A tetra-substituted chrysene: orientation of multiple electrophilic substitution and use of a tetra-substituted chrysene as a blue emitter for OLEDs†

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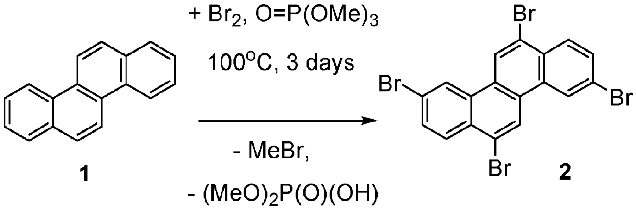
The first tetra-substituted non-fused chrysene, 3,6,9,12-tetrakis(4-*tert*-butylphenyl)chrysene 7 with blue electroluminescence at 450 nm, and with a radiance of 500 cd m^{-2}, was synthesized by a two-step procedure: direct bromination of chrysene in trimethyl phosphate, followed by palladium-catalyzed cross-coupling of tetrabromochrysene 2 and *tert*-butylphenylboronic acid 3.

Polycyclic aromatic hydrocarbons (PAH) have been the focus of research for many years. PAH are found to occur naturally on earth with other sources of carbon,[1] and have even been identified among the most stable compounds in the cosmos.[2] The carcinogenic properties of PAH have raised health concerns,[3] while their fluorescent properties have attracted the interest of chemists and physicists.[4] The large delocalization of p-electrons in PAH are directly responsible for the fluorescent properties of those materials and for some unique bonding modes, *e.g.*, non-covalent, intermolecular aromatic–aromatic π–π stackings.[5–8] However, the low solubility of the parent PAH and a lack of well-established rules for their basic chemical transformations hinder their development as useful materials.

One strategy for improving the solubility and efficiency of the blue emission of PAH is to add aryl, amino or hetero groups onto a parent PAH (*e.g.*, pyrene, perylene, chrysene or coronene).[9] The introduction of these substituents helps break-up π–π stackings, leading to increased solubility and providing a way to adjust the electron density of the PAH. For example, true blue emission can be obtained from di-substituted chrysenes.[10] To date, no tetra-substituted, non-fused chrysene derivatives have been disclosed. Such chrysenes would be expected to have extra thermal and oxidation resistance, which could lead to extended OLED device lifetimes.

In this study, we synthesized the first tetra-substituted, non-fused chrysene. We also determined the order of electrophilic substitution and made simple OLED devices incorporating these tetra-substituted chrysenes.

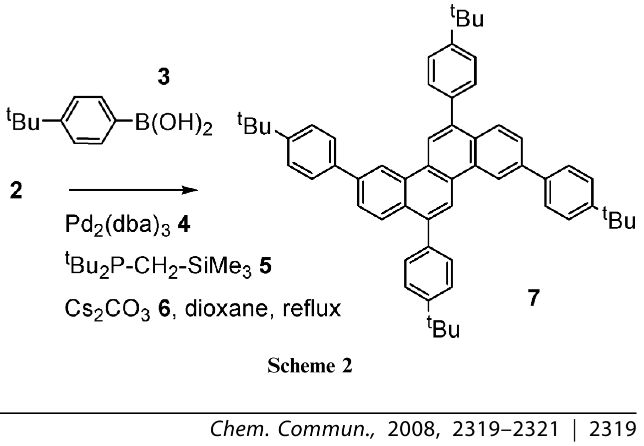
The first step in the synthesis was the high temperature, direct bromination of chrysene in trimethyl phosphate.‡ In this step, 3,6,9,12-tetrabromochrysene (**2**) precipitated from the trimethyl phosphate solution, simplifying purification (Scheme 1).[11]



Scheme 1

Compound **2** is practically insoluble in commonly used solvents, making spectroscopic characterization difficult. Direct probe GC-MS of **2** shows the exact mass at 543.73 g mol^{-1}, corresponding to a tetrabromo-substituted derivative. The next step involved a Suzuki cross-coupling reaction between **2** and *tert*-butylphenylboronic acid (**3**), using di-*tert*-butyl(trimethylsilylmethyl)phosphane (**4**) and Pd_2dba_3 (**5**) as a catalyst in the presence of caesium carbonate (**6**) (Scheme 2).[12] The Suzuki cross-coupling reaction takes place in the *ipso* position of the aromatic carbon without migration of the bromide, resulting in retention of the aromatic substitution pattern.

A crystal of compound **7** was grown from pentane and analyzed by X-ray crystallography§ to establish the pattern of substitution. As can be seen from Fig. 1, the four *tert*-butylphenyl groups are in the 3, 6, 9 and 12 positions of



Scheme 2

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† Electronic supplementary information (ESI) available: Crystallographic data of **7** (CCDC 663240) and experimental details for the preparation and testing of the OLED device of **7**. See DOI: 10.1039/b715386d

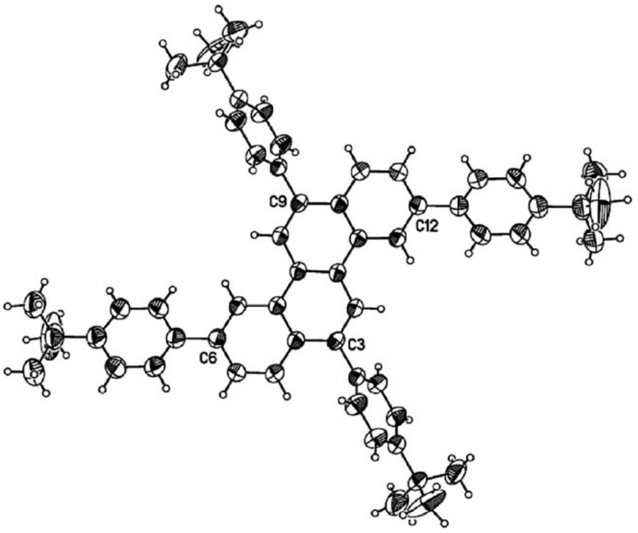
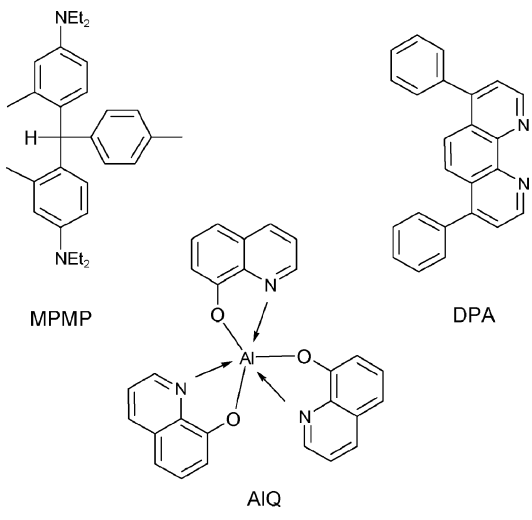


Fig. 1 ORTEP drawing of 3,6,9,12-tetrakis(4-*tert*-butylphenyl)chrysene (**7**). Thermal ellipsoids drawn to the 50% probability level. The phenyl ring connected at C3 is rotationally disordered and nicely resolved to a 0.67 : 0.32 ratio. Only the major conformation is shown.

chrysene **7**. The *tert*-butylphenyl groups in positions 3 and 9 are perpendicular relative to the central ring, while the *tert*-butylphenyl groups in positions 6 and 12 fluctuate around the central chrysene ring, even in the solid state. There are no aromatic–aromatic interactions of the chrysene core of **7**, indicating that the introduction of four *tert*-butylphenyl groups broke the π-stacking. In general, π-stacking has been found to be detrimental to OLEDs. Simple PAH molecules like pyrene and chrysene have a tendency to form excimers that decrease the fluorescence efficiency in condensed media.[9]

The bulky substituents of the substituted PAH are believed to prevent the excimer formation that causes the concentration quenching of fluorescence in the solid state.

Compound **7** shows blue photoluminescence. An OLED device was fabricated from **7** by a thermal evaporation technique. The device configuration consists of ITO as the anode, MPMP (30 nm) as the hole transport material, emitters (40 nm), DPA/AlQ (40 nm) as the electron transport material, and LiF/Al as the cathode. Molecular structures of MPMP, DPA and AlQ are shown in Scheme 3.



Scheme 3

Table 1 Device configuration and efficiency of OLED device using 3,6,9,12-tetrakis(4-*tert*-butylphenyl)chrysene (**7**)

Device configuration	Efficiency/ cd A^{-1}	Radiance/ cd m^{-2}	Peak wavelength/ nm
MPMP(300 Å)/emitter(400 Å)/ DPA(100 Å)/AlQ(300 Å)/ LiF(10 Å)/Al(500 Å)	1.5	500	450

The (*x*,*y*) color coordinates of **7** are based on the 1931 convention, and are found at 0.23 and 0.35. The compound was deposited as a neat film. The electroluminescent spectrum shows a peak at 450 nm, but with a long tail, presumably due to aggregation in the neat film. This long tail could be eliminated if compound **7** were used as dopant in a host matrix.[10] Table 1 summarizes the device configuration and the efficiency of the OLED device made from **7**.

In conclusion, we present here the first example of a tetra-substituted chrysene, in which four aromatic substituents are located in the 3, 6, 9 and 12 positions. The initial OLED device was assembled incorporating chrysene **7**. Further studies to optimize the device architecture will be required to evaluate the potential of tetra-substituted chrysenes in OLEDs.

Notes and references

‡ Synthesis of compounds: 3,6,9,12-tetrabromochrysene (**2**): bromine (85 g, 0.53 mol) in trimethyl phosphate (100 ml) was added dropwise to a stirred solution of chrysene (20.0 g, 0.0876 mol) dissolved in trimethyl phosphate (300 ml) at 60 °C. The reaction temperature was slowly increased to 100 °C and kept for 3 days at that temperature. The resultant precipitate was filtered, washed with methanol (2 × 100 ml) and dried in vacuum. Yield of 3,6,9,12-tetrabromochrysene (**2**) was 39.14 g (82.14%) with no mp below 300 °C (decomposition above 300 °C). Direct probe GC-MS: exact mass found for $C_{18}H_8Br_4$ is 543.73 g mol^{-1}. Calculated mass found for $C_{18}H_8Br_4$ is 543.73 g mol^{-1} for most abundant isotope combination.

3,6,9,12-Tetrakis(4-*tert*-butylphenyl)chrysene (**7**): 3,6,9,12-tetrabromochrysene (**2**) (5.0 g, 0.00919 mol), 4-*tert*-butylphenylboronic acid (**3**) (9.82 g, 0.0552 mol), tris(dibenzylideneacetone) dipalladium(0) (**4**) (1.26 g, 0.00138 mol), di-*tert*-butyl(trimethylsilylmethyl)phosphane (**5**) (0.62 g, 0.02670 mol), caesium carbonate (**6**) (17.97 g, 0.0552 mol) and 1,4-dioxane (100 ml) were refluxed for 48 h. The resultant mixture was poured into 200 ml of water and extracted twice by 200 ml of methylene chloride. The organic phase was dried over magnesium sulfate overnight and filtered. The solvent was removed on a rotary evaporator and the residue was purified by chromatography on silica gel with petroleum ether–diethyl ether (10 : 0.5) as eluant. Yield of 3,6,9,12-tetrakis(4-*tert*-butylphenyl)chrysene (**7**) was 2.05 g (30%) as a white solid with mp 376.48 °C. The melting point was measured by DSC method. Additionally the purity was evaluated by LC-MS method. It was found to be 99.17% based on retention area. ^{1}H NMR (CD_2Cl_2) 1.30 (s, 9H, *t*-Bu), 1.35 (s, 9H, *t*-Bu), 1.50 (s, 18H, *t*-Bu), 7.60–9.20 (m, 24H, arom.-H). GC-MS (direct probe): exact mass found for $C_{58}H_{60}$ is 756.47 g mol^{-1}. Calculated mass found for $C_{58}H_{60}$ is 756.47 g mol^{-1}. The pattern of the substitution of the chrysene ring was confirmed from X-ray analysis.

3,6,9,12-Tetrakis(4-*tert*-butylphenyl)chrysene (**7**) shows blue photoluminescence in toluene solution with a PL peak at 430 nm. The solution quantum yield in toluene is measured to be 0.49 with 350 nm excitation wavelength and quinine sulfate as the standard. For comparison purpose, the solution PL quantum yield of unsubstituted chrysene is 0.12–0.17.[13]

§ *Crystal data* for **7**: $C_{58}H_{60}$, from pentane, colorless, irregular block, ~0.380 × 0.230 × 0.200 mm, monoclinic, $P21/c$, a = 15.3050(15) Å, b = 9.6769(9) Å, c = 14.6721(15) Å, β = 90.280(2)°, U = 2173.0(4) $Å^3$, Z = 2, T = −100 °C, M = 757.06, D_c = 1.157 g cm^{-3}, μ(Mo) = 0.06 mm^{-1}.
Data Collection: Bruker SMART 1K CCD system, Mo Kα radiation, SAINT integration, *hkl* min/max = (−20, 19, −12, 9, −19, 13), data input to shelx = 14 037, unique data = 5147, 2θ range = 2.66 to 56.56°, completeness to 2θ 56.56 = 95.60%, R(int-xl) = 0.0289, SADABS correction applied.
Solution and refinement: structure solved using XS(Shelxtl), refined using shelxtl software package, refinement by full-matrix least squares on F^2, scattering factors from Int. Tab. Vol C Tables 4.2.6.8 and 6.1.1.4, number of data = 5147, number of restraints = 0, number of parameters = 281, data/parameter ratio = 18.32, goodness-of-fit on F^2 = 1.04, R indices[$I > 4\sigma(I)$] $R1$ = 0.0841, w$R2$ = 0.2396, R indices (all data) $R1$ = 0.1356, w$R2$ = 0.2906, max difference peak and hole = 0.602 and −0.336 e $Å^{-3}$. All hydrogen atoms are idealized using a riding model.[14]

1 (*a*) M. Pospisil, K. Pecka and J. Vanura, *Pet. Coal*, 1995, **37**, 34; (*b*) G. Sebor, P. Smidl and J. Mitera, *Fuel*, 1989, **68**, 1285.
2 (*a*) J. Szczepanski and M. Vala, *Astrophys. J.*, 1993, **414**, 646; (*b*) T. Henning and F. Salama, *Science*, 1998, **282**, 2204.
3 (*a*) M. D. Guillen, P. Sopelana and M. A. Partearroyo, *Rev. Environ. Health*, 1997, **12**, 133; (*b*) B. Armstrong, E. Hutchinson, J. Unwin and T. Fletcher, *Environ. Health Perspect.*, 2004, **112**, 970.
4 T. Watabe, T. Ishizuka, M. Isobe and N. Ozawa, *Science*, 1982, **215**, 403.
5 R. Goddard, M. W. Haenel, W. C. Herndon, C. Kruger and M. Zandler, *J. Am. Chem. Soc.*, 1995, **117**, 30.
6 I. Ikemoto and H. Kuroda, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1968, **24**, 383.
7 D. E. Eaton, A. G. Anderson, J. C. Calabrese, W. Tam and Y. Wang, *J. Am. Chem. Soc.*, 1987, **109**, 1886.
8 R. Atencio, K. V. Domasevitch and M. J. Zaworotko, *Cryst. Eng.*, 2000, **3**, 63.
9 W. Sotoyama, H. Sato, M. Kinoshita, T. Takahashi, A. Matsuura, J. Kodama, N. Sawatari and H. Inoue, *SID 03 Digest*, 2003, 1294.
10 (*a*) M. Funahashi and M. Kubota, *PCT Int. Appl.*, WO 2006098080, 2006; (*b*) M. Funahashi, *PCT Int. Appl.*, WO 2006025273, 2006.
11 (*a*) A. H. Cowley, N. C. Norman and M. Pakulski, *Inorg. Synth.*, 1990, **27**, 235; (*b*) A. S. Ionkin, W. J. Marshall and B. Fish, *Organometallics*, 2006, **25**, 1461.
12 (*a*) A. S. Ionkin, W. J. Marshall, D. C. Roe and Y. Wang, *Dalton Trans.*, 200620), 2468; (*b*) A. S. Ionkin and W. J. Marshall, *J. Organomet. Chem.*, 2004, **689**, 1057; (*c*) A. S. Ionkin, Y. Wang, W. J. Marshall and V. A. Petrov, *J. Organomet. Chem.*, 2007, **692**, 4809.
13 S. L. Murov, I. Carmichael and G. L. Hug, *Handbook of photochemistry*, Marcel Dekker, Inc., New York, 2nd edn, 1993, p. 24.
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