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Domino Diels–Alder Cycloadditions of Arynes: New Approach to Elusive Perylene Derivatives

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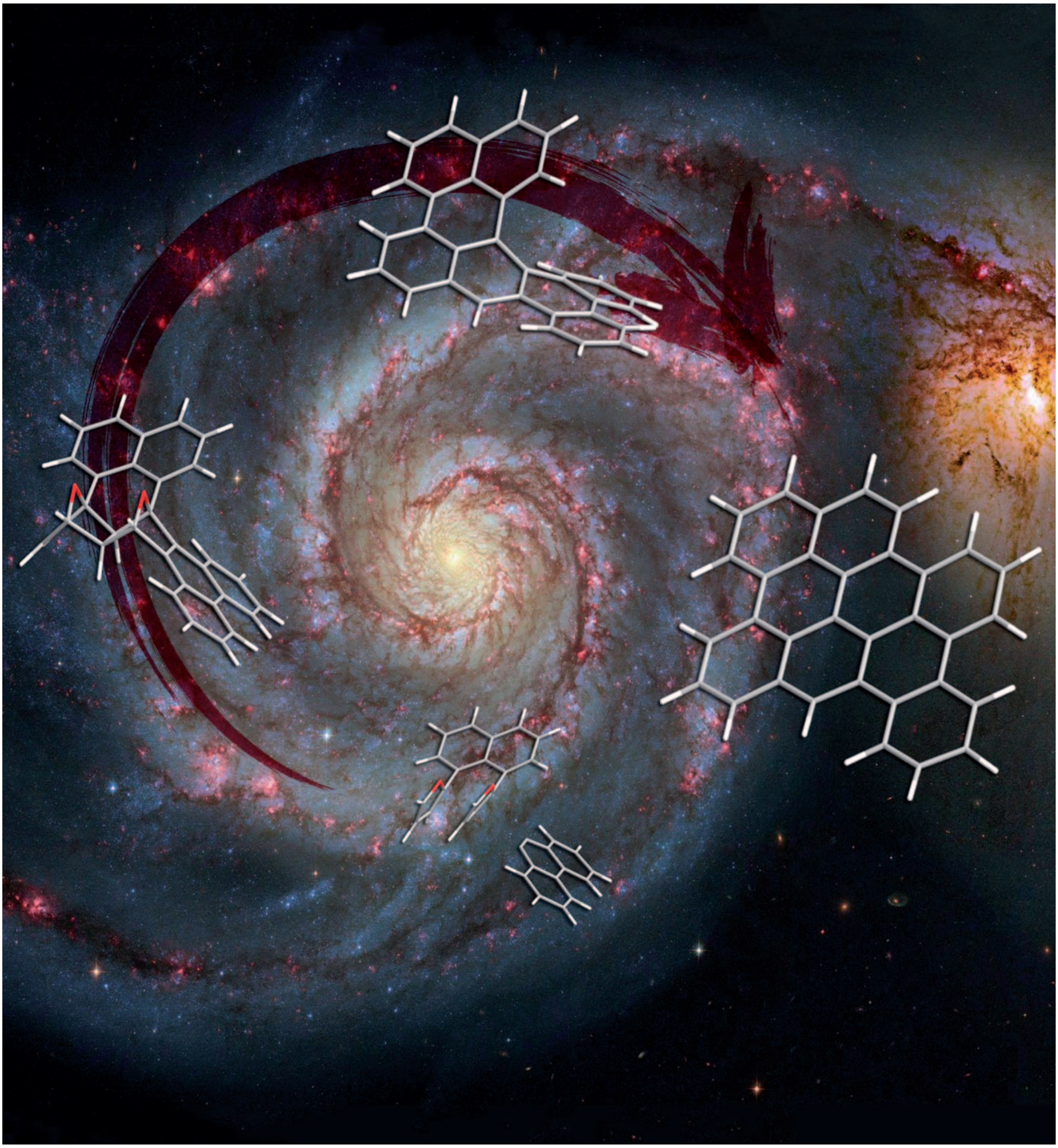
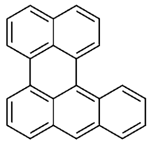
Dedicated to Professor José Barluenga on the occasion of his 70th birthday

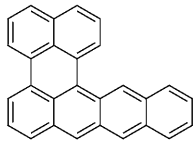


A huge amount of effort is currently dedicated to the design, preparation, and characterisation of new carbon-based electronic materials.[1] Carbon nanotubes, graphenes, and related species are compounds with very interesting electronic properties. However, to exploit the potential of these systems some limitations need to be overcome as there are no selective syntheses of these compounds in a pure form and their processability is hampered by high molecular mass and low solubility. On the other hand, the chemistry of polycyclic aromatic hydrocarbons (PAHs) offers the possibility of tailoring a variety of skeletons and substituents, thus allowing the modulation of properties such as molecular size, solubility, and electronic characteristics. However, only a limited number of platforms based on PAHs are currently under systematic investigation. Among them, oligoacenes have been widely studied.[2,3] In particular, pentacene derivatives are extremely relevant in this field, with more than 1400 papers published since 2000 dealing with their electronic properties.[4] The basic pentacene platform is a paradigmatic molecular semiconductor with a HOMO–LUMO gap of around 2.1 eV, although it is relatively unstable against photo-oxidation. The design and synthesis of pentacene derivatives with a lower gap and higher chemical stability is a very active field of research.[2c,e,4d] Perylene derivatives have also been developed for molecular electronics and molecular photonics, as components of LEDs, photovoltaic cells, and other devices.[5]

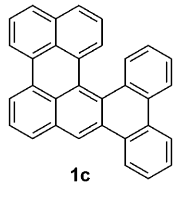
Our experience in aryne chemistry applied to the synthesis of extended PAHs[6] led us to explore the synthesis of novel perylene derivatives with potential applications in molecular electronics. We chose perylenes **1a–c** as initial goals for our study because these compounds are relatively small molecules that contain acene subunits, presumably available in a reduced number of steps, with an expected HOMO–LUMO gap near to or below 2.5 eV, a crucial feature for organic semiconductors. We decided to study the gap of **1a–c** by density functional theory (DFT) at the B3LYP 6-311+G** level on 6-31G(d) optimised geometries. The computed gaps obtained for **1a**, **1b**, and **1c** are 2.54, 2.14, and 2.63 eV, respectively. The first value, 2.54 eV, is in the upper limit of the range for semiconductors. Remarkably, the calculated gap for naphtho[2,3-*a*]perylene (**1b**, 2.14 eV) is slightly lower than the gap calculated for pentacene (2.29 eV) using the same level of theory.[4d] These promising results prompted us to carry out the synthesis of these platforms.



1a

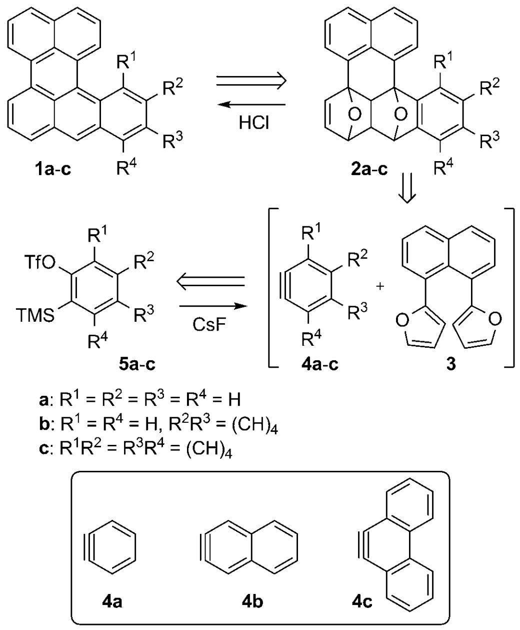


1b



1c

Benzo[*a*]perylene (**1a**) had been prepared by Clar and coworkers by complex and inefficient procedures.[7] To the best of our knowledge, the syntheses of naphtho[2,3-*a*]perylene (**1b**) and phenanthro[9,10-*a*]perylene (**1c**) have not been reported. We devised a new strategy for the synthesis of compounds **1** based on the retrosynthetic analysis shown in Scheme 1.[8] The target molecules **1** should be available by dehydration/deoxygenation of intermediates **2**, obtained by the reaction of 1,8-difurylnaphthalene (**3**) with 1,2-didehydrobenzene (benzyne, **4a**), 2,3-didehydronaphthalene (**4b**), and 9,10-didehydrophenanthrene (**4c**), respectively.[9] 1,8-Difurylnaphthalene (**3**) was prepared in good to excellent yields by double metal-catalysed cross-coupling of 1,8-diiodonaphthalene (**6**) with (1-furyl)zinc chloride (**7a**), (1-furyl)boronic acid (**7b**), or (1-furyl)tributyltin (**7c**, Scheme 2).



Scheme 1. Retrosynthetic analysis.

Didehydroarenes **4a–c** were generated from the corresponding (trimethylsilyl)aryl triflates **5a–c**.[10] Treatment of these triflates with CsF in the presence of **3** afforded adducts **2a–c** in 99, 51, and 53 % yield, respectively (Scheme 3). This key transformation involves two tandem cascade Diels–Alder reactions in a domino mode, with the creation of four new C–C bonds and six new stereogenic centres.[11] Presumably, the intermolecular [4+2] cycloaddition of **3** with arynes **4a–c** would lead to the formation of intermediates

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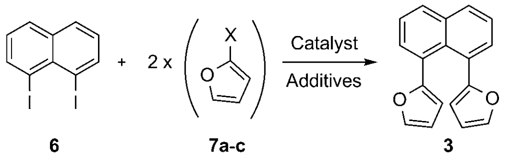
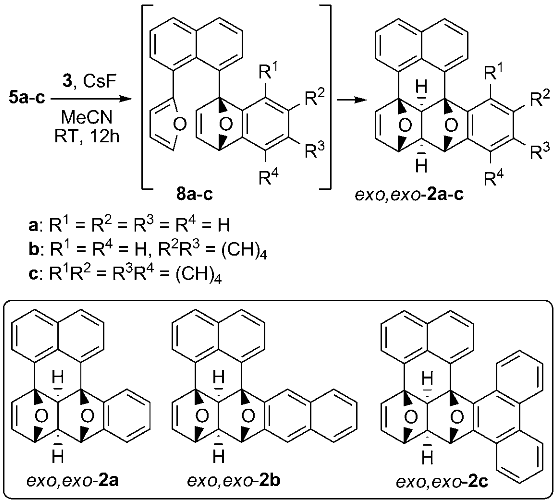


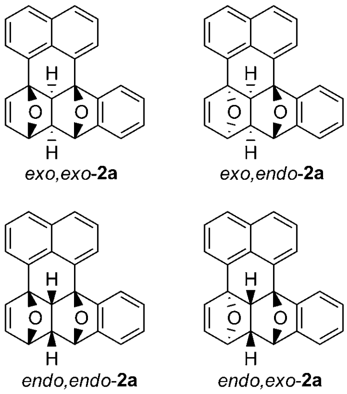
7a-c	X	Catalyst	Additives	Yield (3, %)
7a	ZnCl	[NiCl$_2$(dppp)]	–	54
7b	B(OH)$_2$	[Pd(PPh$_3$)$_4$]	CsF, CuI	92
7c	SnBu$_3$	[Pd(PPh$_3$)$_4$]	Na$_2$CO$_3$	99

Scheme 2. Synthesis of 1,8-difurylnaphthalene (**3**); dppp = 1,3-bis(diphenylphoshino)propane.



Scheme 3. Domino Diels–Alder cycloadditions.

8a–c, which could evolve in situ by intramolecular [4+2] cycloaddition to afford *exo,exo*-**2a–c**, resulting from the *exo* approach of the *exo* face of the dienophile. Remarkably, this is a highly stereoselective transformation: only one diastereoisomer was obtained from four possible products (Scheme 4).[12] This result is in agreement with DFT B3LYP/6-31G(d) calculations, which showed that the *exo,exo*-**2a** adduct is favoured under kinetic or thermodynamic control (Table 1).



Scheme 4. Four possible stereoisomers of **2a**.

Table 1. Calculated relative reaction barriers and enthalpies for the intramolecular Diels–Alder reaction (**8a** to form **2a**).

2a[a]	$\Delta H^{\neq}$[b]	ΔH[b]
exo,exo	13.5	−24.0
exo,endo	18.9	−9.8
endo,endo	34.2	9.8
endo,exo	29.7	−8.4

[a] The first stereochemical prefix indicates the face of the alkene that reacts intramolecularly in **8a**, the second one indicates the approach to the dienophile. [b] Calculated at 298 K (kcal mol^{-1}).

The relative stereochemistry of adduct **2c** was confirmed by single-crystal X-ray diffraction studies (Figure 1). Notably, the torsion angle between the naphthalene and the phenanthrene subunits is 57.6°.

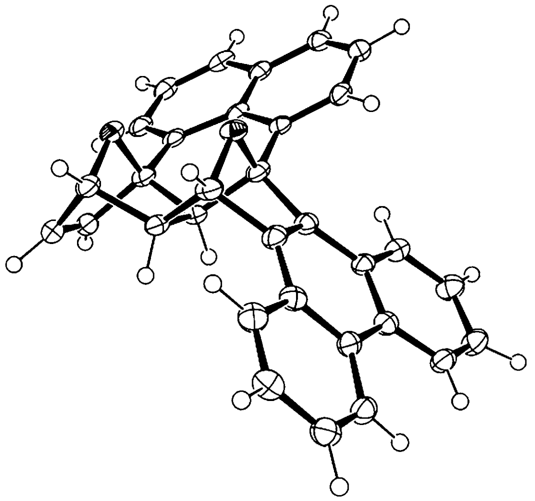


Figure 1. Molecular structure (ORTEP) of **2c** obtained by X-ray diffraction.

Treatment of adducts **2a–c** with concentrated aqueous HCl in refluxing EtOH led to perylene derivatives **1a–c** in 72, 57, and 87 % yield, respectively. UV/Vis spectroscopy was used to explore the electronic properties of these aromatic platforms. In particular, the absorption of the lowest-energy UV/Vis absorption bands of compounds **1a–c** are shown in Table 2, they exhibit a typical vibronic structure. Optical HOMO–LUMO gaps were determined from the onset of these bands and are in very good agreement with the calculated gap determined by time-dependent density functional theory (TDDFT) calculations,[13] at B3LYP/6-31G(d) level. The differences between experimental and TDDFT-calculated values (0.04–0.15 eV) are smaller than those obtained by using DFT calculations (0.12–0.33 eV, vide supra).

Table 2. Absorption and emission data for **1a–c**.

Compound	λ_{max} abs.[a] [nm]	Optical gap[b] [eV]	Calcd gap[c] [eV]	λ_{max} em.[d] [nm]
1a	507	2.36	2.41	518
1b	588	2.02	1.99	604
1c	508	2.30	2.42	544

[a] Lowest-energy UV/Vis absorption band from dichloromethane solutions. [b] Optical HOMO–LUMO gap determined from the onset of λ_{max} abs. [c] Calculated HOMO–LUMO gap determined by TDDFT calculations. [d] Emission maxima from dichloromethane solutions.

It is worth mentioning that compound **1b** has an absorption maximum at 588 nm (Figure 2), corresponding to an optical gap of 2.02 eV, that is, smaller than the gap reported for pentacene (λ_{max} = 582 nm, optical gap = 2.08 eV),[4d] and an emission maximum at 604 nm. For comparison, tetracene and perylene, the two major structural subunits present in compound **1b**, show absorption maxima in solution at 474 and 436 nm, respectively.[14]

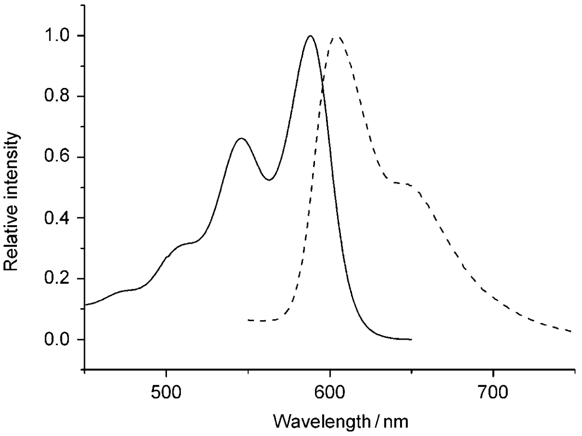
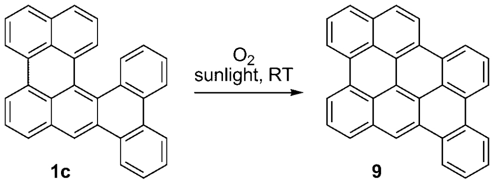


Figure 2. Absorption (solid line) and emission (dashed line) spectra in dichloromethane for compound **1b**.

Exposure of polyarenes **1a** and **1b** in solution to ambient air and sunlight caused a fast photooxidation, probably through the formation of the corresponding $^1O_2$ adducts, which evolved to complex mixtures.[4d] UV/Vis spectra of compounds **1a** and **b** in dichloromethane (30 μM) at room temperature registered at regular intervals showed the fast destruction of the perylene chromophore and the formation of intermediate species, which progressively fade to give final unidentified products. As expected, perylene derivative **1b** has a shorter half-life than **1a** ($t_{1/2}$ = 19.1 min for **1a**, $t_{1/2}$ < 1 min for **1b**). Similar experiments with the exclusion of one of the photooxidation agents, either light or oxygen, resulted in recovery of the starting materials.

Curiously, exposure of tribenzopentahelicene **1c** in solution to ambient air and sunlight did not lead to photooxidation but a rapid photocyclodehydrogenation to afford dibenzo[*cd*,*n*]naphtho[3,2,1,8-*pqra*]perylene (**9**) quantitatively (Scheme 5). This is a remarkable outcome since harsh conditions such as strong oxidants, prolonged UV irradiation, or flash vacuum pyrolysis (FVP) are normally required to perform the cyclodehydrogenation of pentahelicene.[15] Therefore, the three benzene rings fused to the pentahelicene moiety in compound **1c** are the crucial structural motif for this spontaneous cyclodehydrogenation to afford polyarene **9**.



Scheme 5. Photocyclodehydrogenation of pentahelicene **1c**.

In conclusion, we believe that this novel strategy, based on highly stereoselective tandem cascade domino [4+2] cycloadditions involving arynes, opens a new way to access elusive polyarenes and in particular to key molecules for the development of new organic semiconductors. Further work is in progress to obtain substituted derivatives with better solubility/processability, higher kinetic stability against photooxidation, and a reduced gap (<2 eV).

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Keywords: arenes · arynes · cycloaddition · domino reactions · hydrocarbons

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[1] a) A. C. Grimsdale, K. Müllen, *Angew. Chem.* **2005**, *117*, 5732–5772; *Angew. Chem. Int. Ed.* **2005**, *44*, 5592–5629; b) J. Wu, W. Pisula, K. Müllen, *Chem. Rev.* **2007**, *107*, 718–747; c) A. R. Murphy, J. M. J. Fréchet, *Chem. Rev.* **2007**, *107*, 1066–1096; d) K. Müllen, J. P. Rabe, *Acc. Chem. Res.* **2008**, *41*, 511–520; e) J. L. Delgado, M. A. Herranz, N. Martín, *J. Mater. Chem.* **2008**, *18*, 1417–1426; f) L. Zhi, K. Müllen, *J. Mater. Chem.* **2008**, *18*, 1472–1484; g) A. K. Geim, *Science* **2009**, *324*, 1530–1534.

[2] For some recent examples, see: a) M. M. Payne, S. R. Parkin, J. E. Anthony, *J. Am. Chem. Soc.* **2005**, *127*, 8028–8029; b) R. Mondal, R. M. Adhikari, B. K. Shah, D. C. Neckers, *Org. Lett.* **2007**, *9*, 2505–2508; c) D. Chun, Y. Cheng, F. Wudl, *Angew. Chem.* **2008**, *120*, 8508–8513; *Angew. Chem. Int. Ed.* **2008**, *47*, 8380–8385; d) M. L. Tang, S. C. B. Mannsfeld, Y.-S. Sun, H. A. Becerril, Z. Bao, *J. Am. Chem. Soc.* **2009**, *131*, 882–883; e) I. Kaur, N. N. Stein, R. P. Kopreski, G. P. Miller, *J. Am. Chem. Soc.* **2009**, *131*, 3424–3425.

[3] For some recent reviews, see: a) M. Bendikov, F. Wudl, D. F. Perepichka, *Chem. Rev.* **2004**, *104*, 4891–4945; b) R. A. Pascal, Jr., *Chem. Rev.* **2006**, *106*, 4809–4819; c) J. E. Anthony, *Chem. Rev.*

2006, *106*, 5028–5048; d) J. E. Anthony, *Angew. Chem.* **2008**, *120*, 460–492; *Angew. Chem. Int. Ed.* **2008**, *47*, 452–483.

[4] For some recent examples, see: a) J. Jiang, B. R. Kaafarani, D. C. Neckers, *J. Org. Chem.* **2006**, *71*, 2155–2158; b) Q. Miao, X. Chi, S. Xiao, R. Zeis, M. Lefenfeld, T. Siegrist, M. L. Steigerwald, C. Nuckolls, *J. Am. Chem. Soc.* **2006**, *128*, 1340–1345; c) B.-B. Jang, S. H. Lee, Z. H. Kafafi, *Chem. Mater.* **2006**, *18*, 449–457; d) I. Kaur, W. Jia, R. P. Kopreski, S. Selvarasah, M. R. Dokmeci, C. Pramanik, N. E. McGruer, G. P. Miller, *J. Am. Chem. Soc.* **2008**, *130*, 16274–16286.

[5] a) L. Schmidt-Mende, A. Fechtenkötter, K. Müllen, E. Moons, R. H. Friend, J. D. MacKenzie, *Science* **2001**, *293*, 1119–1122; b) B. A. Jones, M. J. Ahrens, M.-H. Yoon, A. Facchetti, T. J. Marks, M. R. Wasielewski, *Angew. Chem.* **2004**, *116*, 6523–6526; *Angew. Chem. Int. Ed.* **2004**, *43*, 6363–6366; c) J. A. A. W. Elemans, R. van Hameren, R. J. M. Nolte, A. E. Rowan, *Adv. Mater.* **2006**, *18*, 1251–1266; d) R. Schmidt, M. M. Ling, J. H. Oh, M. Winkler, M. Könemann, Z. Bao, F. Würthner, *Adv. Mater.* **2007**, *19*, 3692–3695.

[6] a) C. Romero, D. Peña, D. Pérez, E. Guitián, *Chem. Eur. J.* **2006**, *12*, 5677–5684; b) D. Peña, D. Pérez, E. Guitián, *Chem. Rec.* **2007**, *7*, 326–333; c) C. Romero, D. Peña, D. Pérez, E. Guitián, *J. Org. Chem.* **2008**, *73*, 7996–8000.

[7] a) E. Clar, H. Frommel, *Chem. Ber.* **1949**, *82*, 46–60; b) E. Clar, W. Kelly, D. G. Stewart, J. W. Wright, *J. Chem. Soc.* **1956**, 2652–2656.

[8] For a related procedure to prepare benzo[*a*]pyrene by reaction of benzyne with 1,8-diethynylnaphthalene, see: A. Cobas, E. Guitián, L. Castedo, *J. Org. Chem.* **1997**, *62*, 4896–4897.

[9] For some recent reviews on aryne chemistry, see: a) R. Sanz, *Org. Prep. Proced. Int.* **2008**, *40*, 215–291; b) D. Peña, D. Pérez, E. Guitián, *Heterocycles* **2007**, *74*, 89–100; c) D. Peña, D. Pérez, E. Guitián, *Angew. Chem.* **2006**, *118*, 3659–3661; *Angew. Chem. Int. Ed.* **2006**, *45*, 3579–3581; d) H. Pellissier, M. Santelli, *Tetrahedron* **2003**, *59*, 701–730. For some recent examples, see: e) Z. Qiu, Z. Xie, *Angew. Chem.* **2009**, *121*, 5839–5842; *Angew. Chem. Int. Ed.* **2009**, *48*, 5729–5732; f) N. Saito, K. Shiotani, A. Kinbara, Y. Sato, *Chem. Commun.* **2009**, 4284–4286; g) A. A. Cant, G. H. V. Bertrand, J. L. Henderson, L. Roberts, M. F. Greaney, *Angew. Chem.* **2009**, *121*, 5301–5304; *Angew. Chem. Int. Ed.* **2009**, *48*, 5199–5202; h) F. Sha, X. Huang, *Angew. Chem.* **2009**, *121*, 3510–3513; *Angew. Chem. Int. Ed.* **2009**, *48*, 3458–3461; i) T. Gerfaud, L. Neuvulle, J. Zhu, *Angew. Chem.* **2009**, *121*, 580–585; *Angew. Chem. Int. Ed.* **2009**, *48*, 572–577; j) M. Jeganmohan, S. Bhuvaneswari, C.-H. Cheng, *Angew. Chem.* **2009**, *121*, 397–400; *Angew. Chem. Int. Ed.* **2009**, *48*, 391–394; k) R. Webster, M. Lautens, *Org. Lett.* **2009**, *11*, 4688–4691; l) P. T. Lynett, K. E. Maly, *Org. Lett.* **2009**, *11*, 3726–3729; m) S. A. Worlikar, R. C. Larock, *Org. Lett.* **2009**, *11*, 2413–2416.

[10] a) Y. Himeshima, T. Sonoda, H. Kobayashi, *Chem. Lett.* **1983**, 1211–1214; b) H. Yoshida, T. Terayama, J. Ohshita, A. Kunai, *Chem. Commun.* **2004**, 1980–1981; c) D. Peña, A. Cobas, D. Pérez, E. Guitián, *Synthesis* **2002**, 1454–1458; d) D. Peña, D. Pérez, E. Guitián, L. Castedo, *Org. Lett.* **1999**, *1*, 1555–1557.

[11] a) L. F. Tietze, G. Brasche, K. Gericke, *Domino Reactions in Organic Synthesis*, Wiley-VCH, Weinheim, **2006**; b) L. F. Tietze, *Chem. Rev.* **1996**, *96*, 115–136; c) S. E. Denmark, A. Thorarensen, *Chem. Rev.* **1996**, *96*, 137–165; d) J. D. Winkler, *Chem. Rev.* **1996**, *96*, 167–176; e) L. R. Domingo, M. T. Picher, J. Andrés, *J. Org. Chem.* **2000**, *65*, 3473–3477; f) M. Lautens, E. Fillion, *J. Org. Chem.* **1997**, *62*, 4418–4427; g) T. Sasaki, K. Kanematsu, K. Hayakawa, M. Uchide, *J. Chem. Soc. Perkin Trans. 1* **1972**, 2750–2755; h) P. R. Ashton, U. Girreser, D. Giuffrida, F. H. Kohnke, J. P. Mathias, F. M. Raymo, A. M. Z. Slawin, J. F. Stoddart, D. J. Willians, *J. Am. Chem. Soc.* **1993**, *115*, 5422–5429; i) H. Meier, B. Rose, *Liebigs Ann. Chem.* **1997**, 663–669; j) W. D. Neudorff, D. Lentz, M. Anibarro, A. D. Schlüter, *Chem. Eur. J.* **2003**, *9*, 2745–2757.

[12] An intermolecular version of the second domino [4+2] cycloaddition has been reported (see ref. [11g]). Curiously, the *exo*,*endo* isomer was obtained and this evolved to the *exo*,*exo* compound on prolonged heating.

[13] See the Supporting Information for details; a) M. E. Casida, C. Jamorski, K. C. Casida, D. R. Salahub, *J. Chem. Phys.* **1998**, *108*, 4439–4449; b) R. Bauernschmitt, R. Ahlrichs, *Chem. Phys. Lett.* **1996**, *256*, 454–464.

[14] a) S. A. Odom, S. R. Parkin, J. E. Anthony, *Org. Lett.* **2003**, *5*, 4245–4248; b) I. B. Berlman, *Handbook of Fluorescence Spectra of Aromatic Molecules*, Academic Press, New York, **1971**.

[15] X. Xue, L. T. Scott, *Org. Lett.* **2007**, *9*, 3937–3940.

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