Novel red-light-emitting 9,10-bis(phenylethynyl)anthracenes

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Abstract

Novel 9,10-bis(phenylethynyl)anthracenes (BPEA's) **5** were prepared in high yields and purity. They were synthesized by a Pd-catalyzed Sonogashira coupling reaction. These compounds are typical intramolecular charge transfer compounds, which consist of the electron-rich anthracene moiety and an electron acceptor part. Their emissions are all in the red region with λ_{max} ranging between 616-638 nm and they exhibit high fluorescent quantum efficiencies.

Keywords: Red-light emitting, 9,10-bis(phenylethynyl)anthracenes, palladium catalysis

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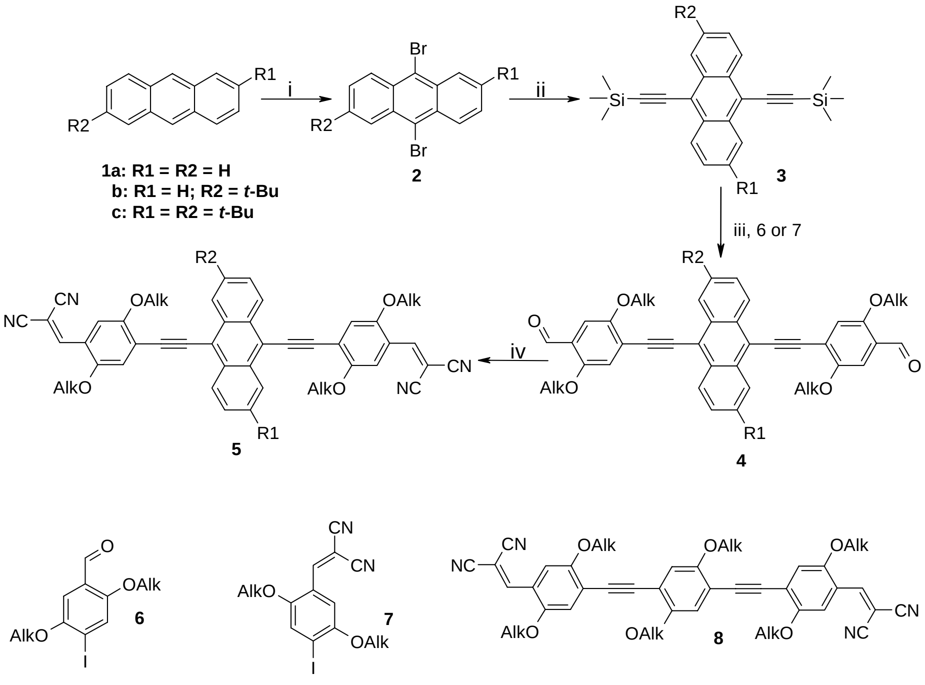
Introduction

9,10-bis(Phenylethynyl)anthracenes (BPEAs) **5** are best known for their interesting fluorescent properties. They are used as conventional chemiluminescent fluorophores.[1-3] The parent compound, BPEA, was applied as a dopant in MOLEDs.[4] Recently, its photophysics and electronic spectroscopy have been thoroughly studied.[5] Also Li *et al*., have prepared a series of substituted BPEAs and provided the absorption and the fluorescence data related to the substitution of the anthracene core.[6] They showed that 1,8-diphenoxy groups gave a greater bathochromic shift than halogenated BPEAs, as compared to the unsubstituted parent system (from 476 to 522 nm). However, to create an extended π-system with a drastically lowered HOMO-LUMO energy gap, sufficient conjugative interaction is needed. Recently, Wong and Hsu constructed a π-conjugated backbone with a significant reduced HOMO-LUMO energy gap and high quantum efficiency by incorporating a highly electronegative pyrimidine ring into the conjugated backbone.[7] Moreover, the presence of a strong electron acceptor and a strong electron donor is indispensable to the proper red aromaticity and saturated red emission.[8] Also, the introduction of different pendant alkyl substituents can lead to a significant increase in solubility and reduction of self-quenching due to the intermolecular π-π overlap.[9-11] Bearing in mind these findings we wish to report herein an easy synthesis of simple and novel π-conjugated systems which are highly luminescent in the red region and have possibilities for use as new red dopants.

Results and Discussion

t-Butylanthracenes **1** (R1, R2 = H or t-butyl) can easily be prepared on a large scale by known procedures (Scheme 1).[12,13] The 9,10-dihalides **2** were synthesized by the reaction of the anthracenes **1** with Br_2 in CCl_4.[14,15] Silylation of **2** by a Pd-catalyzed Sonogashira coupling reaction furnished protected anthracene-9,10-diynes **3**. Removal of the TMS groups and coupling with iodoaldehyde **6**[16] were done in a one-pot reaction, as bis(terminal alkyne)s can be oxidatively unstable during work-up.[17] The obtained aldehydes **4** are insoluble in hexane. We took advantage of their insolubility and purified them by simply washing the crude products several times with hot hexane. The aldehydes **4** exhibit strong orange emission in a solution. However, to shift the emission peaks further to the long wavelength region, a carbaldehyde moiety was converted to a very strong, electron-withdrawing group, dicyanomethylene. This was accomplished quantitatively by condensation of **4** with malonodinitrile in dichloromethane to give the nitriles **5**. The purification of **5** is simple, as they were isolated by careful addition of hexane to the reaction mixture. The direct coupling of the malononitrile **7** with **3** was less efficient and gave **5** in a very low yield. Fluorescence yields of the synthesized red BPEAs **5a-c** were found to range from 0.52 to 0.37, Table 1. Interestingly, the quantum efficiency of the benzo- analogue of **8**, where the anthracene moiety



Scheme 1. (i) Br_2, CCl_4, r.t.; (ii) *i*-Pr_2NH, $Pd(PPh)_3Cl_2$, PPh_3, CuI, trimethylsilylacetylene; (iii) K_2CO_3, $Pd_2(dba)_3$, CuI, PPh_3, **6** (Alk = C_6H_{13}), THF/MeOH (4:1 v/v), 24 h, r.t.; (iv) $CH_2(CN)_2$, piperidine, CH_2Cl_2, 24 h, r.t.

was substituted by a benzene ring, was found to be 82%, but the photoluminescence in a solution was at only 572 nm.[18] The smaller quantum yields for **5** may be explained in terms of the greater relative moment of inertia of the anthracene moiety favouring non-radiative decay processes.[19] Compound **5c** is reasonably luminescent in a solid state. [18] This can be attributed to the presence of bulky *t*-butyl groups, which provide facial encumbrance, necessary for minimizing the aggregation of the planar aromatic planes.

Table 1. Fluorescence and quantum yields of red BPEAs in CH_2Cl_2. [a] Quantum yields were calculated by use of the following equation:[20] $\Phi = [(A_sF_un^2)/(A_uF_sn_o^2)]\Phi_s$; Φ is quantum yield, A is absorbance at the excitation wavelength, F the integrated emission area across the band and n's are respectively the index of refraction of the solvent containing the unknown (n) and the standard (n_o). The reference standard (Nile Red in MeCN) had a quantum yield of 0.78.[21] [b] λ_{ex} = 490 nm

Compound	(PL) λ_{max}, nm	Φ, %^{a,b}
4a (R1, R2 = H)	522, 556	-
4b (R1 = H, R2 = *t*-Bu)	527, 560	-
4c (R1, R2 = *t*-Bu)	531, 564	-
5a (R1, R2 = H)	616	55.2
5b (R1 = H , R2 = *t*-Bu)	626	47.9
5c (R1, R2 = *t*-Bu)	636	37.0

Conclusions

In this paper we synthesized novel red-light-emitting BPEAs in high yields and purity. Fluorescence yields of these BPEAs were found to be in the range from 37-57%. One compound, **5c**, is luminescent in the solid state. However, to prepare highly luminescent solid-state materials based on BPEAs we are going to introduce bulkier substituents within the BPEA framework to minimize the aggregation of the planar aromatic compounds. This approach recently encountered remarkable success in the synthesis of poly(arylene-ethynylene)s.[22,23]

Experimental Section

General Procedures. ^{1}H NMR were recorded on a Bruker AC400 spectrometer. Emission spectra were recorded on a Perkin-Elmer spectrofluorometer, and quantum efficiencies were obtained by the standard method using Nile Red (Φ = 0.78 in acetonitrile) as reference.[21] Mass spectra (FAB) were recorded on a VG70-250S mass spectrometer. Elementary analyses were performed on a Perkin-Elmer 2400 CHN analyzer. 2-*t*-Butylanthracene,[12] 2,6-di-*t*-

butylanthracene,[13] 2-*t*-Butyl-9,10-dibromoanthracene,[15] 2,5-dihexyloxy-4-iodobenzaldehyde,[16] 9,10-bis(Trimethylsilylethynyl)anthracene[24], and $Pd_2(dba)_3$[25] were prepared according to standard procedures.

2,6-Di-*tert*-butylanthracene (1c) (modified procedure)[13]. Anthracene **(1a)** (17.8 g, 0.1 mol), *t*-butyl alcohol (22.2 g, 0.3 mol), and TFAA (100 mL) were heated at reflux overnight. After cooling, the black mixture was treated with solid sodium bicarbonate. Water (200 mL) and hexane (200 mL) were added. The organic phase was separated and methylene chloride was added to obtain a clear solution. The volatiles were removed in vacuo and the residue was treated with hexane and refrigerated. The white solid was filtered and washed with a small amount of cold hexane. The yield of crude **1c** 24.6 g (85%).

2,6-Di-*tert*-butyl-9,10-dibromoanthracene (2c).[14] Compound **1c** 6.08 g (20.93 mmol) was dissolved in carbon tetrachloride (200 mL). To the clear solution, the stochiometric amount of bromine 6.72 g (42 mmol, 2.2 mL) in CCl_4 (20 mL) was added dropwise within 1 hour. The reaction mixture was stirred for an additional 3 hrs. Sodium bisulfite (10%, 50 mL) was added to the solution to remove the orange color. The organic phase was dried over magnesium sulfate. The solvent was removed in vacuo, and the residue was recrystallized from hexane to give pure **2c** as a slightly yellow solid. Yield 6.52 g (69%): mp 209-210 °C; ^{1}H NMR ($CDCl_3$) δ 1.47 [s, 18H, 2x$C(CH_3)_3$], 7.69 (dd, 2H, *J* = 9.3, 1.9 Hz, H-3, H-7), 8.44 (d, 2H, *J* = 1.9, H-1, H-5), 8.49 (d, 2H, *J* = 9.3 Hz, H-4, H-8); EI MS m/z 448 (M^+); Anal. Calcd. C 58.95, H 5.40; found C 59.13, H 5.40.

General procedure for the preparation of 9,10-bis(trimethylsilylethynyl)anthracenes

The dibromo derivative **2b** or **2c** (5 mmol) was refluxed in dry diisopropylamine under N_2 (*ca* 3 hrs) in the presence of $Pd(PPh_3)_2Cl_2$ (2 mol % per halide atom), CuI (4 mol % per halide atom), PPh_3 (4 mol % per halide atom) and trimethylsilylacetylene (1.2 equiv per halide atom). After cooling to room temperature, the solvent was removed under diminished pressure. Hexane was added and diisopropylamine hydroiodide was filtered off. The filtrate was passed through a short column of silica gel and concentrated to deliver the crude 9,10-diynes **3b** and **3c** as yellow solids. They were used without further purification for the next step.

2-*tert*-Butyl-9,10-bis(trimethylsilylethynyl)anthracene (3b). Reddish solid. Yield 1.70 g (80%); mp 98 °C; ^{1}H NMR ($CDCl_3$) δ 0.40 [s, 18H, 2x$Si(CH_3)_3$], 1.47 [s, 9H, $C(CH_3)_3$], 7.53-7.59 (m, 2H, H-6, H-7), 7.70 (dd, 1H, *J* = 9.1, 2.1 Hz, H-3), 8.48 (d, 1H, *J* = 9.1 Hz, H-4), 8.52 (s, 1H, H-1), 8.53-8.56 (m, 2H, H-5, H-8); MS (FAB); m/z 426 (M^+).

2,6-Di-*tert*-butyl-9,10-bis(trimethylsilylethynyl)anthracene (3c). Yellow solid. Yield 1.98 g (83%); mp 110 °C; ^{1}H NMR ($CDCl_3$) δ 0.38 [s, 18H, 2x$Si(CH_3)_3$], 1.45 [s, 18H, 2x$C(CH_3)_3$], 7.66 (dd, 2H, *J* = 9.1, 1.8 Hz, H-3, H-7), 8.46 (s, 2H, H-1, H-5), 8.47 (d, 2H, *J* = 6.6, Hz, H-4, H-8); MS (FAB); m/z 482 (M^+).

Preparation of aldehydes 4a-c

The mixture of silylated alkynes **3a-c** (2mmol), potassium carbonate (3 equiv per TMS), $Pd_2(dba)_3$ (5-10 mol% per TMS),[25] PPh_3 (10-20 mol% per TMS), CuI (5-10 mol% per TMS), **6**[16] (1.2 equiv per TMS) was stirred in THF/MeOH (100 mL, 4:1 v/v).When TLC showed no starting material present (24 hrs), the luminous orange mixture was filtered through a thin pad of silica gel and evaporated to dryness. The residue was recrystallized repeatedly from hexane to afford aldehydes **4a-c** as brown-orange solids.

9,10-bis[4-(Formyl)-2,5-dihexyloxy-phenylethynyl]anthracene (4a). Yield 1.42 g (85%); mp 170-172 °C; ^{1}H NMR ($CDCl_3$) δ 0.84 (t, 6H, *J* = 7.2 Hz, CH_2CH_3), 0.92 (t, 6H, *J* = 6.8 Hz, CH_2CH_3), 1.19-1.41 (m, 16H), 1.45-1.61 (m, 8H), 1.79-1.89 (m, 4H), 1.95-2.05 (m, 4H), 4.15 (t, 8H, *J* = 6.5 Hz, OCH_2CH_2), 7.29 (s, 2H, H_{phenyl}, *ortho* to CHO), 7.39 (s, 2H, H_{phenyl}, *meta* to CHO), 7.63-7.65 (m, 4H, $H_{anthracene}$,), 8.79-8.82 (m, 4H, $H_{anthracene}$), 10.49 (s, 2H, CHO); MS (FAB); m/z 834(M^+); Anal. Calcd. C 80.54 H 7.97; Found C 80.67 H 7.81

2-*tert*-Butyl-9,10-bis[4-(formyl)-2,5-dihexyloxy-phenylethynyl]anthracene (4b). Yield 1.34 g (75%); mp 138-141 °C; ^{1}H NMR ($CDCl_3$) δ 0.80-0.86 (m, 6H), 0.92 (t, H, *J* = 7.1 Hz, 6H), 1.21-1.42 (m, 16H), 1.45-1.61 (m, 8H), 1.56 (s, 9H), 1.86-1.91 (m, 4H), 1.91-2.11 (m, 4H), 4.12-4.18 (m, 8H), 7.28 (s, 1H), 7.29 (s, 1H), 7.40 (s, 1H), 7.41 (s, 1H), 7.59-7.64 (m, 2H, H-6, H-7), 8.73 (dd, 1H, *J* = 9.1, 1.9 Hz, H-3), 8.63 (d, 1H, *J* = 1.8 Hz, H-1), 8.75 (d, 1H, *J* = 9.1 Hz, H-4), 8.76-8.81 (m, 2H, H-5, H-8), 10.49 (s, 2H, CHO); MS (FAB); m/z 890(M^+); Anal. Calcd. C 80.86 H 8.37; Found C 81.32 H 8.13

2,6-Di-*tert*-butyl-9,10-bis[4-(formyl)-2,5-dihexyloxy-phenylethynyl]anthracene (4c). Yield 1.64 g (87%); mp 174-175 °C; ^{1}H NMR ($CDCl_3$) δ 0.82 (t, 6H, *J* = 7.2 Hz, CH_2CH_3), 0.92 (t, 6H, *J* = 7.0 Hz, CH_2CH_3), 1.25-1.45 (m, 14H), 1.45-1.56 (m, 28H, alkyl protons and 2 x *t*-Bu), 1.83-1.92 (m, 4H), 1.95-2.05 (m, 4H), 4.12 (t, 4H, *J* = 6.6 Hz, OCH_2CH_2), 4.16 (t, 4H, *J* = 6.5 Hz, OCH_2CH_2), 7.29 (s, 2H, H_{phenyl}, *ortho* to CHO), 7.40 (s, 2H, H_{phenyl}, *meta* to CHO), 7.71 (dd, 2H, *J* = 9.1, 2.0 Hz, H-3, H-7), 8.60 (d, 2H, *J* = 1.5 Hz, H-1, H-5), 8.73 (d, 2H, *J* = 9.0 Hz, H-4, H-8), 10.49 (s, 2H, CHO); MS (FAB): m/z 946 (M^+); Anal. Calcd. C 81.14 H 8.72; Found C 81.01 H 8.75

Preparations of nitriles 5a-c

Aldehydes 4**a-c** (1mmol), malonodinitrile (1.1 mmol) and 1 drop of piperidine were stirred in dichloromethane (50 mL) at room temperature until no more aldehyde **4a-c** was present. The solution was evaporated and the residue recrystallized from CH_2Cl_2/hexane to furnish the title compounds.

9,10-bis[4-(2,2-Dicyano-vinyl)-2,5-dihexyloxy-phenylethynyl]anthracene (5a). Greenish solid. Yield 855 mg (92%); mp 250-251 °C (from toluene/hexane); ^{1}H NMR ($CDCl_3$) δ 0.83 (t, 6H, *J* = 7.2 Hz, CH_2CH_3), 0.93 (t, 6H, *J* = 6.8 Hz, CH_2CH_3), 1.22-1.63 (m, 24H), 1.82-1.92 (m, 4H), 1.95-2.05 (m, 4H), 4.01 (t, 4H, *J* = 6.5 Hz, OCH_2CH_2), 4.14 (t, 4H, *J* = 6.6 Hz, OCH_2CH_2), 7.20 (s, 2H, H *meta* to $PhHC{=}C(CN)_2$], 7.65-7.67 (m, 4H, $H_{anthracene}$), 7.83 [s, 2H, H *ortho* to

PhHC=C(CN)$_2$], 8.26 [s, 2H, Ph*H*C=C(CN)$_2$], 8.77-8.79 (m, 4H, H$_{\text{anthracene}}$); MS (FAB); m/z 930 (M$^+$); Anal. Calcd. C 79.97 H 7.14 N 6.02; Found C 79.34 H 7.02 N 6.45

2-*tert*-Butyl-9,10-bis[4-(2,2-dicyano-vinyl)-2,5-dihexyloxy-phenylethynyl]anthracene (5b). Greenish solid. Yield 910 mg (92%); mp 244-245 °C (from toluene/hexane); ^{1}H NMR (CDCl$_3$) δ 080-0.85 (m, 6H, CH$_2$C*H*$_3$), 0.93 (t, 6H, *J* = 7.0 Hz, CH$_2$C*H*$_3$), 1.19-1.69 (m, 24H), 1.52 [s, 9H, C(CH$_3$)$_3$], 1.85-2.05 (m, 8H), 4.04-4.11 (m, 4H, OC*H*$_2$CH$_2$), 4.13-4.17 (m, 4H, OC*H*$_2$CH$_2$), 7.19 (s, 1H, H$_{\text{phenyl}}$), 7.20 (s, 1H, H$_{\text{phenyl}}$), 7.59-7.66 (m, 2H, H-6, H-7), 7.75 (dd, 1H, *J* = 9.1, 1.9 Hz, H-3), 7.83 (s, 1H, H$_{\text{phenyl}}$), 7.85 (s, 1H, H$_{\text{phenyl}}$), 8.25 [s, 1H, Ph*H*C=C(CN)$_2$], 8.26 [s, 1H, Ph*H*C=C(CN)$_2$], 8.60 (d, 1H, *J* = 1.6 Hz, H-1), 8.72 (d, 1H, *J* = 9.1 Hz, H-4), 8.71-8.78 (m, 2H, H-5, H-8); MS (FAB); m/z 986 (M$^+$); Anal. Calcd. C 80.29 H 7.55 N 5.67; Found C 80.15 H 7.52 N 5.71

2,6-Di-*tert*-butyl-9,10-bis[4-(2,2-dicyano-vinyl)-2,5-dihexyloxy-phenylethynyl]anthracene (5c). Bronze solid. Yield 945 mg (90%); mp 224-225 °C (from toluene/hexane); ^{1}H NMR (CDCl$_3$) δ 0.82 (t, 6H, *J* = 7.0 Hz, CH$_2$C*H*$_3$), 0.93 (t, 6H, *J* = 7.2 Hz, CH$_2$C*H*$_3$), 1.21-1.43 (m, 16H), 1.51 [s, 18H, C(CH$_3$)$_3$], 1.40-1.86 (m, 8H), 1.82-1.92 (m, 4H), 1.95-2.05 (m, 4H), 4.07 (t, 4H, *J* = 6.6 Hz, OC*H*$_2$H$_2$), 4.17 (t, 4H, *J* = 6.5 Hz, OC*H*$_2$H$_2$), 7.21 [s, 2H, H *meta* to Ph*H*C=C(CN)$_2$], 7.72 (dd, 2H, *J* = 9.1, 1.9 Hz, H-3, H-7), 7.86 [s, 2H, H *ortho* to Ph*H*C=C(CN)$_2$], 8.26 [s, 2H, Ph*H*C=C(CN)$_2$], 8.57 (d, 2H, *J* = 1.9 Hz, H-1, H-5), 8.72 (d, 2H, *J* = 9.1 Hz, H-4, H-8); MS (FAB) m/z 1042 (M$^+$) ; Anal. Calcd. C 80.58 H 7.92 N 5.37; Found C 80.17 H 7.94 N 5.18

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