* = 8.0, 7.2 Hz, 2H), 7.08 (dd, *J* = 1.8, 0.8 Hz, 2H), 6.13 (dd, *J* = 3.3, 1.8 Hz, 2H), 6.06 (dd, *J* = 3.3, 0.8 Hz, 2H), 5.94 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.4 (2C), 153.0 (2C), 141.0 (2CH), 135.1 (2C), 130.1 (2CH), 129.9 (2CH), 129.1 (2CH), 128.9 (2CH), 125.1 (4CH), 110.7 (2CH), 109.4 (2CH), 107.6 (2CH); LRMS (EI), *m*/*z* (%): 452 (12, M^+), 259 (31), 218 (58); HRMS (EI) calcd for $C_{32}H_{20}O_3$: 452.1412, found: 452.1412.

Tandem [4 + 2]/[4 + 2] Cycloadditions of Bisfuran 1a and DMAD. Dimethylacetylenedicarboxylate (DMAD, 0.048 mL, 0.38 mmol) was added to a solution of 1,8-difurylnaphthalene (**1a**, 100 mg, 0.38 mmol) in toluene (6 mL), and the mixture was refluxed for 6 days. Then the mixture was concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2, 9:1 to 1:1 hexane/EtOAc) to obtain compound **11** (12 mg, 8%) as a brown oil and *exo,exo*-**8** (87 mg, 57%) as a brown solid.

*exo,exo-Dimethyl 3,3a,3a^1,4-tetrahydro-3,12b:4,6a-diepoxyperylene-3a,3a^1-dicarboxylate (**8**):* mp 173−175 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 8.3, 0.9 Hz, 2H), 7.78 (dd, *J* = 7.1, 1.1 Hz, 2H), 7.56 (dd, *J* = 8.1, 7.2 Hz, 2H), 7.04 (d, *J* = 5.5 Hz, 2H), 6.86 (dd, *J* = 5.5, 1.7 Hz, 2H), 5.26 (d, *J* = 1.7 Hz, 2H), 3.70 (s, 3H), 3.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4 (C), 170.1 (C), 141.4 (2CH), 139.9 (2CH), 133.6 (C), 130.2 (2CH), 129.3 (C), 128.4 (2C), 128.1 (2CH), 125.8 (2CH), 90.2 (2C), 84.7 (2CH), 74.3 (C), 69.7 (C), 52.2 (CH_3), 52.0 (CH_3); LRMS (CI) *m*/*z* (%): 403 (M^+ + 1, 40), 399 (19), 371 (100); HRMS (CI) calcd for $C_{24}H_{19}O_6$: 403.1182, found: 403.1174.

*Dimethyl 3-(8-(furan-2-yl)naphthalen-1-yl)-6-hydroxyphthalate (**11**):* ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.79 (s, 1H), 7.94 (dd, *J* = 5.9, 2.7 Hz, 1H), 7.90 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.50−7.45 (m, 3H), 7.33 (dd, *J* = 7.1, 1.3 Hz, 1H), 7.09 (dd, *J* = 1.8, 0.8 Hz, 1H), 7.05 (d, *J* = 8.6 Hz, 1H) 6.72 (d, J = 8.6 Hz, 1H), 6.13 (dd, J = 3.2, 0.8 Hz, 1H), 6.03 (dd, J = 3.2, 1.8 Hz, 1H), 3.90 (s, 3H), 3.40 (s, 3H); 13C NMR (100 MHz, $CDCl_3$) δ 169.6 (C), 168.7 (C), 160.1 (2C), 153.0 (C), 141.2 (CH), 136.8 (CH), 135.8 (C), 134.8 (C), 133.3 (C), 132.1 (C), 131.2 (CH), 130.8 (CH), 130.6 (C), 130.0 (CH), 129.2 (CH), 124.9 (CH), 124.8 (CH), 117.7 (CH), 110.8 (CH), 109.8 (CH), 108.5 (C), 52.8 (CH_3), 51.7 (CH_3); LRMS (EI) *m*/*z* (%): 402 (M^+, 35), 371 (100); HRMS (EI) calcd for $C_{24}H_{18}O_6$: 402.1103, found: 402.1106.

General Procedure for the Tandem [4 + 2]/[4 + 2] Cycloadditions of Oligofuran Derivatives 1 and Arynes. Finely powdered anhydrous CsF (1.5 mmol) was added to a solution of aryne precursor (0.5 mmol) and 1,8-difurylnaphthalene (**1a**, 0.5 mmol) in MeCN (10 mL), and the mixture was stirred at r.t. for 24 h. Then, CH_2Cl_2 (10 mL) was added, and the mixture was concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2; 9:1 to 1:1 hexane/EtOAc), affording *exo,exo* adducts.

*exo,exo-3b^1,6,6a,7-Tetrahydro-3b,6:7,11b-diepoxybenzo[a]perylene (**15a**):* 194 mg, 99% yield, yellowish solid, mp 177−179 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03−7.98 (m, 2H), 7.94 (dd, *J* = 7.1, 0.9 Hz, 1H), 7.82 (dd, *J* = 7.0, 1.0 Hz, 1H), 7.64−7.57 (m, 2H), 7.35 (m, 1H), 7.27- 7.19 (m, 3H), 6.77 (d, *J* = 5.6 Hz, 1H), 6.72 (dd, *J* = 5.6, 1.7 Hz, 1H), 5.45 (s, 1H), 5.23 (d, *J* = 1.6 Hz, 1H), 2.36 (d, *J* = 6.1 Hz, 1H), 2.34 (d, *J* = 6.1 Hz, 1H); ^{13}CNMR (100 MHz, $CDCl_3$) δ 148.5 (C), 147.7 (C), 140.3 (CH), 139.9 (CH), 134.0 (C), 130.6 (C), 130.2 (CH), 130.1 (CH), 129.6 (C), 128.6 (CH), 128.2 (CH), 127.9 (C), 126.6 (2CH), 125.9 (CH), 125.8 (CH), 119.8 (CH), 119.7 (CH), 85.9 (C), 85.8 (C), 82.1 (CH), 80.7 (CH), 53.5 (CH), 51.0 (CH); LRMS (EI), *m*/*z* (%): 336 (36), 307 (95), 289 (100); HRMS (EI) calcd for $C_{24}H_{16}O_2$: 336.1150, found: 336.1152.

*exo,exo-6,7-Di-p-tolyl-3b1,6,6a,7-tetrahydro-3b,6:7,11b-diepoxybenzo[a]perylene (**15b**):* 210 mg, 83% yield, yellowish solid, mp 188−190 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09−8.02 (m, 3H), 7.88 (dd, *J* = 7.0, 0.8 Hz, 1H), 7.68 (dd, *J* = 7.9, 7.4 Hz, 1H), 7.62 (dd, *J* = 7.3, 7.2 Hz, 1H), 7.28−7.25 (m, 1H), 7.19 (t, *J* = 7.3 Hz, 1H), 7.12 (dt, *J* = 7.40, 0.7 Hz, 1H), 7.23−7.08 (m, 5H), 6.90 (d, *J* = 5.5 Hz, 1H), 6.85 (d, *J* = 5.5 Hz, 1H), 6.73 (d, *J* = 8.0 Hz, 2H), 6.69 (d, *J* = 7.6 Hz, 2H), 3.09 (d, *J* = 6.0 Hz, 1H), 2.86 (d, *J* = 6.0 Hz, 1H), 2.20 (s, 3H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.4 (C), 148.8 (C), 143.9 (CH), 141.0 (CH), 135.8 (C), 135.3 (C), 134.1 (C), 133.6 (C), 132.5 (C), 130.7 (C), 130.2 (CH), 130.1 (CH), 129.8 (C), 129.1 (CH), 128.7 (CH), 128.1 (2CH), 128.0 (2CH), 128.0 (C), 126.57 (CH), 126.55 (CH), 126.0 (2CH), 125.95 (CH), 125.89 (CH), 125.8 (2CH), 119.8 (CH), 119.4 (CH), 93.0 (C), 90.3 (C), 85.6 (C), 84.8 (C), 57.9 (CH), 57.0 (CH), 21.0 (CH_3), 20.9 (CH_3); LRMS (EI) *m*/*z* (%): 516 (10, M^+), 397 (70), 276 (20), 119 (100); HRMS (EI) calcd for $C_{38}H_{28}O_2$: 516.2089, found: 516.2091.

*exo,exo-6,7-Dimesityl-3b^1,6,6a,7-tetrahydro-3b,6:7,11b-diepoxybenzo[a]perylene (**15c**):* 34 mg, 15% yield, white solid, mp 266 °C dec; ^{1}H NMR (400 MHz, $CDCl_3$.) δ 8.07−8.02 (m, 2H), 7.92 (dd, *J* = 7.1, 1.1 Hz, 1H), 7.83 (dd, *J* = 7.00, 1.2 Hz, 1H), 7.69 (dd, *J* = 8.2, 7.2 Hz 1H), 7.63 (dd, *J* = 8.2, 7.1 Hz 1H), 7.33 (d, *J* = 5.6 Hz, 1H), 7.27−7.24 (m, 1H), 7.20 (dt, *J* = 7.2, 1.4 Hz, 1H), 7.11 (dd, *J* = 7.2, 1.0 Hz, 1H), 7.09−7.06 (m 1H), 6.92 (d, *J* = 5.6 Hz, 1H), 6.68 (s, 1H), 6.51 (s, 1H), 6.26 (s, 1H), 6.16 (s, 1H), 3.71 (d, *J* = 6.0 Hz, 1H), 2.81 (d, *J* = 6.0 Hz, 1H), 2.57 (s, 3H), 2.39 (s, 3H), 2.27 (s, 3H), 2.11 (s, 3H), 2.10 (s, 3 H), 2.09 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.8 (C), 149.3 (C), 144.6 (CH), 141.5 (CH), 139.3 (C), 137.7 (C), 135.3 (C), 135.1 (C), 134.6 (C), 133.7 (C), 132.5 (C), 131.4 (CH), 130.8 (C), 130.7 (CH), 130.59 (C), 130.57 (C), 130.2 (C), 129.64 (CH), 129.62 (CH), 129.5 (CH), 129.2 (C), 128.7 (CH), 128.3 (CH), 128.1 (CH), 126.3 (CH), 125.9 (CH), 125.8 (2CH), 121.7 (CH), 119.6 (CH), 96.5 (C), 93.7 (C), 84.1 (C), 83.7 (C), 59.8 (CH), 55.1 (CH), 26.6 (CH_3), 25.7 (CH_3), 24.6 (CH_3), 23.8 (CH_3), 20.5 (CH_3), 20.4 (CH_3); LRMS (EI) *m*/*z* (%): 572 (76, M^+), 496 (27), 147 (100); HRMS (EI) calcd for $C_{42}H_{36}O_2$: 572.2715, found: 572.2715.

*exo,exo-9,10-Difluoro-3b^1,6,6a,7-tetrahydro-3b,6:7,11b-diepoxybenzo[y]perylene (**34a**):* 396 mg, 53% yield, yellowish solid, mp 215−7 °C dec; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.7 Hz, 1H), 8.01 (d, *J* = 8.3 Hz, 1H), 7.88 (dd, *J* = 7.3, 1.2 Hz, 1H), 7.82 (dd, *J* = 7.1, 1.2 Hz, 1H), 7.64 (d, *J* = 8.6 Hz, 1H), 7.61 (d, *J* = 8.5 Hz, 1H), 7.18 (dd, J_{H-F} = 8.9, 6.8 Hz, 1H), 7.08 (dd, J_{H-F} = 9.0, 6.7 Hz, 1H), 6.78 (d, *J* = 5.6 Hz, 1H), 6.74 (dd, *J* = 5.6, 1.7 Hz, 1H), 5.42 (s, 1H), 5.22 (d, *J* = 1.6 Hz, 1H), 2.41 (d, *J* = 6.1 Hz, 1H), 2.39 (d, *J* = 6.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.0 (d, J_{C-F} = 12.9 Hz, C), 148.03 (d, J_{C-F} = 12.7 Hz, C), 144.2 (C), 143.8 (C), 140.3 (CH), 139.9 (C), 134.0 (CH), 130.5 (CH), 130.3 (C), 130.2 (CH), 129.3 (C), 128.4 (CH), 128.3 (CH), 127.0 (C), 126.0 (CH), 125.8 (CH), 109.9 (d, J_{C-F} = 20.2 Hz, CH), 109.7 (d, J_{C-F} = 19.8 Hz, CH), 86.0 (C), 85.8 (C), 81.9 (CH), 80.2 (CH), 53.4 (CH), 51.0 (CH); LRMS (EI) *m*/*z* (%): 372 (M^+, 41), 354 (100), 325 (63), 288 (29); HRMS (EI) calcd for $C_{24}H_{14}F_2O_2$: 372.0962, found: 372.0953.

*exo,exo-9,10-Difluoro-6,7-di-p-tolyl-3b^1,6,6a,7-tetrahydro-3b,6:7,11b-diepoxybenzo[a]perylene (**34b**):* 234 mg, 56% yield, yellowish solid, mp 224 °C dec; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.3 Hz, 1H), 8.05 (d, *J* = 8.3 Hz, 1H), 7.98 (d, *J* = 7.0 Hz, 1H), 7.88 (d, *J* = 7.0 Hz, 1H), 7.69 (dd, *J* = 7.9, 7.4 Hz, 1H), 7.63 (dd, *J* = 8.0, 7.3 Hz, 1H), 7.08 (dd, J_{H-F} = 8.8 Hz, 6.9 Hz, 1H), 6.99−6.93 (m, 4H), 6.91 (d, *J* = 5.5 Hz, 1H), 6.87 (d, *J* = 5.5 Hz, 1H), 6.83 (dd, J_{H-F} = 9.0 Hz, 6.9 Hz, 1H), 6.75 (d, *J* = 8.0 Hz, 2H), 6.68 (d, *J* = 7.6 Hz, 2H), 3.07 (d, *J* = 6.0 Hz, 1H), 2.84 (d, *J* = 6.0 Hz, 1H), 2.21 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.2 (d, J_{C-F} = 250 Hz, C), 149.0 (d, J_{C-F} = 250 Hz, C), 147.5 (C), 144.02 (CH),

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143.9 (C), 141.0 (CH), 136.02 (C), 135.80 (C), 134.1 (C), 133.2 (C), 131.7 (C), 130.6 (CH), 130.5 (C), 130.2 (CH), 129.5 (C), 128.9 (CH), 128.8 (CH), 128.3 (2CH), 128.1 (2CH), 127.2 (C), 126.1 (CH), 126.0 (CH), 125.8 (4CH), 110.0 (d, J_{C-F} = 18.3 Hz, CH), 109.4 (d, J_{C-F} = 19.5 Hz CH), 93.0 (C), 90.0 (C), 85.5 (C), 84.8 (C), 57.81 (CH), 56.94 (CH), 21.0 (CH_3), 20.9 (CH_3); LRMS (EI) *m*/*z* (%): 552 (9, M^+), 433 (36), 416 (12), 119 (100); HRMS (EI) calcd for $C_{38}H_{26}F_2O_2$: 552.1901, found: 552.1881.

*exo,exo-6,6a,7,9,10,11-Hexahydro-3b¹H-3b,6:7,12b-diepoxyindeno[5,6-a]perylene (**35**):* 107 mg, 82% yield, yellowish solid, mp 200 °C dec; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05−7.94 (m, 3H), 7.82 (d, *J* = 7.0 Hz, 1H), 7.65−7.57 (m, *J* = Hz, 2H), 7.21 (s, 1H), 7.10 (s, 1H), 6.76 (d, *J* = 5.6 Hz,1H), 6.73 (dd, *J* = 5.6, 1.6 Hz, 1H), 5.39 (s, 1H), 5.22 (d, *J* = 1.5 Hz, 1H), 2.97−2.80 (m, 4H), 2.42 (d, *J* = 6.1 Hz, 1H), 2.40 (d, *J* = 6.2 Hz, 1H), 2.18−2.06 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.1 (C), 146.3 (C), 142.53 (C), 142.51 (C), 140.2 (CH), 139.8 (CH), 134.0 (C), 130.6 (C), 130.02 (CH), 129.97 (CH), 129.7 (C), 128.6 (CH), 128.2 (C), 128.1 (CH), 125.8 (CH), 125.7 (CH), 116.2 (CH), 116.0 (CH), 85.85 (C), 85.6 (C), 82.0 (CH), 80.6 (CH), 53.8 (CH), 51.3 (CH), 32.71 (CH_2), 32.62 (CH_2), 25.70 (CH_2); LRMS (EI) *m*/*z* (%): 376 (M^+, 22), 358 (100), 347 (62), 330 (37); HRMS (EI) calcd for $C_{27}H_{20}O_2$: 376.1463, found: 376.1462.

*exo,exo-3b¹,6,6a,7-Tetrahydro-3b,6:7,12b-diepoxydibenzo-[6,7:11,12]tetrapheno[2,3-d][1,3]dioxol (**36**):* 20 mg, 88% yield, yellowish solid, mp 160 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 6.3, 1.4 Hz, 1H), 8.00 (dd, *J* = 6.3, 1.4 Hz, 1H), 7.93 (dd, *J* = 7.1, 1.2 Hz, 1H), 7.81 (dd, *J* = 7.0, 1.2 Hz, 1H), 7.64−7.58 (m, 2H), 6.87 (s, 1H), 6.77 (d, *J* = 5.7 Hz, 2H), 6.76 (s, 1H), 6.72 (dd, *J* = 5.6, 1.7 Hz, 1H), 6.01 (d, *J* = 1.4 Hz, 1H), 5.95 (d, *J* = 1.4 Hz, 1H), 5.35 (s, 1H), 5.19 (d, *J* = 1.7 Hz, 1H), 2.39 (d, *J* = 6.1 Hz, 1H), 2.37 (d, *J* = 6.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.2 (2C), 142.3 (C), 141.6 (C), 140.3 (CH), 139.9 (CH), 134.0 (C), 130.5 (C), 130.2 (CH), 130.1 (CH), 129.6 (C), 128.5 (CH), 128.2 (CH), 127.9 (C), 125.81 (CH), 125.79 (CH), 102.3 (CH), 102.0 (CH), 101.3 (CH_2), 85.9 (C), 85.8 (C), 81.9 (CH), 80.6 (CH), 53.9 (CH), 51.3 (CH); LRMS (CI) *m*/*z* (%): 381 (M^+ + 1, 100), 363 (37), 347 (10); HRMS (CI) calcd for $C_{25}H_{16}O_4$: 381.1127, found: 381.1127.

*exo,exo-11-Methoxy-3b¹,6,6a,7-tetrahydro-3b,6:7,11b-diepoxybenzo[a]perylene (**37**):* 21 mg, 95% yield, yellowish solid, mp 180 °C dec; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.98 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.84 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.79 (dd, *J* = 7.0, 1.2 Hz, 1H), 7.59 (dd, *J* = 8.2, 7.2, Hz, 1H), 7.57 (dd, *J* = 8.2, 7.0, Hz, 1H), 7.23 (dd, *J* = 8.3, 7.2 Hz, 1H), 6.99 (d, *J* = 7.1 Hz, 1H), 6.790 (d, *J* = 8.2 Hz, 1H), 6.786 (d, *J* = 5.6 Hz, 1H), 6.70 (dd, *J* = 5.6, 1.7 Hz, 1H), 5.41 (s, 1H), 5.20 (d, *J* = 1.7 Hz, 1H), 3.64 (s, 3H), 2.49 (d, *J* = 6.1 Hz, 1H), 2.40 (d, *J* = 6.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.8 (C), 150.8 (C), 140.03 (CH), 140.00 (CH), 133.7 (C), 133.6 (C), 130.5 (CH), 130.1 (CH), 130.0 (C), 129.6 (CH), 129.5 (C), 128.9 (CH), 127.8 (CH), 127.7 (C), 125.5 (CH), 125.3 (CH), 112.5 (CH), 110.9 (CH), 86.3 (C), 86.1 (C), 81.9 (CH), 80.7 (CH), 55.2 (CH_3), 53.8 (CH), 50.8 (CH); LRMS (EI) *m*/*z* (%):366 (M^+, 19), 348 (100), 305 (15); HRMS (EI) calcd for $C_{25}H_{18}O_3$: 366.1256, found: 366.1257.

*exo,exo-3b¹,6,6a,7-Tetrahydro-3b,6:7,13c-diepoxynaphto[1,2-a]perylene (**38a**):* 123 mg, 55% yield, yellowish solid, mp 211 °C dec; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04−7.99 (m, 3H), 7.91 (d, *J* = 8.3 Hz, 1H), 7.90 (d, *J* = 8.3 Hz, 1H), 7.82 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.64 (dd, *J* = 8.1, 7.2 Hz, 1H), 7.61 (dd, *J* = 8.2, 7.6 Hz, 1H), 7.54 (dd, *J* = 6.9, 1.2 Hz, 1H), 7.47 (dd, *J* = 7.0, 1.1 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 6.76 (d, *J* = 3.9 Hz, 1H), 6.72 (dd, *J* = 5.6, 1.8 Hz, 1H), 5.97 (s, 1H), 5.30 (d, *J* = 1.8 Hz, 1H), 2.44 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.6 (C), 145.5 (C), 140.4 (CH), 140.1 (CH), 134.1 (C), 132.8 (C), 130.6 (C), 130.2 (CH), 130.1 (CH), 129.7 (C), 128.9 (CH), 128.8 (CH), 128.3 (CH), 128.1 (C), 127.4 (CH), 126.7 (C), 126.6 (CH), 125.9 (CH), 125.8 (CH), 125.6 (CH), 123.3 (CH), 118.5 (CH), 86.8 (C), 86.0 (C), 82.1 (CH), 79.3 (CH), 53.28 (CH), 52.4 (CH); LRMS (EI) *m*/*z* (%): 386 (M^+, 33), 368 (100), 339 (51), 302 (20); HRMS (EI) calcd for $C_{28}H_{18}O_2$: 386.1307, found: 386.1307.

*exo,exo-3b¹,6,6a,7-Tetrahydro-3b,6:7,13b-diepoxynaphtho[2,1-a]perylene (**39a**):* 62 mg, 34% yield, yellowish solid, mp 189−191 °C dec; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.1 Hz, 1H), 8.04 (d, *J* = 8.2 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.9 (d, *J* = 6.9 Hz, 1H), 7.83 (d, *J* = 6.9 Hz, 1H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.64−7.56 (m, 2H), 7.54 (d, *J* = 8.1 Hz, 1H), 7.44 (d, *J* = 8.4 Hz, 1H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.20 (t, *J* = 7.62 Hz, 1H), 6.80 (d, *J* = 5.6 Hz, 1H), 6.71 (d, *J* = 5.5 Hz, 1H), 5.57 (s, 1H), 5.21 (s, 1H), 2.46 (d, *J* = 6.0 Hz, 1H), 2.41 (d, *J* = 6.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.9 (C), 143.4 (C), 126.7 (C), 140.4 (CH), 139.9 (CH), 134.0 (C), 133.5 (C), 130.5 (CH), 130.2 (2CH), 130.1 (C), 129.7 (C), 129.0 (CH), 128.5 (C), 128.2 (CH), 128.1 (CH), 125.8 (CH), 125.7 (CH), 125.7 (CH), 125.0 (CH), 123.6 (CH), 118.3 (CH), 87.1 (C), 85.9 (C), 81.9 (CH), 80.8 (CH), 55.3 (CH), 50.9 (CH); LRMS (EI) *m*/*z* (%): 386 (M^+, 69), 368 (158), 357 (100), 339 (87); HRMS (EI) calcd for $C_{28}H_{18}O_2$: 386.1307, found: 386.1316.

*exo,exo-6,7-Di-p-tolyl-3b¹,6,6a,7-tetrahydro-3b,6:7,13c-diepoxynaphtho[1,2-a]perylene (**38b**):* 35% yield (calculated by NMR), white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (dd, *J* = 7.3, 1.1 Hz, 1H), 8.09 (dd, *J* = 7.3, 1.2 Hz, 1H), 7.99 (dd, *J* = 7.1, 1.1 Hz, 1H), 7.91 (dd, *J* = 7.0, 1.2 Hz, 1H), 7.86 (d, *J* = 8.3 Hz, 1H), 7.71−7.62 (m, 3H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.37 (ddd, *J* = 8.2, 6.8, 1.2 Hz, 1H), 7.27−7.19 (m, 1H), 7.22 (d, *J* = 8.2 Hz, 1H), 7.07 (d, *J* = 7.7 Hz, 2H), 6.99 (d, *J* = 8.3 Hz, 2H), 6.94 (d, *J* = 5.5 Hz, 1H), 6.86 (d, *J* = 5.5 Hz, 1H), 6.77 (d, *J* = 7.8 Hz, 2H), 6.69 (d, *J* = 7.8 Hz, 2H), 3.07 (d, *J* = 6.0 Hz, 1H), 2.93 (d, *J* = 6.0 Hz, 1H), 2.23 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.5 (C), 144.1 (CH), 143.6 (C), 141.1 (CH), 135.9 (C), 135.4 (C), 134.2 (C), 133.5 (C), 133.4 (C), 132.4 (C), 131.0 (CH), 130.3 (C), 130.22 (CH), 130.18 (CH), 129.8 (C), 129.0(CH), 128.60 (C), 128.57 (CH), 128.1 (3CH), 128.04 (2CH), 127.97 (CH), 126.5 (C), 126.3 (2CH), 125.8 (4CH), 125.1 (CH), 123.9 (CH), 118.2 (CH), 93.0 (C), 90.4 (C), 86.0 (C), 85.7 (C), 59.6 (CH), 57.0 (CH), 21.03 (CH_3), 20.97 (CH_3); LRMS (EI) *m*/*z* (%): 566 (22, M^+), 447 (84), 327 (20), 119 (100); HRMS (EI) calcd for $C_{42}H_{30}O_2$: 566.2246, found: 566.2247.

*exo,exo-6,7-Di-p-tolyl-3b¹,6,6a,7-tetrahydro-3b,6:7,13b-diepoxynaphtho[2,1-a]perylene (**39b**):* 17% yield (calculated by NMR), white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12−8.07 (m, 2H), 8.04 (dd, *J* = 8.3, 1.0 Hz, 1H), 7.86 (dd, *J* = 7.0, 1.1 Hz, 1H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.80 (d, *J* = 8.8 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.73 (dd, *J* = 8.79, 7.72 Hz, 1H), 7.61 (dd, *J* = 8.2, 7.1 Hz, 1H), 7.40 (d, *J* = 8.1 Hz, 1H), 7.32−7.28 (m, 1H), 7.18 (ddd, *J* = 8.8, 7.7, 1.2 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 5.5 Hz, 1H), 6.94 (d, *J* = 5.5 Hz, 1H), 6.67 (d, *J* = 7.8 Hz, 2H), 3.32 (d, *J* = 5.9 Hz, 1H), 2.84 (d, *J* = 5.9 Hz, 1H), 2.25 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.4 (c), 146.1 (C), 143.3 (CH), 140.9 (CH), 136.2 (C), 134.6 (C), 134.1 (C), 133.5 (C), 134.1 (C), 130.1 (CH), 130.0 (CH), 129.8 (C), 129.6 (CH), 129.0 (CH), 128.6 (CH), 128.4 (CH), 128.2 (2CH), 128.1 (C), 128.0 (C), 127.9 (C), 127.4 (2CH), 126.2 (CH), 126.0 (CH), 125.8 (CH), 124.8 (CH), 122.8 (CH), 117.8 (CH), 93.6 (C), 92.7 (C), 85.2 (C), 84.8 (C), 58.5 (CH), 57.8 (CH), 21.1 (CH_3),21.0 (CH_3); LRMS (EI) *m*/*z* (%): 566 (22, M^+), 447 (56), 119 (100); HRMS (EI) calcd for $C_{42}H_{30}O_2$: 566.2246, found: 566.2257.

*exo,exo- 3b¹,6,6a,7-Tetrahydro-3b,6:7,13b-diepoxydibenzo-[fg,uv]pentaphene (**40a**):* 61 mg, 51% yield, yellowish solid, mp 160 °C dec; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09−8.01 (m, 3H), 7.89−7.79 (m, 3H), 7.74 (s, 1H), 7.67 (dd, *J* = 8.0, 7.4 Hz, 1H), 7,63 (d, *J* = 7,4 Hz, 1H), 7.61 (d, *J* = 7,6 Hz, 1H), 7.51−7.47 (m, 2H), 6.77 (d, *J* = 5.6 Hz, 1H), 6.73 (dd, *J* = 5.6, 1.5 Hz, 1H), 5.30 (d, *J* = 1.4 Hz, 1H), 5.58 (s, 1H), 2.50 (d, *J* = 6.2 Hz, 1H), 2.48 (d, *J* = 6.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.7 (C), 145.3 (C), 140.2 (CH), 139.7 (CH), 134.0 (C), 132.7 (2C), 130.5 (C), 130.2 (CH), 130.1 (CH), 129.5 (C), 128.6 (CH), 128.3 (CH), 128.2 (CH), 128.1 (CH), 127.7 (C), 126.0 (CH), 125.91 (CH), 125.95 (CH), 125.8 (CH), 118.1 (CH), 117.8 (CH), 86.0 (C), 85.6 (C), 82.2 (CH), 80.5 (CH), 53.4 (CH), 50.8 (CH); MS (EI), *m*/*z* (%): 386 (33), 368 (100); HRMS (EI) $C_{28}H_{18}O_2$, calcd 386.1307, found: 386.1307.

*exo,exo-6,7-Di-p-tolyl-3b1,6,6a,7-tetrahydro-3b,6:7,11b-diepoxybenzo[a]perylene (**40b**):* 160 mg, 59% yield, yellowish solid, mp 206 °C dec; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (dd, *J* = 7.1, 1.0 Hz, 1H),

8.11 (dd, J = 8.2, 0.9 Hz, 1H), 8.07 (dd, J = 8.3, 1.0 Hz, 1H), 7.90 (dd, J = 7.02, 1.07 Hz, 1H), 7.81−7.77 (m, 1H), 7.75−7.69 (m, 2H), 7.64 (dd, J = 7.25, 6.17 Hz, 2H), 7.46−7.39 (m, 2H), 7.37 (s, 1H), 7.08 (d, J = 7.5 Hz, 2H), 7.01 (d, J = 8.2 Hz, 2H), 6.90 (d, J = 5.5 Hz, 1H), 6.86 (d, J = 5.5 Hz, 1H), 6.78 (d, J = 8.0 Hz, 2H), 6.71 (d, J = 7.7 Hz, 2H), 3.15 (d, J = 6.1 Hz, 1H), 2.92 (d, J = 6.1 Hz, 1H), 2.24 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.1 (C), 145.9 (C), 143.9 (CH), 140.9 (CH), 135.9 (C), 135.2 (C), 134.2 (C), 133.5 (C), 132.7 (2C), 132.6 (C), 130.8 (C), 130.3 (CH), 130.2 (CH), 129.7 (C), 129.1 (CH), 128.7 (CH), 128.3 (CH), 128.2 (2CH), 128.1 (2CH), 127.9 (C), 126.1 (2CH), 126.0 (CH), 125.9 (2CH), 125.9 (4CH), 118.38 (CH), 117.7 (CH), 93.2 (C), 90.1 (C), 85.7 (C), 84.7 (C), 57.9 (CH), 56.69 (CH), 21.0 (CH_3), 20.9 (CH_3); LRMS (EI) m/z (%): 566 (35, M^+), 447 (100), 430 (55); HRMS (EI) $C_{42}H_{30}O_2$, calcd 566.2246, found: 566.2233.

*exo,exo-7,7a,7a^1,8-Tetrahydro-7,16b:8,10a-diepoxyphenanthro-[2,1-a]perylene (**41**):* 84 mg, 50% yield, white solid, mp 258−260 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.68 (t, J = 8.7 Hz, 2H), 8.08 (d, J = 8.3 Hz, 2H), 7.90 (dd, J = 3.9, 1.0 Hz, 1H), 7.87 (dd, J = 3.6, 0.9 Hz, 1H), 7.79 (d, J = 8.7 Hz, 1H), 7.70 − 7.56 (m, 5H), 7.44 (d, J = 9.2 Hz, 1H), 7.36 (d, J = 9.2 Hz, 1H), 6.82 (d, J = 5.6 Hz, 1H), 6.72 (dd, J = 5.6, 1.7 Hz, 1H), 5.64 (s, 1H), 5.25 (d, J = 1.6 Hz, 1H), 2.54 (d, J = 6.1 Hz, 1H), 2.45 (d, J = 6.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.19 (C), 144.14 (C), 140.44 (CH), 139.84 (CH), 134.02 (C), 131.20 (C), 130.76 (C), 130.48 (CH), 130.18 (2CH), 130.05 (C), 129.95 (C), 129.66 (C), 128.60 (CH), 128.07 (CH), 126.87 (CH), 126.84 (CH), 126.50 (CH), 125.75 (2CH), 125.23 (C), 122.91 (CH), 122.44 (CH), 122.38 (CH), 118.25 (CH), 87.11 (C), 85.91 (C), 82.00 (CH), 80.52 (CH), 55.08 (CH), 50.84 (CH); LRMS (EI) m/z (%): 435.9 (M^+, 36), 416.9 (100), 399.9 (66), 388.9 (43), 375.9 (24); HRMS (EI) calcd for $C_{32}H_{20}O_2$: 436.1463, found: 436.1464

*exo,exo-3b^1,6,6a,7-Tetrahydro-3b,6:7,15c-diepoxyphenanthro-[1,2-a]perylene (**42**):* 70 mg, 42% yield, white solid, mp 283−285 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.69 (d, J = 8.1 Hz, 1H), 8.62 (d, J = 8.3 Hz, 1H), 8.08 (s, 1H), 8.06−8.02 (m, 2H), 7.92 (dd, J = 7.7, 1.3 Hz, 1H), 7.85 (dd, J = 7.1, 1.2 Hz, 1H), 7.82 (s, 2H), 7.70−7.58 (m, 5H), 6.79 (d, J = 5.6 Hz, 1H), 6.74 (dd, J = 5.6, 1.7 Hz, 1H), 6.04 (s, 1H), 5.35 (d, J = 7 Hz, 1H), 2.49 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.23 (C), 146.07 (C), 140.37 (CH), 140.05 (CH), 134.06 (C), 131.74 (C), 130.72 (C), 130.57 (C), 130.30 (CH), 130.19 (CH), 129.65 (C), 129.36 (C), 128.86 (2CH), 128.63 (C), 128.33 (CH), 127.96 (CH), 127.04 (CH), 126.62 (CH), 125.94 (CH), 125.88 (CH), 125.04 (C), 122.94 (CH), 122.15 (CH), 121.82 (CH), 118.55 (CH), 86.77 (C), 85.99 (C), 82.17 (CH), 79.45 (CH), 53.26 (CH), 52.12 (CH); LRMS (EI) m/z (%): 436.2 (M^+, 13), 418.2 (100), 402.2 (20), 389.2 (26), 376.2 (9); HRMS (EI) calcd for $C_{32}H_{20}O_2$: 436.1463, found: 436.1467.

*exo,exo-3b^1,6,6a,7-Tetrahydro-3b,6:7,15c-diepoxyphenanthro-[9,10-a]perylene (**43**):* 60 mg, 76% yield, yellowish solid, mp 214−216 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83−8.73 (m, 2H), 8.14−7.99 (m, 3H), 7.92 (d, J = 6.8 Hz, 1H), 7.86 (d, J = 6.7 Hz, 1H), 7.72−7.54 (m, 6H), 7.32 (m, 1H), 6.82 (dd, J = 5.6, 0.7 Hz, 1H), 6.71 (ddd, J = 5.6, 1.7, 0.7 Hz, 1H), 6.05 (s, 1H), 5.30 (d, J = 1.6 Hz, 1H), 2.57 (d, J = 5.8 Hz, 1H), 2.48 (dd, J = 6.1, 0.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8 (C), 141.8 (C), 140.4 (CH), 139.9 (CH), 134.1 (C), 130.7 (CH), 130.6 (C), 130.4 (C), 130.20 (CH), 130.16 (CH), 130.1 (C), 129.7 (C), 128.6 (C), 128.1 (CH), 127.0 (CH), 126.6 (CH), 126.3 (C), 126.1 (CH), 125.92 (C), 125.87 (CH), 125.75 (CH), 125.72 (CH), 124.4 (CH), 124.0 (CH), 123.7 (CH), 123.5 (CH), 88.0 (C), 86.0 (C), 81.9 (CH), 79.1 (CH), 55.0 (CH), 52.1 (CH); LRMS (EI), m/z (%): 436 (12), 417 (100); HRMS (EI) $C_{32}H_{20}O_2$, calcd: 436.1463, found: 436.1461.

*exo,exo-9,18-Diphenyl-3b^1,6,6a,7-tetrahydro-3b,6:7,19b-di-epoxytetrabenzo[fg,o,q,yz]hexaphene (**44**):* 59 mg, 38% yield, yellowish solid, mp 240 °C dec; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (d, J = 7.8 Hz, 2H), 8.03 − 7.98 (m, 3H), 7.84 (s, 1H), 7.81 (d, J = 1.1 Hz, 1H), 7.71 (s, 1H), 7.69 − 7.49 (m, 11H), 7.40 − 7.32 (m, 5H), 7.01 (dd, J = 7.1 y 1.1 Hz, 1H), 6.97 (dd, J = 7.1 y 1.1 Hz, 1H), 6.76 (d, J = 5.6 Hz, 1H), 6.73 (dd, J = 5.6 y 1.6 Hz, 1H), 5.52 (s, 1H), 5.27 (d, J = 1.5 Hz, 1H), 2.55 (d, J = 6.2 Hz, 1H), 2.50 (d, J = 6.2 Hz, 1H); ^{13}C NMR DEPT (125 MHz, $CDCl_3$) δ 145.57 (C), 144.70 (C), 141.88 (C), 141.71 (C), 140.22 (CH), 139.75 (CH), 135.87 (C), 135.71 (C), 133.95 (C), 132.75 (CH), 132.72 (CH), 132.48 (CH), 132.11 (CH), 131.84 (C), 131.80 (C), 131.15 (C), 131.12 (C), 131.10 (C), 130.99 (C), 130.50 (C), 130.34 (CH), 130.24 (CH), 130.20 (CH), 130.10 (CH), 129.54 (C), 129.33 (CH), 129.20 (CH), 129.16 (C), 129.06 (C), 128.83 (CH), 128.65 (CH), 128.54 (CH), 128.24 (CH), 127.63 (2CH), 126.73 (2CH), 125.81 (CH), 125.77 (CH), 125.74 (2CH), 123.28 (2CH), 117.02 (CH), 116.49 (CH), 86.06 (C), 85.87 (C), 82.23 (CH), 80.70 (CH), 53.41 (CH), 50.71 (CH); LRMS (EI) m/z (%): 688.3 (M^+, 100), 670.2 (69), 654.2 (20), 335.1 (23); HRMS (EI) calcd for $C_{52}H_{32}O_2$: 688.2402, found: 688.2415

*exo,exo,exo,exo-4b^1,10c,10c^1,11,19c,20-Hexahydro-4b,20:10b,19b:11,13a-tri-epoxytribenzo[de,hi,op]naphtho[3,2,1-st]-pentacene (**45**):* 58 mg, 56% yield, white solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.32 (d, J = 6.8 Hz, 1H), 8.26 (d, J = 6.5 Hz, 1H), 8.05 (d, J = 8.3 Hz, 1H), 8.04 (d, J = 7.0 Hz, 1H), 8.01−7.97 (m, 3H), 7.85 (d, J = 7.00 Hz, 1H), 7.67−7.56 (m, 4H), 7.46 (d, J = 7.09 Hz, 1H), 7.36−7.24 (m, 3H), 6.86 (d, J = 5.66 Hz, 1H), 6.66 (dd, J = 5.64, 1.87 Hz, 1H), 6.31 (s, 1H), 6.01 (d, J = 1.99 Hz, 1H), 2.72 (d, J = 6.55 Hz, 1H), 2.68 (d, J = 6.56 Hz, 1H), 2.59 (d, J = 6.7 Hz, 1H), 2.57 (d, J = 6.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.1 (C), 147.0 (C), 139.9 (2CH), 134.3 (C), 134.0 (C), 130.9 (C), 130.5 (CH), 130.2 (CH), 130.0 (C), 129.6 (CH), 129.4 (CH), 129.1 (C), 128.6 (2CH), 128.1 (CH), 127.6 (CH), 127.4 (C), 127.0 (CH), 126.9 (CH), 125.8 (CH), 125.7 (CH), 125.5 (2CH), 120.3 (CH), 119.7 (CH), 87.2 (C), 86.9 (2C), 81.8 (C), 81.7 (CH), 81.1 (C), 80.5 (CH), 62.0 (CH), 59.7 (CH), 56.4 (CH), 54.51 (C); LRMS (EI) m/z (%): 528 (13, M^+), 510 (34), 482 (9), 231 (100); HRMS (EI) calcd for $C_{38}H_{24}O_3$: 528.1725, found: 528.1727.

General Procedure for the Synthesis of Perylene Derivatives. Concentrated HCl solution (100 μL, 37.5% in water) was added to a solution of aryne adducts (0.30 mmol) in EtOH (6 mL), and the mixture was stirred under argon in the absence of light at 78 °C for 5 h. Then, H_2O (1 mL) was added and the mixture was concentrated under reduced pressure. The residue was purified by column chromatography (under argon in the absence of light; SiO_2; 9:1 hexane/CH_2Cl_2), affording perylene derivatives.

*Benzo[a]perylene (**46a**):*[35] 72 mg, 72% yield, red solid, mp 116 °C dec;[7] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (d, J = 9.5 Hz, 1H), 8.27 (d, J = 6.6 Hz, 1H), 8.25 (s, 1H), 8.24 (d, J = 8.0 Hz, 1H), 8.14 (d, J = 7.3 Hz, 1H), 7.98 (d, J = 9.7 Hz, 1H), 7.89 (d, J = 8.4 Hz, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.73 (d, J = 8.1 Hz, 1H), 7.55 (t, J = 7.7 Hz, 1H), 7.54 (t, J = 7.8 Hz, 1H), 7.50 (t, J = 7.9 Hz, 1H), 7.47−7.44 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.3 (C), 133.4 (C), 131.5 (C), 131.3 (C), 131.2 (C), 131.1 (C), 130.0 (C), 128.8 (C), 128.7 (CH), 128.3 (C), 128.2(CH), 127.6 (C), 127.44 (CH), 127.46 (CH), 127.2 (CH), 126.8 (CH), 126.5 (CH), 126.4 (2CH), 126.0 (CH), 125.6 (CH), 125.4 (CH), 120.4 (CH), 120.3 (CH); LRMS (EI) m/z (%): 302 (M^+, 100), 150 (14); HRMS (EI) calcd for $C_{24}H_{14}$: 302.1095, found: 302.1096.

*9,10-Difluorobenzo[a]perylene (**47a**):* 180 mg, 50% yield, red solid, mp 162−164 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.53 (dd, J_{H-F} = 13.5, 8.2 Hz, 1H), 8.24 (d, J = 7.4 Hz, 1H), 8.14 (m, 3H), 7.84 (d, J = 8.3 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.77 (d, J = 8.1 Hz, 1H), 7.64 (dd, J_{H-F} = 10.6, 8.7 Hz, 1H), 7.61−7.52 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 134.3 (C), 130.85 (d, J_{C-F} = 234 Hz, C), 130.83 (d, J_{C-F} = 236 Hz, C), 130.99 (C), 130.97 (C), 130.91 (C), 130.8 (C), 130.7 (C), 128.4 (C), 127.8 (CH), 127.7 (CH), 127.59 (C), 127.58 (C), 127.4 (CH), 127.2 (CH), 126.8 (CH), 126.2 (2CH), 125.6 (dd, J_{C-F} = 6.6, 3.2 Hz, CH), 120.8 (CH), 120.7 (CH), 113.2 (d, J_{C-F} = 15.9 Hz, CH), 112.8 (d, J_{C-F} = 19.7 Hz, CH); LRMS (EI) m/z (%): 338 (100, M^+), 318 (9), 168 (25); HRMS (EI) calcd for $C_{24}H_{12}F_2$: 338.0901, found: 338.0907; UV/vis (CH_2Cl_2), λ_{max} (ε): 501 (55104), 469 (40495), 276 (120441) nm (mol^{-1} dm^3 cm^{-1}).

*10,11-Dihydro-9H-indeno[5,6-a]perylene (**48**):* 55 mg, 57% yield, red solid, mp 130−2 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.65 (s, 1H), 8.27 (d, J = 7.5 Hz, 1H), 8.21 (d, J = 7.5 Hz, 1H), 8.14 (s, 1H), 8.09 (d, J = 7.2 Hz, 1H), 7.83 (d, J = 8.3 Hz, 1H), 7.76 (d, J = 7.6 Hz, 2H), 7.71 (d, J = 8.1 Hz, 1H), 7.55 (t, J = 7.8 Hz, 2H), 7.51−7.43 (m, 1H),

3.09 (dt, J = 7.1, 2.6 Hz, 4H), 2.18 (p, J = 7.2 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.0 (C), 143.3 (C), 134.4 (C), 133.4 (C), 131.8 (C), 131.4 (C), 131.1 (C), 131.0 (C), 130.3 (C), 128.9 (C), 127.7 (CH), 127.5 (C), 127.4 (CH), 127.3 (C), 127.2 (CH), 126.8 (CH), 126.5 (CH), 126.0 (2CH), 125.2 (CH), 122.4 (CH), 120.4 (CH), 120.2 (CH), 120.0 (CH), 33.0 (CH_2), 32.4 (CH_2), 26.2 (CH_2); LRMS (EI), m/z (%): 342 (100, M^+), 313 (7), 171 (9); HRMS (EI) calcd for $C_{27}H_{18}$: 342.1407, found: 342.1409; UV/vis (CH_2Cl_2), λ_{max} (ε): 510 (25680), 478 (15720), 280 (3718) nm (mol^{-1} dm^3 cm^{-1}).

Dibenzo[6,7:11,12]tetrapheno[2,3-d][1,3]dioxol (**49**): 14 mg, 23% yield, red solid, mp 157 °C dec; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (d, J = 7.0 Hz, 1H), 8.18 (d, J = 7.2 Hz, 1H), 8.14 (s, 1H), 8.07 (d, J = 7.3 Hz, 1H), 8.00 (s, 1H), 7.76 (t, J = 7.7 Hz, 1H), 7.70 (d, J = 8.1 Hz, 1H), 7.57−7.42 (m, 3H), 7.15 (s, 1H), 6.06 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.7 (C), 147.5 (C), 134.4 (C), 131.7 (C), 131.6 (C), 131.3 (C), 130.9 (C), 130.7 (C), 130.2 (C), 127.3 (C), 127.2 (CH), 127.04 (C), 127.01 (CH), 126.97 (CH), 126.88 (CH), 126.79 (C), 126.5 (CH), 125.9 (CH), 125.31 (CH), 125.26 (CH), 120.1 (CH), 120.0 (CH), 103.1 (CH), 102.1 (CH), 101.2 (CH_2); LRMS (EI), m/z (%): 346 (100, M^+), 287 (48), 173 (24), 144 (47); HRMS (EI) calcd for $C_{25}H_{14}O_2$: 346.0990, found: 346.0990; UV/vis (CH_2Cl_2), λ_{max} (ε): 500 (33740), 470 (245000), 272 (44700) nm (mol^{-1} dm^3 cm^{-1}).

11-Methoxybenzo[a]perylene (**50**): 22 mg, 35% yield, red solid, mp 190 °C dec; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (d, J = 7.4 Hz, 1H), 8.23 (s, 1H), 8.14 (d, J = 7.2 Hz, 1H), 7.86 (d, J = 8.3 Hz, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.71 (d, J = 7.5 Hz, 1H), 7.63 (d, J = 8.3 Hz, 1H), 7.56 − 7.41 (m, 5H), 6.88 (d, J = 7.4 Hz, 1H), 3.79 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.50 (C), 135.28 (C), 133.51 (C), 131.72 (C), 131.46 (C), 131.27 (CH), 131.06 (CH), 129.43 (C), 128.84 (C), 128.25 (C), 127.42 (C), 126.81 (2CH), 125.95 (C), 125.84 (CH), 125.79 (CH), 125.48 (CH), 125.03 (CH), 121.88 (CH), 120.60 (C), 120.25 (CH), 120.16 (CH), 105.13 (CH), 54.56 (CH_3); LRMS (EI), m/z (%): 332.2 (M^+, 100), 316.1 (90), 158.0 (54); HRMS (EI) calcd for $C_{25}H_{16}O$: 332.1201, found: 332.1202; UV/vis (CH_2Cl_2), λ_{max} (ε): 516 (25341), 482 (18295), 450 (7552), 350 (3729), 299 (25588), 281 (50265) nm (mol^{-1} dm^3 cm^{-1}).

Naphtho[1,2-a]perylene (**51**): 39 mg, 46% yield, red solid, mp 206−8 °C dec; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.72 (d, J = 8.4 Hz, 1H), 8.35 (d, J = 7.5 Hz, 1H), 8.19 (dd, J = 7.4, 0.9 Hz, 1H), 8.08 (dd, J = 7.4, 0.8 Hz, 1H), 7.97 (s, 1H), 7.78 (d, J = 8.2 Hz, 1H), 7.72 (d, J = 8.0 Hz, 1H), 7.68 (dd, J = 8.0, 1.4 Hz, 1H), 7.62 (d, J = 8.0 Hz, 1H), 7.60 − 7.45 (m, 4H), 7.36 (ddd, J = 8.0, 7.0, 1.1 Hz, 1H), 7.14 (t, J = 7.9 Hz, 1H), 7.03 (ddd, J = 8.5, 7.0, 1.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.34 (C), 133.14 (C), 132.90 (C), 132.09 (C), 131.97 (C), 131.38 (C), 131.22 (C), 131.14 (C), 129.77 (C), 129.39 (C), 129.26 (C), 129.00 (CH), 128.60 (CH), 127.87 (CH), 127.58 (CH), 127.43 (CH), 127.37 (C), 127.29 (CH), 127.14 (CH), 126.96 (CH), 126.76 (CH), 126.55 (CH), 126.00 (CH), 125.82 (CH), 125.53 (CH), 124.28 (CH), 120.73 (CH), 120.22 (CH); LRMS (EI) m/z (%): 352.2 (M^+, 69), 350.2 (100), 176.0 (16), 175.1 (77); HRMS (EI) calcd for $C_{28}H_{16}$: 352.1252, found: 352.1256; UV/vis (CH_2Cl_2), λ_{max} (ε): 513 (14259), 484 (12051), 463 (9321), 365 (8030), 348 (8383), 328 (17210), 274 (55841) nm (mol^{-1} dm^3 cm^{-1}).

Naphtho[2,1-a]perylene (**52**): 13 mg, 29% yield, red solid, mp 195−6 °C dec; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.96 (s, 1H), 8.78 (d, J = 8.1 Hz, 1H), 8.53 (d, J = 9.5 Hz, 1H), 8.25 (dd, J = 7.5, 0.9 Hz, 1H), 8.20 (dd, J = 7.4, 0.8 Hz, 1H), 8.15 (d, J = 7.4 Hz, 1H), 7.98 (d, J = 8.2 Hz, 1H), 7.83 (dd, J = 7.6, 1.6 Hz, 1H), 7.79 (d, J = 8.4 Hz, 1H), 7.76 (d, J = 8.9 Hz, 1H), 7.69 (dd, J = 7.1, 1.6 Hz, 1H), 7.66 − 7.51 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.31 (C), 131.79 (C), 131.72 (C), 131.17 (C), 131.09 (C), 130.85 (C), 130.71 (C), 130.64 (C), 130.13 (C), 129.04 (CH), 127.94 (CH), 127.79 (C), 127.72 (CH), 127.49 (2CH), 127.40 (CH), 127.18 (CH), 126.97 (C), 126.85 (CH), 126.53 (CH), 126.02 (2CH), 125.98 (CH), 123.12 (CH), 121.36 (CH), 120.46 (2CH); LRMS (EI) m/z (%): 352.2 (M^+, 100), 175.1 (72); HRMS (EI) calcd for $C_{28}H_{16}$: 352.1252, found: 352.1255. λ_{max} (ε):495 (24546), 464 (17953), 437 (7969), 336 (38780), 321 (25450), 308 (14815), 269 (24886), 249 (48630) nm (mol^{-1} dm^3 cm^{-1}).

Dibenzo[fg,uv]pentaphene (**53a**): 74 mg, 57% yield, violet solid, mp 152−4 °C; ^{1}H NMR (400 MHz, $CDCl_2CDCl_2$) δ 9.48 (s, 1H), 8.61 (s, 1H), 8.54−8.42 (m, 2H), 8.28 (d, J = 7.2 Hz, 1H), 8.11 (d, J = 7.0 Hz, 1H), 8.01 (d, J = 7.3 Hz, 2H), 7.92 (d, J = 8.4 Hz, 1H), 7.84 (d, J = 7.9 Hz, 1H), 7.80 (d, J = 7.8 Hz, 1H), 7.65 (d, J = 8.1 Hz, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.53−7.42 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.5 (C), 135.5 (C), 134.9 (C), 134.8 (C), 134.5 (C), 134.4 (C), 134.3 (C), 134.1 (C), 133.0 (C), 132.0 (CH), 131.1 (CH), 131.0 (CH), 130.9 (C), 130.8 (CH), 130.7 (CH), 130.4 (CH), 130.3 (C), 130.2 (C), 130.0 (CH), 129.7 (CH), 129.6 (CH), 129.5 (CH), 129.0 (CH), 128.9 (CH), 128.7 (CH), 128.5 (CH), 123.8 (CH), 123.5 (CH); HRMS $C_{28}H_{16}$: 352.1254, found: 352.1252; UV/vis (CH_2Cl_2), λ_{max} (ε): 589 (13920), 546 (9340), 295 (45780) nm (mol^{-1} dm^3 cm^{-1}).

Phenanthro[1,2-a]perylene (**54**): 32 mg, 41% yield, red solid, mp 264 °C dec; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.67 (d, J = 8.4 Hz, 1H), 8.50 (d, J = 9.1 Hz, 1H), 8.43 (d, J = 9.1 Hz, 1H), 8.27 (d, J = 7.5 Hz, 1H), 8.17 (d, J = 6.5 Hz, 1H), 8.16 (s, 1H), 8.07 (d, J = 7.5 Hz, 1H), 7.90 (d, J = 8.3 Hz, 1H), 7.88 (d, J = 7.0 Hz, 1H), 7.80 (dd, J = 6.5, 1.3 Hz, 1H), 7.76 (d, J = 8.1 Hz, 1H), 7.66 − 7.52 (m, 5H), 7.38 (d, J = 9.2 Hz, 1H), 7.15 (t, J = 7.8 Hz, 1H); ^{13}C NMR (500 MHz, $CDCl_3$) δ 134.26 (C), 132.74 (C), 132.53 (C), 132.24 (C), 131.92 (C), 131.42 (C), 131.29 (C), 130.52 (C), 129.61 (C), 129.41 (CH), 129.33 (C), 129.26 (C), 129.24 (C), 129.12 (C), 128.27 (CH), 127.91 (CH), 127.58 (CH), 127.48 (CH), 127.30 (CH), 127.05 (CH), 126.61 (CH), 126.50 (CH), 126.40 (CH), 126.00 (CH), 125.75 (CH), 125.71 (CH), 124.13 (CH), 123.30 (CH), 121.85 (CH), 120.77 (CH), 120.33 (CH); LRMS (EI) m/z (%): 402.2 (M^+, 63), 400.2 (100), 398.2 (18), 200.1 (64); HRMS (EI) calcd for $C_{32}H_{18}$: 402.1409, found: 402.1405; UV/vis (CH_2Cl_2), λ_{max} (ε): 522 (21203), 489 (16120), 332 (42232), 291 (66013), 283 (69039) nm (mol^{-1} dm^3 cm^{-1}).

Phenanthro[2,1-a]perylene (**55**): 12 mg, 32% yield, red solid, mp 262−4 °C dec; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.14 (s, 1H), 8.87 (t, J = 8.6 Hz, 2H), 8.76 (d, J = 8.3 Hz, 1H), 8.60 (d, J = 9.7 Hz, 1H), 8.30 (dd, J = 7.3 y 2.9 Hz, 2H), 8.26 (d, J = 7.3 Hz, 1H), 8.07 (t, J = 8.6 Hz, 2H), 8.03 (d, J = 7.9 Hz, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.80 (d, J = 8.1 Hz, 1H), 7.73 (t, J = 7.5 Hz, 1H), 7.67 − 7.58 (m, 4H); ^{13}C NMR-DEPT (125 MHz, $CDCl_3$) δ 134.8 (C), 132.90 (C), 132.3 (C), 131.6 (C), 131.54 (C), 131.52 (C), 131.4 (C), 130.61 (C), 130.59 (C), 129.5 (C), 129.3 (CH), 128.82 (CH), 128.80 (C), 128.26 (C), 128.21 (CH), 128.19 (C), 128.0 (C), 127.92 (CH), 127.89 (CH), 127.78 (CH), 127.0 (CH), 126.9 (2CH), 126.7 (CH), 126.40 (CH), 126.38 (CH), 123.5 (CH), 122.3 (CH), 122.2 (CH), 121.8 (CH), 120.9 (CH), 120.80 (CH); LRMS (EI) m/z (%): 402.2 (M^+, 100), 200.0 (28); HRMS (EI) calcd for $C_{32}H_{18}$: 402.1409, found: 402.1405; UV/vis (CH_2Cl_2), λ_{max} (ε): 509 (22535), 476 (16493), 449 (7361), 330 (38280), 260 (72810) nm (mol^{-1} dm^3 cm^{-1}).

Phenanthro[9,10-a]perylene (**56**): 70 mg, 87% yield, red solid, mp 231−3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (s, 1H), 8.57−8.43 (m, 3H), 8.28 (t, J = 7.5 Hz, 2H), 8.24 (d, J = 7.4 Hz, 1H), 8.17 (d, J = 7.4 Hz, 1H), 7.87 (d, J = 8.1 Hz, 1H), 7.72 (d, J = 8.0 Hz, 1H), 7.67−7.59 (m, 3H), 7.54 (d, J = 7.8 Hz, 1H), 7.52 (d, J = 7.7 Hz, 1H), 7.38 (t, J = 7.6 Hz, 1H), 7.13 (t, J = 7.8 Hz, 1H), 6.99 (t, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.4 (C), 132.3 (C), 132.2 (C), 131.6 (C), 131.2 (C), 131.1 (C), 131.01 (C), 130.95(C), 130.8 (C), 130.4 (CH), 130.0 (C), 129.9 (CH), 129.7 (C), 129.5 (C), 129.4 (C), 127.9 (C), 127.7 (2CH), 127.65 (CH), 127.63 (CH), 127.57 (CH), 127.51 (CH), 126.5 (CH), 126.3 (CH), 125.7 (CH), 125.4 (CH), 124.0 (CH), 123.9 (CH), 123.2 (CH), 120.6 (CH), 120.2 (CH), 120.1 (CH); LRMS (EI) m/z (%): 402 (100), 401 (99), 400 (88), 200 (40); HRMS calcd for $C_{32}H_{18}$: 402.1406, found: 402.1409; UV/vis (CH_2Cl_2), λ_{max} (ε): 507 (1160), 327 (28400), 287 (*sh*, 45580), 250 (51320) nm (mol^{-1} dm^3 cm^{-1}).

9,18-Diphenyltetrabenzo[fg,o,q,yz]hexaphene (**57**): 8 mg, 12% yield, green solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.57 (s, 1H), 8.61 (s, 1H), 8.37 (s, 1H), 8.25 (d, J = 7.4 Hz, 1H), 8.17 (d, J = 8.1 Hz, 2H), 8.11 (d, J = 7.1 Hz, 1H), 8.03 (d, J = 7.4 Hz, 1H), 7.84 (d, J = 8.4 Hz, 1H), 7.74 (dd, J = 13.2 y 7.5 Hz, 3H), 7.66 − 7.45 (m, 13H), 7.32 (dd, J = 13.4 y 6.9 Hz, 2H), 7.18 (t, J = 7.8 Hz, 1H), 6.96 (dd, J = 12.4 y 7.5

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Hz, 2H); ^{13}C NMR DEPT (125 MHz, $CDCl_3$) δ 132.74 (2CH), 132.42 (2CH), 130.94 (CH), 130.80 (CH), 129.21 (2CH), 129.10 (2CH), 127.87 (CH), 127.84 (CH), 127.74 (CH), 127.69 (CH), 127.51 (CH), 127.21 (CH), 127.16 (CH), 127.10 (CH), 126.81 (CH), 126.55 (CH), 126.13 (CH), 126.02 (CH), 126.99 (CH), 125.96 (CH), 125.74 (CH), 125.52 (CH), 123.46 (CH), 123.42 (CH), 120.53 (CH), 120.24 (CH); LRMS (EI) m/z (%): 654.0 (M^+, 100), 327. (14); HRMS (EI) calcd for $C_{52}H_{30}$: 654.2348, found: 654.2349; UV/vis (CH_2Cl_2), λ_{max} (ε): 643 (10995), 593 (7501), 549 (3287), 446 (6116), 420 (4397), 365 (68396), 349 (61220) nm (mol^{-1} dm^3 cm^{-1}).

General Procedure for the Stepwise Reduction/Deoxygenation of Adducts 15b, 36b, and 42b. Ni Raney was washed with H_2O and MeOH, and then suspended into MeOH (0.5 mL). The suspension was added to a solution of *exo,exo*-adduct (1 equiv) in CH_2Cl_2 (0.01−0.02 M) and the mixture was shaken under H_2 (5 atm) for 18 h. The mixture was filtered through cellite, which was then washed with AcOEt/CH_2Cl_2 (1:1) and the filtrates were evaporated in vacuo. The residue was purified by column chromatography (SiO_2).

The reduced product was deoxygenated following the general procedure used for the one-pot deoxygenation of adducts.

*6,7- Di-p-tolyl-3b^1,4,5,6,6a,7-hexahydro-3b,6:7,11b-diepoxybenzo[a]perylene (**58**):* 45 mg, 90% yield, yellowish solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08−8.00 (m, 4H), 7.66 (dd, J = 8.2, 7.2 Hz, 1H), 7.31 (d, J = 7.2 Hz, 1H), 7.62 (dd, J = 8.2, 7.3 Hz, 1H), 7.23 (dt, J = 7.3, 1.0 Hz, 1H), 7.15 (dt, J = 7.4, 1.1 Hz, 1H), 7.00 (d, J = 7.3 Hz, 1H), 6.97−6.88 (m, 4H), 6.72 (d, J = 8.0 Hz, 2H), 6.36 (*br s*, 2H), 3.06 (d, J = 6.5 Hz, 1H), 2.81 (d, J = 6.5 Hz, 1H), 2.77 (dt, J = 12.1, 5.2 Hz, 1H), 2.40 (ddd, J = 11.9, 9.1, 5.1 Hz, 1H), 2.21 (s, 3H), 2.16 (s, 3H), 2.08 (dt, J = 12.2, 3.9 Hz, 1H), 1.94 (ddd, J = 11.8, 9.1, 4.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.8 (C), 146.9 (C), 136.5 (C), 135.6 (C), 135.1 (C), 134.2 (C), 132.6 (C), 130.7 (C), 130.2 (CH), 130.0 (C), 129.7 (CH), 128.8 (4CH), 128.1 (C), 128.0 (2CH), 126.7 (2CH), 126.4 (CH), 126.0 (2CH), 125.8 (CH), 125.7 (CH), 119.51 (CH), 119.5 (2CH), 90.9 (C), 89.6 (C), 85.3 (C), 81.4 (C), 59.6 (CH), 55.7 (CH), 39.6 (CH_2), 35.4 (CH_2), 21.0 (CH_3), 20.9 (CH_3); LRMS (EI) m/z (%): 518 (12, M^+), 408 (41), 399 (54), 382 (79), 119 (100); HRMS (EI) calcd for $C_{38}H_{30}O_2$: 518.2246, found: 518.2249.

*9,10-Difluoro-6,7-di-p-tolyl-3b^1,4,5,6,6a,7-hexahydro-3b,6:7,11b-diepoxybenzo[a]perylene (**59**):* 155 mg, 66% yield, yellowish solid 280 °C dec; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 7.6 Hz, 1H), 8.06−8.00 (m, 2H), 7.97 (dd, J = 7.0, 0.8 Hz, 1H), 7.68 (dd, J = 8.0, 7.4 Hz, 1H), 7.63 (dd, J = 7.9, 7.5 Hz, 1H), 7.12 (dd, J_{H-F} = 8.9 Hz, 6.8 Hz, 1H), 6.88 (d, J = 6.9 Hz, 4H), 6.80 (dd, J_{H-F} = 9.0 Hz, 6.9 Hz, 1H), 6.73 (d, J = 8.0 Hz, 2H), 6.37 (br s, 2H), 3.03 (d, J = 6.5 Hz, 1H), 2.78 (d, J = 6.4 Hz, 1H), 2.77 (dt, J = 12.1, 5.1 Hz, 1H), 2.40 (ddd, J = 12.1, 9.1, 5.1 Hz, 1H), 2.21 (s, 3H), 2.16 (s, 3H), 2.09 (dt, J = 12.1, 3.9 Hz, 1H), 1.95 (ddd, J = 12.8, 9.1, 4.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.5 (d, J_{C-F} = 250 Hz, C), 149.3 (d, J_{C-F} = 251 Hz, C), 146.8 (dd, J_{C-F} = 4.8, 3.2 Hz, C), 142.9 (dd, J_{C-F} = 5.5, 3.1 Hz, C), 136.2 (C), 135.8 (2C), 135.6 (2C), 134.2 (C), 131.8 (C), 130.6 (CH), 135.8 (C), 129.9 (CH), 129.7 (C), 128.5 (CH), 128.2 (4CH), 127.3 (C), 126.5 (CH), 126.0 (CH), 125.8 (CH), 125.7 (4CH), 109.6 (d, J_{C-F} = 19.5 Hz, CH), 109.4 (d, J_{C-F} = 19.7 Hz, CH), 90.7 (C), 85.3 (C), 59.4 (CH), 55.6 (CH), 39.5 (CH_2), 35.3 (CH_2), 21.0 (CH_3), 20.9 (CH_3). LRMS (EI) m/z (%): 554 (11, M^+), 536 (11), 444 (16), 418 (32), 119 (100); HRMS (EI) calcd for $C_{38}H_{28}F_2O_2$: 554.2057, found: 554.2057.

*6,7-Di-p-tolyl-3b^1,4,5,6,6a,7-hexahydro-3b,6:7,13b-diepoxydibenzo[fg,uv]pentaphene (**60**):* 225 mg, 66% yield, white solid, mp 263 °C dec; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 (d, J = 7.1 Hz, 1H), 8.09 (d, J = 8.2 Hz, 1H), 8.07−8.01 (m, 2H), 7.81 (d, J = 7.7 Hz, 1H), 7.73−7.64 (m, 2H), 7.66 (s, 1H), 7.65−7.60 (m, 1H), 7.46−7.38 (m, 2H), 7.33 (s, 1H), 6.99 (d, J = 6.7 Hz, 2H), 6.96−6.88 (m, 2H), 6.75 (d, J = 7.9 Hz, 2H), 6.55−6.22 (m, 2H), 3.15 (d, J = 6.6 Hz, 1H), 2.90 (d, J = 6.6 Hz, 1H), 2.77 (dt, J = 12.1, 5.0 Hz, 1H), 2.43−2.34 (m, 1H), 2.23 (s, 3H), 2.17 (s, 3H), 2.08 (dt, J = 12.1, 3.8 Hz, 1H), 1.98−1.89 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.7 (C), 145.1 (C), 136.4 (C), 135.6 (C), 135.2 (C), 134.2 (C), 132.7 (2C), 132.6 (C), 130.7 (C), 130.3 (CH), 129.9 (C), 129.8 (CH), 128.8 (CH), 128.3 (CH), 128.14 (2CH), 128.10 (3CH), 128.0 (C), 126.4 (CH), 126.0 (CH), 125.9 (CH), 125.8 (6CH), 118.0 (CH), 117.7 (CH), 90.8 (C), 89.9 (C), 85.1 (C), 81.6 (C), 60.0 (CH), 56.0 (CH), 39.6 (CH_2), 35.4 (CH_2), 21.0 (CH_3), 20.9 (CH_3); LRMS (EI) m/z (%): 568 (14, M^+), 550 (24), 449 (50), 431 (100); HRMS (EI) calcd for $C_{42}H_{32}O_2$: 568.2402, found: 568.2385.

*6,7-Di-p-tolylbenzo[a]perylene (**46b**):* 96 mg, 42% yield, red solid, mp 171−172 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.77 (d, J = 8.7 Hz, 1H), 8.30 (d, J = 7.5 Hz, 1H), 8.23 (d, J = 7.4 Hz, 1H), 8.17 (d, J = 7.5 Hz, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.78 (d, J = 8.1 Hz, 1H), 7.65−7.57 (m, 3H), 7.46−7.41 (m, 1H), 7.30−7.24 (m, 2H), 6.82 (s, 4H), 6.77 (d, J = 8.3 Hz, 2H), 6.74 (d, J = 7.9 Hz, 2H), 2.29 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.7 (C), 140.8 (C), 137.1 (C), 135.7 (C), 137.4 (C), 134.6 (C), 134.1 (C), 133.4 (C), 132.2 (2CH), 131.6 (2C), 130.4 (CH), 130.0 (C), 129.8 (C), 129.7 (C), 129.6 (2CH), 129.0 (CH), 128.6 (C), 128.5 (C), 128.3 (C), 127.9 (2CH), 127.5 (2CH), 127.15 (CH), 127.09 (CH), 127.00 (2CH), 126.8 (CH), 126.1 (CH), 125.8 (CH), 125.3 (CH), 120.6 (CH), 120.0 (CH), 21.2 (CH_3), 21.1 (CH_3); LRMS (EI) m/z (%): 482 (100, M^+), 390 (13), 376 (21); HRMS (EI) calcd for $C_{38}H_{26}$: 482.2035, found: 482.2034; UV/vis (CH_2Cl_2), λ_{max} (ε): 527 (80216), 494 (59359), 285 (138117) nm (mol^{-1} dm^3 cm^{-1}).

*9,10-Difluoro-6,7-di-p-tolylbenzo[a]perylene (**47b**):* 57 mg, 39% yield, red solid, mp 175−177 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.51 (dd, J_{H-F} = 13.1, 8.7 Hz, 1H), 8.29 (d, J = 7.4 Hz, 1H), 8.17 (d, J = 7.6 Hz, 1H), 8.13 (d, J = 7.4 Hz, 1H), 7.84 (d, J = 8.4 Hz, 1H), 7.82 (d, J = 8.4 Hz, 1H), 7.63 (dd, J = 7.9, 7.7 Hz, 1H), 7.62 (dd, J = 7.7, 7.6 Hz, 1H), 7.33−7.25 (m, 2H), 6.83 (d, J = 7.9 Hz, 2H), 6.81−6.75 (m, 4H), 6.73 (d, J = 8.0 Hz, 2H), 2.29 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.3 (C), 140.5 (C), 136.9 (C), 136.2 (C), 134.8 (C), 134.1 (C), 131.8 (2CH), 131.3 (C), 131.2 (2C), 130.7 (CH), 129.9 (C), 129.8 (C), 129.6 (2CH), 129.5 (C), 128.5 (C), 128.3 (C), 128.2 (2CH), 128.1 (CH), 127.6 (2CH), 127.5 (CH), 127.3 (CH), 127.0 (CH), 126.6 (C), 126.2 (CH), 125.6 (C), 120.7 (CH), 120.3 (CH), 112.6 (d, J_{C-F} = 19.3 Hz CH), 112.5 (d, J_{C-F} = 18.5 Hz CH), 21.1 (CH_3), 21.0 (CH_3); LRMS (EI) m/z (%): 518 (100, M^+), 536 (11), 431 (29), 412 (17); HRMS (EI) calcd for $C_{38}H_{24}F_2$: 518.18459, found: 518.1846; UV/vis (CH_2Cl_2), λ_{max} (ε): 519 (31349), 488 (23420), 283 (54950) nm (mol^{-1} dm^3 cm^{-1}).

*6,7-Di-p-tolyldibenzo[fg,uv]pentaphene (**53b**):* 40 mg, 19% yield, red solid, mp 118−120 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.44 (s, 1H), 8.38 (d, J = 7.4 Hz, 1H), 8.32 (d, J = 7.4 Hz, 1H), 8.26 (s, 1H), 8.11 (d, J = 7.5 Hz, 1H), 7.92 (d, J = 8.4 Hz, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.79 (d, J = 8.1 Hz, 1H), 7.75 (d, J = 8.5 Hz, 1H), 7.62 (t, J = 7.8 Hz, 2H), 7.40−7.34 (m, 1H), 7.34−7.28 (m, 1H), 7.22 (d, J = 7.4 Hz, 1H), 6.92 (d, J = 7.9 Hz, 2H), 6.88 (d, J = 7.8 Hz, 2H), 6.78 (d, J = 8.0 Hz, 2H), 6.75 (d, J = 7.9 Hz, 2H), 2.34 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.8 (C), 140.7 (C), 137.5 (C), 137.0 (C), 135.8 (2C), 134.6 (2C), 134.2 (C), 132.4 (2CH), 132.2 (C), 132.1 (C), 131.8 (C), 131.6 (C), 131.2 (C), 130.0 (C), 130.2 (CH), 129.7 (C), 129.6 (C), 129.4 (2CH), 128.8 (CH), 128.6 (CH), 128.3 (CH), 128.0 (2CH), 127.6 (2CH), 127.2 (CH), 127.1 (C), 127.0 (CH), 126.9 (CH), 126.3 (CH), 125.8 (CH), 125.4 (CH), 125.3 (CH), 125.1 (CH), 120.7 (CH), 119.9 (CH), 21.2 (CH_3), 21.0 (CH_3); LRMS (EI) m/z (%): 532 (100, M^+), 441 (21), 424 (12); HRMS (EI) calcd for $C_{42}H_{28}$: 532.2194, found: 532.2191; UV/vis (CH_2Cl_2), λ_{max} (ε): 610 (28780), 566 (19393), 320 (56812), 300 (66939) nm (mol^{-1} dm^3 cm^{-1}).

Photo-cyclo-dehydrogenation of Phenanthro[9,10-*a*]perylene (56). A solution of phenanthro[9,10-*a*]perylene (**56**, 2 mg) in $CDCl_2CDCl_2$ (1 mL) was exposed at r.t. to ambient sunlight and air for 1 h, affording dibenzo[*cd,n*]naphtho[3,2,1,8-*pqra*]perylene (**61**) quantitatively as a red solid.

*Benzo[cd]naphtho[3,2,1,8-pqra]perylene (**61**):* 100% yield, orange solid, mp 366−8 °C; ^{1}H NMR (400 MHz, $CDCl_2CDCl_2$, 353 K) δ 9.38 (s, 1H), 9.30 (d, J = 8.5 Hz, 1H), 9.11 (d, J = 8.9 Hz, 1H), 9.06 (d, J = 7.9 Hz, 1H), 9.00−8.96 (m, 3H), 8.88 (m, 1H), 8.49 (d, J = 8.0 Hz, 1H), 8.31−8.27 (m, 2H), 8.23 (d, J = 7.9 Hz, 1H), 8.12 (t, J = 7.6 Hz, 1H), 8.02 (t, J = 7.6 Hz, 1H), 7.88- 7.77 (m, 2H); LRMS (EI), $m/$

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z (%): 400 (100), 200 (22); HRMS calcd for $C_{32}H_{16}$: 400.1255, found: 400.1252; UV/vis (CH_2Cl_2), λ_{max} (ε): 452 (18960), 424 (12580), 327 (49560), 313 (sh, 36020), 246 (46800) nm (mol^{-1} dm^3 cm^{-1}).

■ ASSOCIATED CONTENT

Supporting Information

Stereochemical notation, computational details, X-ray crystallographic data, and NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(11) A minor product **11** was isolated in 8% yield (see Scheme 8).

(12) For an explanation of the stereochemical nomenclature see the Supporting Information.

(13) For further details see the Supporting Information.

(14) The formation of intermolecular *pincer* furan-DMAD cycloadducts has been proven to be reversible at 100 °C (see ref 9). To force the retro-Diels−Alder fragmentation in some intramolecular *pincer* adducts requires 165 °C (see ref 10a). For retro-Diels−Alder reactions of some *domino* furan cycloadducts see Löffler, M.; Packe, R.; Schlüter, A.-D. *Macromolecules* **1992**, *25*, 4213.

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