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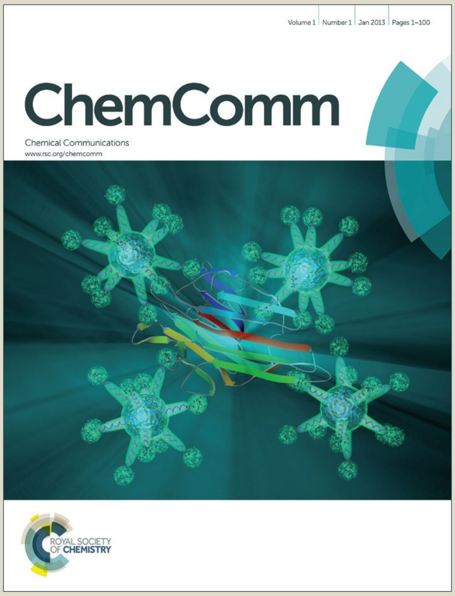

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A Planarized 9-Phenylanthracene: A Simple Electron-Donating Building Block for Fluorescent Materials†

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A 9-phenylanthracene, constrained in a coplanar fashion by two methylene tethers, was synthesized and its optoelectronic properties were investigated. The rigid planarization increased its electron-donating character and induced a bathochromic shift of its absorption, as well as an increased molar absorption coefficient and intense fluorescence. These properties render this compound a promising building block for fluorescent materials.

The structural constraint of π-conjugated skeletons in a planar fashion induces characteristic electronic properties, and thus represents a powerful design principle to extend π-conjugation effectively. To date, a variety of fascinating planarized π-electron materials have been developed this way.[1] This design approach is also able to effectively stabilize Lewis acidic tricoordinate boron compounds.[2] Based on this principle, we have already synthesized a series of stable planarized triarylboranes and disclosed their characteristic features as models for boron-doped graphene.[3] As a part of this study, we synthesized phenyl-substituted borataanthracene **1**, which is constrained in a planar fashion by two methylene tethers.[4] In combination with a cryptand-coordinated K^+ counterion, this anion showed attractive photophysical properties in THF, specifically an orange emission (λ_{em} = 584 nm) concomitant with a high quantum yield (Φ_F = 0.45). Therefore, we became interested in its carbon congener **2**, which is a planarized derivative of 9-phenylanthracene **3** (Fig. 1).

Anthracene is one of the most fundamental fluorescent skeletons and especially the introduction of substituents at its 9 and 10-positions significantly alters its electronic properties. Accordingly, 9,10-disubstituted anthracenes have been extensively employed as building blocks in materials for organic light-emitting diodes,[5] two-photon absorption fluorescent dyes,[6] and organic field-effect transistors.[7] For example, Müllen and co-workers reported the synthesis of the attractive 9,10-diphenylanthracene derivative **4**, which was partially constrained by a methylene tether on one side of each phenyl substituent, and its subsequent use as a monomer in π-conjugated polymers.[8,9] While **4** showed intriguing optoelectronic properties, such as a red-shifted absorption and fluorescence relative to the parent 9,10-diphenylanthracene, the structure of this skeleton is still substantially deviated from planarity, due to the steric congestion in the non-substituted cove region. In contrast, twofold methylene-tethered phenylanthracene **2** should exhibit a completely planarized π-conjugated skeleton, and the rigid π-framework should effectively suppress the nonradiative decay from the excited state, giving thus rise to an intense fluorescence. The presence of two methylene tethers should moreover alter the electronic structure. In this paper, we report the synthesis, as well as the structural, photophysical, and electrochemical properties of planarized 9-phenylanthracene **2**. We also demonstrate the potential of this simple skeleton as a useful building block for the generation of fluorescent π-conjugated materials.

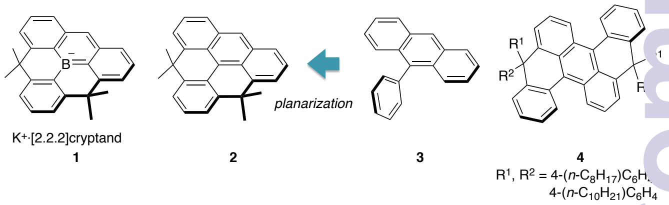

Fig. 1 Chemical structures of **1**-**4**.

Initially, we synthesized planarized 9-phenylanthracene **2** (Scheme 1) according to our previously reported synthesis of a planarized triphenylborane via the twofold intramolecular Friedel-Crafts cyclization of a 2,6-di(2-propenyl)phenyl-substituted precursor in the presence of $Sc(OTf)_3$.[2] For this purpose, di(2-propenyl)phenyl-substituted precursor **5** was prepared in 44% yield from the reaction of anthrone with 2,6-di(2-propenyl)phenyllithium, followed by aromatization.[10]

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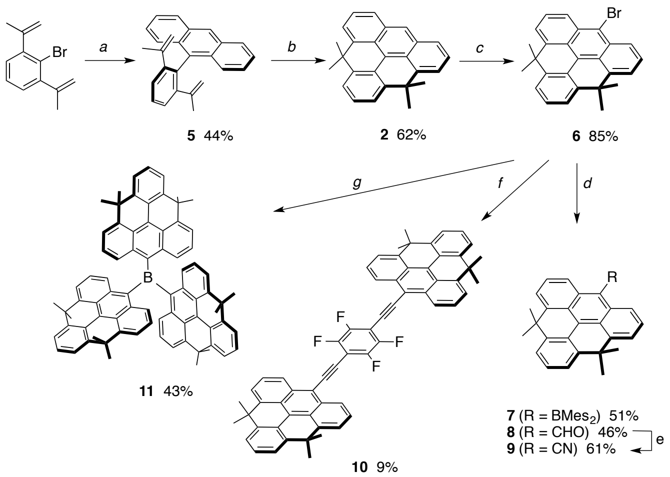

Scheme 1 Synthesis of planarized 9-phenylanthracene **2** and its derivatives **7**-**11**: (a) i, *t*-BuLi, Et_2O, –78 °C; ii, anthrone, toluene, reflux; iii, sat. NH_4Cl aq.; (b) $Sc(OTf)_3$, 1,2-dichloroethane, reflux; (c) NBS, CH_2Cl_2; (d) i, *t*-BuLi, THF, –78 °C; ii, electrophile (**7**: Mes_2BF; **8**: DMF); (e) I_2, 28% NH_3 aq., THF, 60 °C; (f) 1,4-diethynyltetrafluorobenzene, $Pd(PhCN)_2Cl_2/P(t\text{-}Bu)_3$, CuI, *i*-$Pr_2NH$, toluene; (g) i, *t*-BuLi, THF, –78 °C; ii, $BF_3{\cdot}OEt_2$, –78 °C to rt.

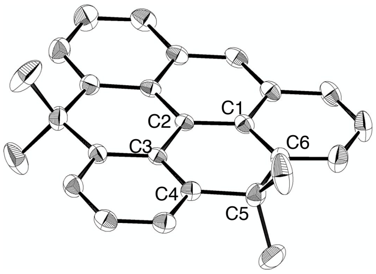

Fig. 2 Molecular structure of planarized 9-phenylanthracene **2** (atomic displacement parameters set at 50% probability). Hydrogen atoms are omitted for clarity and only selected atoms are labelled.

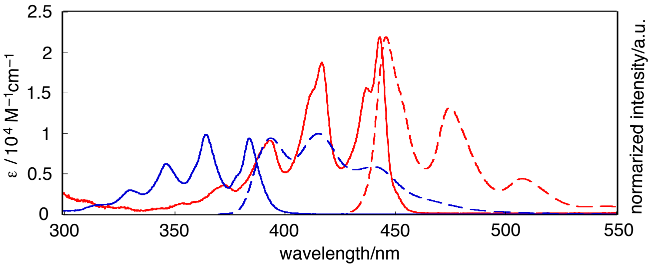

Fig. 3 UV-vis absorption (solid lines) and fluorescence (dashed lines) spectra of **3** (blue) and **2** (red) in cyclohexane.

Subsequent heating of **5** and $Sc(OTf)_3$ in 1,2-dichloroethane successfully furnished **2** in 62% yield.

Using NBS, planarized 9-phenylanthracene **2** was readily brominated at the 10-position to produce **6**, which was used as a versatile precursor to generate various derivatives. As **2** exhibited an electron-donating character (*vide infra*), we were particularly interested in introducing electron-accepting groups at the 10-position. Consequently, bromide **6** was lithiated with *t*-BuLi in THF at –78 °C, followed by a treatment with Mes_2BF or DMF to furnish **7** and **8** in 51% and 46% yield, respectively. Aldehyde **8** was further transformed into cyano-substituted **9** (61%) by treatment with iodine and an aqueous solution of ammonia.[11] Moreover, π-extended derivatives with an electron-accepting diethynyltetrafluoro-phenylene spacer (**10**) or a tricoordinate boron atom (**11**) were synthesized.[12,13]

By slow evaporation of an ether solution, we successfully obtained single crystals of the planarized 9-phenylanthracene **2**, suitable for X-ray crystallographic analysis. For comparison, the crystal structure of parent 9-phenylanthracene **3** was also determined. The X-ray diffraction analysis confirmed that **2** adopts a nearly planar structure in the crystalline state (Fig. 2). Between the anthracene and phenyl mean planes of **2**, a dihedral angle of 1.17(9)° was observed, while the corresponding angle in **3** is 73.2(5)°. Importantly, the C2–C3 bond (1.473(2) Å) in **2** is shorter than that in **3** (1.501(5) Å). This is probably due to a distorted hexagon structure, involving the sp^3-hybridized carbon atom C5. Even though the C4–C5–C6 angle is 113.27(12)°, which is wider than the ideal bond angle for an sp^3 hybridized carbon atom (109.5°), it is still below 120°. Consequently, the six-membered ring (C1–C6) is distorted from a regular hexagon geometry, resulting in a contracted C2–C3 bond.

The planarized structure of **2** has significant impact on its photophysical properties, compared to those of parent congener **3** (Fig. 3). In cyclohexane, both **2** and **3** showed similarly structured absorption and fluorescence spectra that are characteristic for the anthracene moiety. However, planarized **2** showed a substantially red-shifted absorption band (λ_{abs} = 443 nm, ε = 2.19 × 10^4 $M^{-1}cm^{-1}$) relative to **3** ($\Delta\lambda_{abs}$ = 59 nm), whereby the molar absorption coefficient of **2** is almost twice as large as that of **3**. While the fluorescence spectrum of **2** showed an intense blue emission (λ_{em} = 446 nm) with a high quantum yield (Φ_F = 0.92), **3** exhibited purple fluorescence (λ_{em} = 393 nm) with a lower quantum yield (Φ_F = 0.51).[14] The observed Stokes shift of 152 cm^{-1} for **2** is consistent with a rigid and planar skeleton.

In order to study the fluorescence property differences between **2** and **3**, we measured their fluorescence lifetimes (τ) in cyclohexane and determined the radiative (k_r) and nonradiative (k_{nr}) decay rate constants based on the Φ_F and τ values (Table S1 in the ESI). While we observed a slight increase in the k_r values from **3** (7.73 × 10^7 s^{-1}) to **2** (9.48 × 10^7 s^{-1}), the k_{nr} value of **2** (8.25 × 10^6 s^{-1}) is by an order of magnitude lower than that of **3** (7.42 × 10^7 s^{-1}). This result demonstrated that the rigidly planarized structure in **2** effectively suppresses the nonradiative decay process from the excited state, resulting in the observed intense fluorescence.

The red-shifted λ_{abs} and λ_{em}, as well as the increased molar absorption coefficient of **2** relative to **3** suggested substantial perturbations of the electronic structure arising from the planarization enforced by the two methylene tethers in **2**. In order to further investigate the differences between **2** and **3**, structural optimization and TD-DFT calculations were carried out at the B3LYP/6-31G(d) level of theory (Fig. 4).

Whereas the HOMO and LUMO of **3** are essentially localized on the anthracene moiety, the corresponding orbitals

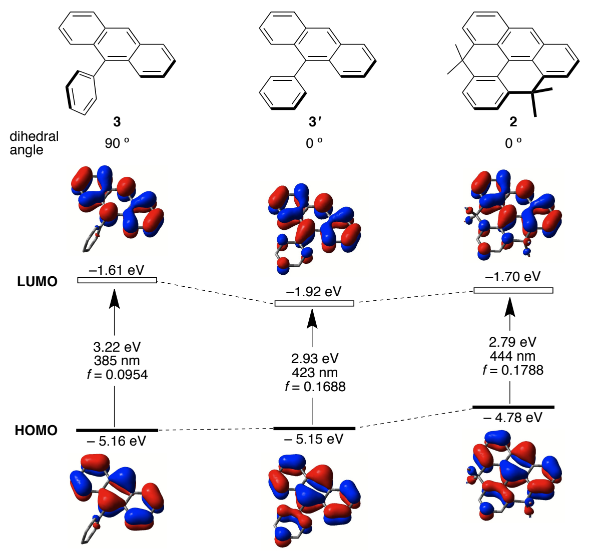

Fig. 4 HOMO and LUMO energy levels, as well as excitation energies for **3**, **3′**, and **2**, calculated at the B3LYP/6-31G(d) level of theory.

Table 1 Photophysical Properties of Planarized 9-Phenylanthracene Derivatives **7-11** in Cyclohexane

Compd	λ_{abs} (nm)	ε (10^4 $M^{-1}cm^{-1}$)	λ_{em} (nm)	$\Phi_F{}^a$	Stokes shift (cm^{-1})
7	486	1.90	527	0.88	1601
8	469	1.38	573	0.45	3870
9	477	1.30	489	0.94	514
10[b]	554	7.73	571	0.72	538
11	547	2.34	632	0.21	2459

[a]Absolute emission quantum yields were determined by a calibrated integrating sphere system within an error of ±3%. [b]In toluene.

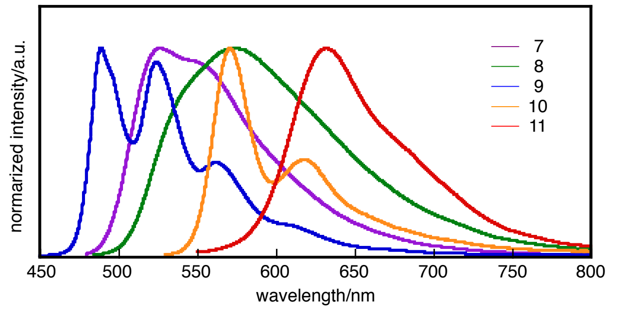

Fig. 5 Fluorescence spectra of **7**-**9**,**11** in cyclohexane and of **10** in toluene.

of **2** are delocalized over the anthracene and the planarized benzene moieties. In both cases, the excitation to the lowest excited singlet state (S_1) was assigned to the HOMO–LUMO (π–π*) transition. The calculated excitation energy for **2** (2.79 eV, 444 nm) was significantly smaller than that of **3** (3.22 eV, 385 nm), and the oscillator strength of **2** (*f* = 0.1788) was substantially larger than that of **3** (*f* = 0.0954). These results are commensurate with the experimentally observed differences between **2** and **3**.

In order to assess the impact of the structural constraint on the frontier orbitals, phenylanthracene **3** and its planarized derivative **3′** were also examined theoretically and compared with **2** (Fig. 4). The structural optimization of **3** at the B3LYP/6-31G(d) level revealed an orthogonal alignment of the phenyl and anthracene planes, comprising a dihedral angle of 90°. The structure of planarized **3′** was calculated by using a fixed dihedral angle of 0°, while all other structural parameters calculated for **3** remained constant. The orientational change of the phenyl group from a perpendicular (**3**) to a coplanar geometry (**3′**) resulted in a decrease of the LUMO energy by 0.31 eV, while the energy level of the HOMO remained unchanged. The oscillator strength was also significantly increased from **3** (*f* = 0.0954) to **3′** (*f* = 0.1688). Conversely, the introduction of two methylene tethers from **3′** to **2** increased both the HOMO and LUMO energy levels by 0.37 eV and 0.22 eV, respectively. As a consequence of the planarization and the inductive effect of the methylene tethers, **2** exhibited a higher HOMO and a slightly lower LUMO level compared to **3**, which explains the substantially red-shifted λ_{abs} and λ_{em} values of **2**.

The characteristic electronic structure of **2** is also reflected in the cyclic voltammetry in THF (Fig. S6; ESI). For **2**, a reversible redox wave at $E_{1/2}$ = +0.49 V with an anodic peak potential (E_{pa}) at +0.58 V (vs. Fc/Fc^+) was observed for an oxidation process, together with an irreversible wave at a cathodic peak potential (E_{pc}) of –2.54 V for a reduction process. Compound **3** showed irreversible oxidation and reduction waves[15] at E_{pa}= +0.96 V and E_{pc} = –2.96 V, respectively. These results demonstrate that the simple structural modification of planarization is able to significantly alter the electronic structure of phenylanthracenes.

Focusing our attention on the electron-donating character of the planarized phenylanthracene, we became interested in introducing electron-accepting groups at the 10-position, as this design approach should induce intriguing fluorescence properties. Consequently, we synthesized a series of derivatives **7**–**9** and examined their photophysical properties, which are summarized in Table 1. All of these derivatives showed substantially red-shifted λ_{abs} and λ_{em} values compared to **2**. For example, cyano- and dimesitylboryl-substituted **9** and **7** showed green (λ_{em} = 489 nm) and yellowish green (λ_{em} = 527 nm) emissions in cyclohexane, while maintaining high Φ_F values of 0.94 and 0.88, respectively. Formyl derivative **8** exhibited an even larger red-shift and a broad emission band around λ_{em} = 573 nm in cyclohexane. Despite its small π-conjugated skeleton, **8** exhibited a reddish orange emission (λ_{em} = 617 nm) in DMF and showed a relatively large solvent dependence of its fluorescence compared to **7** and **9** (Fig. S2 and Table S2 in the ESI). Based on the Lippert-Mataga plot (Fig. S4 in the ESI), the dipole moment present in the excited state was estimated to be 13.7 D, while that in the ground state was estimated to be 4.9 D. To gain further insight into the origin of the significantly red-shifted emission of **8**, structural optimization calculations for the lowest excited singlet state (S_1) were carried out at the CAM-B3LYP/6-31G(d) level of theory. The obtained structure exhibited a distorted anthracene skeleton that deviated from planarity, while a coplanar geometry was maintained between the CHO and the anthracene moiety (Fig. S10 in the ESI). This structural deformation in S_1 may be responsible for the significantly red-shifted and relatively unstructured emission band.

In order to demonstrate the utility of the planarized phenylanthracene as a building block for more extended π-electron materials, **10** and **11** were prepared. The combination of **2** with an electron-accepting diethynylarene spacer in **10** gave rise to a significantly red-shifted absorption band (λ_{abs} = 554 nm; ε = 7.73 × 10^4 $M^{-1}cm^{-1}$) in toluene. Reflecting the large molar absorption coefficient, this compound emitted a bright orange fluorescence (λ_{em} = 571 nm) with a high quantum yield (Φ_F = 0.72). It should be noted that these properties are very different from those of non-planarized phenylanthracene congener **12** (Fig. 6), which exhibits in the same solvent λ_{abs} and λ_{em} values of 479 nm and 495 nm, respectively (ε = 3.57 × 10^4 $M^{-1}cm^{-1}$; Fig. S5 and Table S2 in the ESI). Attachment of three planarized phenylanthracene units to a boron atom in **11** induced an even more red-shifted fluorescence (λ_{em} = 632 nm) in cyclohexane.

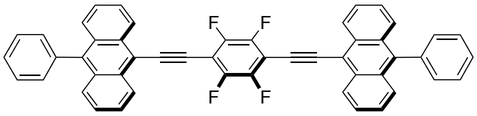

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Fig. 6 Chemical structure of **12**.

Conclusions

We synthesized a series of planarized 9-phenyanthracene derivatives, in which the planar and rigid structure induces effective π-conjugation and reduces the nonradiative decay process from the excited state. These effects should cause red-shifted absorptions, increased molar absorption coefficients, and intense fluorescence. Planarized 9-phenylanthracenes should thus represent a useful electron-donating building block for the generation of fluorescent materials. The combination of this skeleton with electron-accepting moieties enabled us to produce fluorescent molecules with various emission colours. These results clearly demonstrate the significant impact of the planar constraint imposed by the methylene tethers on the properties of the π-conjugated skeleton.

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