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Introduction

Anthracene derivatives nowadays are used in a large variety of chemical, photophysical and medical applications. The most important applications encompass fluorescence probes and chemosensors,¹ anticancer agents,² efficient organic scintillators³ as well as numerous optoelectronic devices including anthracene-based thin-film transistors,^{4–6} solar cells,^{7,8} and organic light-emitting diodes (OLEDs).^{9–15} The liquid anthracenes are believed to have prospects for future applications such as low-power color-tunable and light upconversion devices.^{16–18} Owing to the high stability and high-efficiency deep-blue fluorescence of anthracene compounds they were found to be particularly attractive for OLED applications.¹⁹ Recently, the interest in anthracenes has risen even more because of the demonstration of OLED efficiency boosting

Non-symmetric 9,10-diphenylanthracene-based deep-blue emitters with enhanced charge transport properties[†]

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Realization of efficient deep-blue anthracene-based emitters with superior film-forming and charge transport properties is challenging. A series of non-symmetric 9,10-diphenylanthracenes (DPA) with phenyl and pentyl moieties at the 2nd position and alkyl groups at *para* positions of the 9,10-phenyls were synthesized and investigated. The non-symmetric substitution at the 2nd position enabled to improve film forming properties as compared to those of the unsubstituted DPA and resulted in glass transition temperatures of up to 92 °C. Small-sized and poorly conjugated substituents allowed to preserve emission in the deep blue range (<450 nm). Substitution at the 2nd position enabled to achieve high fluorescence quantum yields (up to 0.7 in solution, and up to 0.9 in the polymer host), although it caused an up to 10-fold increase in the intersystem crossing rate as compared to that of the unsubstituted DPA. Further optimization of the film forming properties achieved by varying the length of the alkyl groups attached at the 9,10-phenyls enabled to attain very high hole drift mobilities (~5 × 10⁻³-1 × 10⁻² cm² V⁻¹ s⁻¹) in the solution-processed amorphous films of the DPA compounds.

capabilities *via* utilization of triplet–triplet annihilation (or triplet fusion)^{12,14} and thermally-activated delayed fluorescence.¹⁵ The latter phenomenon enabled to achieve a very high external quantum efficiency (16.5%) in anthracene-based OLED.

Generally, the unsubstituted anthracene is of less practical use in optoelectronics as it suffers from low fluorescence quantum yield (30%) in solution and ready crystallization in the films.¹ To overcome these shortcomings structural modifications of anthracene are commonly used. The most popular way to evade a high intersystem crossing rate is an introduction of various substituents into the 9th and 10th positions of molecular anthracene. This substitution enhances the strength of an allowed optical transition $S_0 \rightarrow S_1$ with the transition dipole moment lying along the short axis of the anthracene molecule.^{20,21} A well-known 9,10-diphenylanthracene (DPA) serves as a nice example of such enhancement boosting fluorescence quantum efficiency up to 95%.²² Although outof-plane twisted 9,10-phenyl moieties cause only a minimal decrease in the emission energy, which is important for preserving emission in the deep-blue range, they are insufficient to prevent crystallization of DPA films. The crystallization is detrimental as it severely limits the efficiency of OLED devices.²³ It was demonstrated that film forming properties of DPA can be improved either by introducing more bulky aryl-based substituents at the 9th and 10th positions^{9,11} or by

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incorporating additional moieties at the 2nd and 6th positions.^{24,25} Unfortunately, most of the DPA derivatives subjected to such modifications and exhibiting a glassy state showed poor hole drift mobility ($\mu_{\rm h}$), in the order of 10⁻⁷ cm V⁻¹ s⁻¹.^{26,27} Nevertheless, observations of remarkably higher μ_h for a few DPA derivatives were also reported.²⁸ For instance, DPA functionalized with arylamino²⁹ or pyridine³⁰ moieties resulted in carrier drift mobilities exceeding 10⁻³ cm² V⁻¹ s⁻¹. However, the downside of the bulky aromatic substituents was the extension of the π -conjugated electron system, which shifted the compound emission to longer wavelengths (>450 nm). Therefore, one of the challenges from the optoelectronic application point of view could be the realization of anthracenebased deep-blue emitters featuring fluorescence efficiencies close to DPA, though, in contrast to DPA, demonstrating good film forming properties and high carrier drift mobilities. Excellent emission and charge transport properties realized in the same functional layer accompanied with solution processability could make the anthracene emitters promising for simplified architecture deep-blue OLEDs.

To this end, a series of structurally modified non-symmetric 9,10-diphenylanthracene derivatives (Fig. 1) were synthesized and investigated. To enhance film forming properties of the DPA derivatives they were non-symmetrically substituted at the 2nd position by using either phenyl or pentyl moiety. The impact of different length alkyl groups attached at the *para* position of 9,10-phenyls on the fluorescence efficiency, concentration quenching and carrier drift mobility was also studied. The influence of various substituents on the electron density distribution in molecular orbitals, the energy spectrum of singlet and triplet manifolds, and oscillator strengths of the studied DPA derivatives was evaluated by density functional theory calculations, which were compared with experimental data.



Fig. 1 Chemical structures of the DPA derivatives studied in this work.

Experimental methods

Instrumentation

H1, C13 NMR spectra were measured using BRUKER ASCEND 400 (400 MHz) and Varian Unity Inova 300 (300 MHz) spectrometers. Purity of the synthesized materials was analyzed using Agilent Technologies 6890N Network GC System and Agilent Technologies 7890C GC systems gas chromatographs. Mass spectra were set using the Agilent Technologies 5975C gas chromatograph/mass selective detector (GC/MSD) system with the triple-axis detector. HRMS mass spectrometry analyses were carried out on a quadrupole, time-of-flight mass spectrometer (micrOTOF-Q II, Bruker Daltonik GmbH). Melting points of the materials were determined using the Thermo Scientific 9100 apparatus. Differential scanning calorimetry (DSC) measurements were carried out using the DSC 8500 (PerkinElmer) thermal analysis system at a heating–cooling rate of 10 °C min⁻¹ under nitrogen flow. Optical properties of the DPA derivatives were assessed in dilute 10^{-6} M tetrahydrofuran (THF) solutions and wet-casted films prepared from 5×10^{-3} M THF solutions. Absorption spectra were recorded on a UV-Vis-NIR Lambda 950 spectrophotometer (Perkin-Elmer). Fluorescence of the investigated compounds was excited by a 365 nm wavelength light from a Xe lamp (FWHM < 10 meV) and measured using a back-thinned CCD spectrometer PMA-11 (Hamamatsu) at room temperature. Fluorescence transients were measured using a time-correlated single photon counting system PicoHarp 300 (PicoQuant) utilizing a semiconductor diode laser (repetition rate 1 MHz, pulse duration 70 ps, emission wavelength 375 nm) as an excitation source. Fluorescence quantum yields $(\Phi_{\rm F})$ of the solutions were estimated using the integrated sphere method.³¹ An integrating sphere (Sphere Optics) coupled to the CCD spectrometer via optical fiber was also employed to measure $\Phi_{\rm F}$ of the films. Fluorescence concentration quenching effects of the DPA derivatives were analyzed by dispersing molecules in an inert polymer (polystyrene, PS) matrix and estimating $\Phi_{\rm F}$ dynamics vs. molecule concentration in the range of 0.1-100 wt%. The DPA derivatives dispersed in polystyrene films were prepared by dissolving the DPA derivatives and PS at appropriate ratios in THF solutions and then wet-casting the solutions on quartz substrates. Cyclic voltammetry experiments were performed on the Edaq ER466 Integrated Potentiostat System. Platinum wire, glassy carbon disk $[\emptyset$ 1.6 mm, \emptyset 3.0 mm], and Ag/AgCl were used as counter, working, and reference electrodes, respectively. In all cases, CV experiments were performed in DMF (N,N-dymethylformamide) with tetrabutylammonium perchlorate - as the supporting electrolyte (0.1 M) under Ar flow; concentrations of compounds were 0.002 M. The scan rate was 50 mV s⁻¹. Carrier drift mobility in the wet-casted neat films was measured by the xerographic time of flight (XTOF) method.³²⁻³⁴ The samples for the charge carrier mobility measurements were prepared as described earlier.35 The film thickness was in the range of 3–6 μ m. The ionization potentials (I_p) of the compound films were measured by the electron photoemission in air method as described elsewhere.36



Materials

The DPA derivatives **1–6** (see Fig. 1) were prepared according to the scheme presented in Fig. 2. A substituted benzene was acylated using phthalic anhydride, the resulting substituted benzoylbenzoic acid underwent an intramolecular cyclization upon the action of an inorganic acid, which led to the formation of 2-substituted anthraquinone. It reacted with arylmagnesium bromide; the resulting 9,10-diaryl-9,10-dihydroxydihydroanthracene was reduced, thus forming 2,9,10-trisubstituted anthracene.

(4-Phenylbenzoyl)-2-benzenecarboxylic acid. A 2 L glass bulb equipped with mechanical stirrer, thermometer and reflux condenser was placed in an ice bath and charged with 1.2 L dichloroethane, then cooled down to 0-5 °C. While stirring 139 g (0.9 mol) biphenyl, 120 g (0.9 mol) aluminium trichloride and 133 g (0.9 mol) phthalic anhydride were added at such a rate that the temperature remained within the 0 to +5 $^{\circ}$ C range. After all the reagents were introduced, the mixture was stirred for 0.5 h, then the ice bath was changed to a water bath and heated up to +40 °C. 120 g (0.9 mol) of aluminium chloride was added portionwise and the temperature kept in the 40-45 °C range. The hydrogen chloride released through the reflux condenser was absorbed in the sodium hydroxide solution. After all the aluminium chloride had been introduced, the reaction mixture was stirred at the same 40-45 °C for 2 h, then poured into an ice and 0.2 L hydrochloric acid mixture. The solid product was filtered off, washed three times with water and dried at 100 °C. 253 g of 2-(4-phenylbenzoyl)benzenecarboxylic acid was obtained, which was used in the next step without additional purification.

2-Phenylanthraquinone. A 2 L glass bulb was charged with 800 g of polyphosphoric acid and heated up to 160 $^{\circ}$ C, then in 20 min, 253 g (0.836 mol) of 2-(4-phenylbenzoyl)benzene-carboxylic acid was added and stirred for 4.5 h at 160–166 $^{\circ}$ C.

After this the mixture was cooled down to +140 $^{\circ}$ C and poured into 5 L of hot water and left for a night to cool down. The mixture was filtered, the solid was placed into a 10% aqueous potassium hydroxide solution, the mixture boiled for 0.5 h, filtered, the solid washed with water and filtered again. The solid was extracted with 1.3 L of toluene, concentrated; the remainder was distilled under vacuum, b.p. 220–275 $^{\circ}$ C/1 Torr. 126 g (0.443 mol) 2-phenylanthraquinone was obtained, yield 53%. M.p. 162–163 $^{\circ}$ C.

2-Pentylanthraquinone. 2-Pentylanthraquinone was prepared in a similar way; just the cyclization of 2-(4-pentylbenzoyl)benzenecarboxylic acid was carried out not in polyphosphoric acid, but in 5% oleum at 80 °C. M.p. 85 °C.

2-Pentyl-9,10-bis(4-methylphenyl)anthracene. A round 250 mL glass bulb was charged with 3.19 g (0.131 mol) magnesium powder and 100 mL dry tetrahydrofuran. 21.4 g (0.125 mol) 4-bromotoluene was added dropwise with constant stirring, then refluxed for 3 h till most of the magnesium dissolved. A solution of 3.5 g (0.0125 mol) 2-pentylanthraquinone in 30 mL tetrahydrofuran was added to this mixture dropwise at room temperature, then the resulting mixture was refluxed for 4 h. The mixture was cooled down to room temperature and poured into a saturated aqueous solution of ammonium chloride. The mixture was extracted using dichloromethane, then an organic layer separated and was evaporated.

To the residue 17 g (0.102 mol) potassium iodide, 14.7 g (0.167 mol) sodium dihydrophosphite and 50 mL anhydrous acetic acid were added and the whole mixture was heated at reflux for 3 h. The mixture was poured into water, extracted by dichloromethane and purified by column chromatography on silica gel, toluene was used as the eluent. The collected product was crystallized from acetone. 0.7 g (1.6 mmol) of a light yellow powder, m.p. 78-80 °C, was obtained, in 13% yield from 2-pentylanthraquinone. GC-MS: m/z 428.3. C₃₃H₃₂, calculated: FW 428.61. ¹H-NMR (400 MHz, CDCl₃): δ 7.744-7.675 (m, 3H), 7.493-7.383 (m, 9H), 7.329-7.285 (m, 2H), 7.234-7.208 (dd, $J_1 = 8.8$ Hz, $J_2 = 1.6$ Hz, 1H), 2.658 (t, J = 8 Hz, 2H), 2.575 (m, 6H), 1.607 (m, 3H), 1.318 (m, 3H), 0.890 (t, 3H). ¹³C-NMR (400 MHz, CDCl₃): δ 139.36, 136.95, 136.86, 136.82, 136.20(2), 131.27, 131.22, 130.20, 129.57, 129.10, 129.07, 128.89, 127.02, 126.98, 126.93(2), 124.72, 124.69, 124.43, 36.27, 31.53, 30.81, 22.53, 21.45, 21.42, 14.04.

According to the same procedure the rest of the 2,9,10-trisubstituted anthracenes were obtained.

2,9,10-Triphenylanthracene. A light yellow powder, crystallized twice from acetic acid and once from hexane was obtained. Yield 35%. M.p. 175–177 °C. GC-MS: m/z 406.3. $C_{32}H_{22}$, calculated: FW 406.52. ¹H-NMR (300 MHz, CDCl₃): δ 7.37–7.46 (m, 5H), 7.57–7.88 (m, 16H), 7.98 (s, 1H). ¹³C-NMR (300 MHz, CDCl₃): δ 124.8, 125.3, 125.4, 127.2, 127.3, 127.5, 127.6, 127.8(2), 127.9, 128.7, 129.1, 129.3, 130.3, 130.4, 130.6, 131.6, 131.7, 137.3, 137.6, 137.7, 139.2, 139.3, 141.4.

2-Phenyl-9,10-bis(4-methylphenyl)anthracene. A light yellow powder, crystallized from acetic acid and three times from hexane was obtained. Yield 22%. M.p. 209–211 °C. GC-MS: m/z 434.3. C₃₄H₂₆, calculated: FW 434.57. ¹H-NMR (300 MHz, CDCl₃): δ 7.98

(s, 1H), 7.87–7.29 (m, 19H), 2.58–2.59 (s, 6H). ¹³C-NMR (300 MHz, CDCl₃): δ 141.5, 137.7, 137.5, 137.4, 137.3, 139.3, 136.2, 136.1, 131.4, 130.4, 129.4(2), 129.0, 127.9, 127.6, 127.4, 127.3, 125.2, 125.1, 124.9, 21.6.

2-Phenyl-9,10-bis(4-*n***-hexylphenyl)anthracene.** A light yellow powder, crystallized from acetic acid and twice from hexane was obtained. Yield 26%. M.p. 105–107 °C.

GC-MS: m/z 574.5. $C_{44}H_{46}$, calculated: FW 574.84. ¹H-NMR (300 MHz, CDCl₃): δ 7.98 (s, 1H), 7.85–7.60 (m, 6H), 7.46–7.29 (m, 13H), 2.87–2.81 (t, J = 1.2 Hz, 4H), 1.83 (m, 4H), 1.53–1.43 (m, 12H), 1.00 (t, J = 2.4 Hz, 6H). ¹³C-NMR (300 MHz, CDCl₃): δ 142.4, 142.3, 141.5, 137.8, 137.3, 137.2, 136.3, 136.2, 131.4, 130.7, 130.4, 129.4, 129.0, 128.7(2), 128.0, 127.6, 127.4, 127.3, 125.2, 125.1, 124.9, 36.2(2). 32.1, 31.8, 31.6, 29.4(2), 22.9, 14.4.

2-Pentyl-9,10-diphenylanthracene. A light yellow powder, crystallized from acetone, was obtained. Yield 28%. M.p. 87–89 °C. GC-MS: m/z 400.3. C₃₁H₂₈, calculated: FW 400.55. ¹H-NMR (400 MHz, CDCl₃): δ 7.725–7.572 (m, 9H), 7.522–7.518 (d, J = 1.6 Hz, 4H), 7.501 (s, 1H), 7.450–7.215 (m, 3H), 1.612–1.580 (m, 4H), 1.326–1.289 (m, 4H), 0.881 (t, 3H). ¹³C-NMR (400 MHz, CDCl₃): δ 139.50, 139.30, 139.26, 136.88, 136.23, 131.39, 131.33, 130.06, 130.04, 129.42, 128.75, 128.39, 128.36, 127.39, 127.34, 127.07, 126.94, 126.89, 126.84, 124.85, 124.59, 124.57, 36.24, 31.48, 30.71, 22.50, 14.02.

2-Pentyl-9,10-bis(4-*n***-hexylphenyl)anthracene.** A light yellow powder, crystallized twice from acetone was obtained. Yield 23%. M.p. 64–65 °C. GC-MS: *m/z* 568.5. $C_{43}H_{52}$, calculated: FW 568.87. ¹H-NMR (400 MHz, CDCl₃): δ 7.744–7.675 (m, 3H), 7.482–7.394 (m, 9H), 7.330–7.286 (m, 2H), 7.234–7.208 (m, 1H), 2.852–2.797 (q, *J* = 8 Hz, 4H), 2.687–2.649 (t, *J* = 7.2 Hz, 2H), 1.851–1.795 (m, 4H), 1.639–1.575 (m, 2H), 1.511–1.298 (m, 17H), 0.995–0.906 (2t, 9H). ¹³C-NMR (400 MHz, CDCl₃): δ 142.02, 141.91, 139.26, 136.89, 136.38, 136.36, 136.25, 131.22, 131.18, 130.20(2), 129.58, 128.91, 128.36, 128.34, 127.06, 127.00, 126.96, 126.91, 124.69, 124.41, 36.21, 35.95, 31.83, 31.54, 31.48, 30.66, 29.21, 29.19, 22.69, 22.53, 14.15, 14.04.

Computational methods

Quantum chemical calculations of the DPA derivatives were performed using the density functional theory B3LYP method implemented in the Gaussian09 software package.³⁷ Ground-state geometries of molecular structures were optimized in a 6/31G basis set. Electronic excitation energies, oscillator strengths of the singlet and triplet transitions and spatial distributions of electron density for HOMO and LUMO for "freezed" structures were calculated using the semiempirical ZINDO procedure (for singlets only and for triplets only, respectively).

Results and discussion

Theoretical calculations

Fig. 3 demonstrates spatial electron density distribution in the HOMO and LUMO of the DPA derivatives **1–6** with optimized geometries. Phenyl groups at the 9th and 10th positions in the unsubstituted DPA are known to form a right angle with the



Fig. 3 HOMO and LUMO of the DPA compounds **1–6** calculated using the B3LYP/6-31G basis set. The positions of the short (denoted as S_0-S_1) and long (denoted as S_0-S_2) molecular axes of anthracene molecule are denoted in the top of the picture.

anthracene core, whereas in the studied non-symmetrically substituted DPA compounds **1–6** this angle in some cases reduces to about 80°. The 2-phenyl group in the compounds **1–3** is twisted with respect to the core by about 55°. Generally, the spatial distribution of electron density in the ground and excited states resembles that of the unsubstituted anthracene.³⁸ Only a small fraction of molecular orbitals extends towards the substituents. This extension towards the 2-phenyl group is somewhat more noticeable than towards the 9,10-phenyls.

The $S_0 \rightarrow S_1$ optical transition dipole moment of the anthracene lies along the short axis of the molecule, while the transition dipole moment of $S_0 \rightarrow S_2$ lies along the long axis. Therefore, introduction of various substituents at the

Table 1 Calculated transition energies for $S_0 \to S_1$ and $S_0 \to T_1/T_2$, and oscillator strengths for $S_0 \to S_1$ and $S_0 \to S_2$

Comp.	Transition energy of $S_0 \rightarrow S_1$ (eV)	Transition energy of $S_0 \rightarrow T_1/T_2$ (eV)	Oscillator strength of $S_0 \rightarrow S_1$	Oscillator strength of $S_0 \rightarrow S_2$
1	3.091	0.981/1.956	0.326	0.09
2	3.069	0.98/1.96	0.356	0.093
3	3.076	0.98/1.959	0.361	0.093
4	3.124	0.994/2.037	0.361	0.067
5	3.115	0.996/2.032	0.385	0.067
6	3.12	0.995/2.027	0.388	0.068
DPA	3.14	0.995/2.053	0.376	0.072
	Comp. 1 2 3 4 5 6 DPA	$\begin{array}{rl} & {\rm Transition} \\ {\rm energy \ of} \\ {\rm S}_0 \rightarrow {\rm S}_1 \\ {\rm Comp.} & ({\rm eV}) \end{array}$ $\begin{array}{rl} & 3.091 \\ {\rm 2} & 3.069 \\ {\rm 3} & 3.076 \\ \\ {\rm 4} & 3.124 \\ {\rm 5} & 3.115 \\ {\rm 6} & 3.12 \\ {\rm DPA} & 3.14 \end{array}$	$\begin{array}{c cccc} Transition & Transition \\ energy of \\ S_0 \rightarrow S_1 & S_0 \rightarrow T_1/T_2 \\ \hline Comp. & (eV) & (eV) \\ \hline 1 & 3.091 & 0.981/1.956 \\ 2 & 3.069 & 0.98/1.96 \\ 3 & 3.076 & 0.98/1.959 \\ \hline 4 & 3.124 & 0.994/2.037 \\ 5 & 3.115 & 0.996/2.032 \\ \hline 6 & 3.12 & 0.995/2.027 \\ DPA & 3.14 & 0.995/2.053 \\ \hline \end{array}$	$\begin{array}{c cccc} Transition & Transition \\ energy of \\ S_0 \rightarrow S_1 & energy of \\ (eV) & (eV) & S_0 \rightarrow T_1/T_2 \\ (eV) & (eV) & S_0 \rightarrow S_1 \end{array} \\ \begin{array}{c cccc} 0.326 \\ 0.381/1.956 & 0.326 \\ 0.381/1.956 & 0.326 \\ 0.381/1.959 & 0.361 \\ 0.981/1.959 & 0.361 \\ 0.981/1.959 & 0.361 \\ 0.981/1.959 & 0.361 \\ 0.991/2.037 & 0.361 \\ 0.996/2.032 & 0.385 \\ 0.312 & 0.995/2.027 & 0.388 \\ DPA & 3.14 & 0.995/2.053 & 0.376 \\ \end{array}$

9th and 10th positions increases the oscillator strength of the $S_0 \rightarrow S_1$ optical transitions, whereas the modifications at 2, 3, 6 and 7 positions mainly affect the $S_0 \rightarrow S_2$ transition. Table 1 displays calculated oscillator strengths and energies of the lowest singlet and triplet transitions of the DPA derivatives 1–6 and of the unsubstituted DPA. The $S_0 \rightarrow S_1$ transition energy of the DPA is estimated to be 3.14 eV. The energy reduces down to 3.115-3.124 eV with the introduction of the 2-pentyl substituent (compounds 4-6) and slightly more down to 3.069-3.091 eV with the introduction of the more conjugated 2-phenyl substituent (compounds 1-3). Calculated energies of the two lowest triplet states T₁ and T₂ of the DPA derivatives correlated well with the first singlet transition energies and were found to depend on the substitution at the 2nd position. For the compounds 4-6 possessing the 2-pentyl substituent the triplet energies were rather similar to those of the unsubstituted DPA (0.995/2.05 eV for T_1/T_2), whereas for the compounds 1-3 the T_1/T_2 energies were somewhat lower (0.98/1.9605 eV for T_1/T_2) due to the more conjugated 2-phenyl group. Although the differences in singlet and triplet energies of the compounds 1-3 and 4-6 are not significant, they can notably affect the rate of intersystem crossing thereby severely impacting photophysical and photoelectrical properties of the compounds. The oscillator strength of the dominating singlet transitions $S_0 \rightarrow S_1$ was found to be at least 4 times as large as that of the nearest $S_0 \rightarrow S_2$ transitions. The oscillator strength of the $S_0 \rightarrow S_1$ transition of the DPA derivatives 1-6 showed variations depending on the nature of substituents. The highest oscillator strength was obtained for the unsubstituted DPA (0.376) and for 2-pentyl-substituted compounds (0.361-0.388), meanwhile 2-phenyl-substituted DPA derivatives exhibited a slightly lower oscillator strength (0.326-0.361). The oscillator strength was slightly larger for the DPA compounds with longer alkyl groups attached at the para position of 9,10-phenyls due to the increased dipole moment of the $S_0 \rightarrow S_1$ transition. In contrast, the largest oscillator strength of the $S_0 \rightarrow S_2$ transition (having the dipole moment oriented along the longer molecular axis) was found for the 2-phenyl-substituted derivatives as compared to 2-pentyl-substituted analogues.

Fig. 4 illustrates the optimized geometry as well as the total energy and oscillator strength of the compounds **3** and **6**. The total energy and oscillator strength as a function of the dihedral



Fig. 4 (a) Molecular structures of the compounds **3** and **6**. β , the dihedral angle between the planes of anthracene and 4-hexylphenyl substituents. Bottom graphs: the calculated total energy of the ground state S_0 and the first excited state S_1 (upper picture) and oscillator strength of the $S_0 \rightarrow S_1$ transition (lower picture) as a function of the dihedral angle β for the compound **3** (b) and compound **6** (c). Vertical dashed lines mark energy minima of the S_1 state.

angle β (between the anthracene core and the phenyl substituents at 9th and 10th positions) are shown in Fig. 4(b). Since the twist angle of the labile phenyl group at the 2nd position of anthracene was previously shown to have a small effect on the transition energies and oscillator strengths,³⁹ the angle β served as the main reaction coordinate in the geometry optimization of the DPA compounds. The optimization of the total energies indicated flat energy minima of the So state with respect to the angle β persisting from about 70° to 110°, whereas the S₁ state exhibited two slightly non-symmetrical energy minima at the angles β of 70° and 110°. The barrier height between the minima was about 40 meV, which is close to the thermal energy (25 meV) at room temperature. The asymmetry in energy minima is obviously caused by the non-symmetrical substitution of the DPA compounds. The oscillator strengths had minima at the right angles β , though a rapid increase in the strengths was clearly observed with a larger deviation from this angle.

Thus theoretical calculations show that substitution at the 2nd position of DPA by phenyl or pentyl moieties weakly perturbs electronic transitions, while the 2,9,10-substitution ensures a complex geometry of the molecules, which can significantly influence film-forming and thereby charge transport properties.

Table 2 Thermal properties of DPA derivatives 1-6

Comp.	$T_{\rm m}^{\ a}$ (°C)	T_{g}^{b} (°C)		
1	209	71		
2	213	92		
3	101	7		
4	86	-1		
5	63	-10		
6	60	-24		
<i>a</i>				

^{*b*} The melting temperature. ^{*b*} The glass transition temperature.

Thermal properties

Thermal properties of the non-symmetric DPA derivatives were assessed by utilizing DSC. Melting (T_m) and glass transition (T_g) temperatures of the derivatives are summarized in Table 2. The typical DSC curves for the compounds 2 and 5 are presented in Fig. 5 and the rest of the thermograms are presented in Fig. S1 in the ESI.[†]

All the DPA compounds 1-6 exhibited similar DSC thermograms by demonstrating a melting signal only in the first heating scan with peaks centered at 101–209 $^\circ C$ and 60–86 $^\circ C$ for compounds 1-3 and 4-6, respectively. The additional low intensity melting signals at 174 $^\circ C$ and 106 $^\circ C$ were observed for compounds 2 and 3, respectively, which are possibly due to the presence of a different crystalline phase. An absence of crystallization peaks during the cooling indicated that the compounds were transformed into an amorphous phase. The second heating scan revealed glass transition temperatures of 7-92 °C for compounds 1-3 and -24-(-1) °C for compounds 4-6. The introduction of the 2-pentyl substituent remarkably lowered the $T_{\rm m}$ and $T_{\rm g}$. The continuous decrease of $T_{\rm m}$ and $T_{\rm g}$ was also observed with the increasing length of the alkyl groups attached at the 9,10-phenyls. It should be noted, that fluorescence measurements above the $T_{\rm g}$ temperature for samples 3-6 had just a minor impact on its properties (see Fig. S2 in the ESI[†]).

Absorption and fluorescence spectra

Absorption and emission spectra of the dilute solutions and neat films of the DPA derivatives **1–6** are displayed in Fig. 6. The detailed optical properties of all the derivatives and also of the



Fig. 5 DSC curves of the DPA compounds 2 (a) and 5 (b).



Fig. 6 Absorption (dashed line) and fluorescence (solid line) spectra of the DPA derivatives **1** (a), **2** (b), **3** (c), **4** (d), **5** (e) and **6** (f) in dilute 10^{-6} M THF solutions and neat films (thin solid lines).

unsubstituted DPA, which served as the reference compound, are summarized in Table 3. Note that for the compounds **3–6** optical measurements were performed at temperatures exceeding their glass transition temperatures. Absorption spectra of the DPA compounds **1–6** contain clearly resolved vibronic structures with the dominant 1st vibronic replica similarly to that observed in the spectra of unsubstituted DPA (see Fig. S3 in the ESI[†]) or

Table 3 Absorption and fluorescence data of the DPA derivatives $1\!-\!6$ and unsubstituted DPA in dilute ($\sim\!10^{-6}$ M) THF solutions and neat films

	Dilute solutior	Neat film		
Comp.	$\lambda_{\rm abs}^{\max a}$ (nm)	$\varepsilon^b (l \text{ mol}^{-1} \text{ cm}^{-1})$	$\lambda_{\rm FL}^{\max c}$ (nm)	$\lambda_{\rm FL}^{\max d}$ (nm)
1	363, 383, 404	13 000	422	453
2	365, 384, 405	12 500	425	456
3	365, 384, 405	10700	426	454
4	352, 370, 390	10050	416	441
5	353, 371, 391	11 500	419	444
6	353, 372, 391	13 100	421	450
DPA	355 374 394	13430	410	441

^{*a*} Absorption band maximum. ^{*b*} Molar absorption coefficient of the 0th vibronic transition maximum. ^{*c*} Fluorescence band maximum of dilute THF solution. ^{*d*} Fluorescence band maximum of the neat film.

Table 4 Fluorescence decay time constants, quantum yields, radiative and non-radiative decay time constants of the DPA derivatives **1–6** in 10⁻⁶ M THF solutions, neat films and 0.1 wt% in PS films

		Dilute solution			Neat film		PS matrix (0.1 wt% in PS)				
	Comp.	$\tau_{\rm F}^{\ a}$ (ns)	τ_{r}^{b} (ns)	$\tau_{\rm nr}^{\ c} ({\rm ns})$	${\Phi_{\mathrm{F}}}^d$	$\tau_{\rm F}^{\ e} ({\rm ns})$	${\Phi_{ m F}}^d$	$\tau_{\rm F}^{\ a}$ (ns)	$\tau_r^{\ b}$ (ns)	$\tau_{\rm nr}^{\ c} ({\rm ns})$	$\Phi_{\mathrm{F}}{}^{d}$
2-Phenyl	1	5.2	11.6	9.5	0.45	0.45 [70%] 0.95 [26%] 4.09 [4%]	0.06	8	14.5	17.8	0.55
	2	5.1	10.6	9.7	0.48	4.09 [470] 0.24 [57%] 1.07 [30%]	0.03	6.45	10.9	15.3	0.59
	3	5	10.2	9.8	0.49	$\begin{array}{c} 3.48 \\ [14\%] \\ 0.83 \\ [55\%] \\ 3.41 \\ [45\%] \end{array}$	0.06	6.96	10.7	19.9	0.65
2-Pentyl	4	6.2	9.1	19.4	0.68	2.98 [82%] 1.03 [13%]	0.27	9.69	11	80.8	0.88
	5	5.8	8.5	18	0.68	12.48 [6%] 0.66 [9%] 3.05 [76%] 8.55 [15%]	0.3	8.75	11.1	41.7	0.79
	6	5.6	7.9	19.3	0.71	1.15 [7%] 5.86 [76%] 16.56 [18%]	0.43	8.36	10	51.3	0.84
DPA		6	6.4	100	0.94	0.64 [17%] 2.66 [44%] 7.62 [39%]	0.26	8.1	8.3	405	0.98

^a Fluorescence decay time. ^b Radiative decay time. ^c Non-radiative decay time. ^d Fluorescence quantum yield. ^e Fluorescence decay time of neat films.

other various DPA derivatives due to the presence of the rigid anthracene core.^{40–42} Non-symmetric substitution at the 2nd position obviously increases lability of the anthracene structure thus making vibronic replica less pronounced.⁴⁰ The lowest energy vibronic bands in the absorption spectrum of the 2-phenyl substituted DPA compounds **1–3** peak at 405 nm, whereas the bands of the 2-pentyl substituted counterparts **4–6** are shifted more in the UV (at about 391 nm) due to the worse π -conjugation of the substitutent. The molar extinction coefficient of the derivatives does not exceed that of the unsubstituted DPA ($\varepsilon = 13400 \text{ Lmol}^{-1} \text{ cm}^{-1}$) and varies between 10 000 and 13 000 L mol⁻¹ cm⁻¹.

Emission spectra of the DPA compounds **1–6** in the dilute solution also express vibronic bands; however a lack of mirror images between absorption and emission implies flexibility of the molecules and geometrical transformations occurring in the excited state in agreement with DFT calculation results. In accordance with the absorption spectra, fluorescence bands of more conjugated 2-phenyl-substituted DPA derivatives **1–3** are located at 422–426 nm, and thus are slightly redshifted as compared to those of the less conjugated 2-pentyl-substituted DPA counterparts **4–6** peaking at 416–421 nm. To compare, the 0th vibronic replica of the unsubstituted DPA in a solution was observed at 409 nm.

Fluorescence spectra of the neat films of the DPA derivatives **1–6** are slightly redshifted as compared to the spectra of their dilute solutions, which is due to the enhanced intermolecular interactions in the solid state. The films of the compounds **1–3** and **4–6** emit in the deep blue region with maxima positioned at 453–456 nm and 441–450 nm, respectively. CIE color coordinates of the emitters are displayed in Fig. S4 in the ESI.† A noticeable vibronic structure in the fluorescence bandshapes

of the DPA derivatives 1–4 points out dense molecular packing in the films, whereas nearly structureless shapes observed for the compounds 5–6 imply more random molecular arrangement, which is typical for amorphous films. A weak long-wavelength tail observed in the fluorescence spectra of compounds 1–3, which is especially well pronounced in the compound 2 showing a small shoulder at 580 nm, is likely caused by excimer states formed as a result of denser molecule packing of the 2-phenyl-substituted DPA. Excimer bands typically lower the fluorescence quantum yield (Φ_F), which is exactly the case of compounds 1–3, yielding 5 to 10 times lower Φ_F values as compared to that of 4–6 compounds bearing 2-pentyl substituents (see Table 4). This also adversely affects color purity of the films by shifting color coordinates closer to the white point of the chromaticity diagram.

Thus, in spite of enhanced electron–vibronic interaction, introduction of poorly-conjugated substituents at the 2nd position weakly affects electronic transition energies ensuring deep-blue emission in both non-interacting molecules and aggregate states. The small differences in transition energies, however might result in dramatic changes of excited state relaxation pathways, as discussed below.

Excited state relaxation

Estimated fluorescence quantum yields ($\Phi_{\rm F}$) of the DPA derivatives in dilute solutions were found to range from 0.45 to 0.49 for the compounds **1–3** and from 0.68 to 0.71 for the compounds **4–6** (see Table 3). As compared to $\Phi_{\rm F}$ of the unsubstituted DPA, which is close to 1.0, significantly lower quantum yields of the DPA derivatives indicate a moderately high rate of the non-radiative recombination processes. It is known that in planar and rigid molecules like anthracene,

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the non-radiative decay is caused entirely by the intersystem crossing to triplet states.^{21,43} Efficient intersystem crossing results from the proximity of higher-lying triplet states (T₂ or higher) and the singlet state S₁. For example, in the case of crystalline anthracene, the S₁ is located below the T₁ level, and thus $\Phi_{\rm F}$ is increased to almost 1.0. Simple alteration of the anthracene core, like introduction of phenyl groups at 9th and 10th positions, as in 9,10-diphenylanthracene, can easily realign singlet and triplet energies resulting in close to unity quantum yields.³⁰ However, conversion of the symmetric DPA structure to non-symmetric, for instance, by additional substitution at the 2nd position with the phenyl group (compounds 1-3) might not only affect energy alignment, but also enhance the electron-vibronic coupling, which can efficiently deactivate the excited state *via* non-radiative intramolecular torsions.^{44,45} Indeed, 2-phenyl-substituted DPA compounds 1-3, exhibit somewhat lower fluorescence efficiencies as compared to those of 2-pentyl-substituted analogues suggesting the presence of the torsional motions. To discriminate between the two effects additional experiments, where one of the effects is fully eliminated, are needed. The results of these experiments will be discussed below.

 $\Phi_{\rm F}$ values of the neat films of the DPA derivatives were found to be considerably lower as those of their dilute solutions. $\Phi_{\rm F}$ values of only 0.03-0.06 were obtained in 2-phenyl-substituted DPA compounds 1-3, whereas 0.27-0.42 values were estimated for the 4-6 compounds with 2-pentyl groups. Intermolecular interactions in the films, which are known to promote exciton migration, and thus enhance the possibility for the excitons to be captured by the quenching sites (lattice distortions, impurity traps or other defects) are responsible for this $\Phi_{\rm F}$ lowering and depend on intermolecular separation. Obviously, only a 2-fold drop in $\Phi_{\rm F}$ observed for the neat films of compounds 4–6 as compared to their solution in contrast to a roughly 10-fold drop observed for the compound 1-3 neat films indicates that the 2-pentyl moieties more effectively suppress aggregate formation as the 2-phenyl groups. This result is well supported by the long-wavelength tails observed in the fluorescence spectra of the neat films of compounds 1-3 being attributed to the excimer emission (see Fig. 6) and signifying a reduced average intermolecular distance.

Excited state relaxations dynamics of the DPA derivatives was assessed by measuring fluorescence decay transients. The transients of the compound dilute solutions and neat films are shown in Fig. 7, whereas extracted fluorescence lifetimes (τ_F) are listed in Table 4. Fluorescence transients of the DPA derivatives **1–6** in dilute solutions follow a single-exponential decay profile with τ_F of 5.0–6.2 ns similar to that of the unsubstituted DPA ($\tau_F = 6.0$ ns). In contrast, fluorescence transients of the neat DPA films exhibit highly non-exponential decay profiles. The non-exponential temporal profile accompanied by the redshifted fluorescence bands of the solid films is a clear signature of energy transfer occurring *via* exciton hopping through the localized states in disordered or partly disordered media.^{46,47} The fluorescence decay profiles were fitted by using the three-component exponential decay model to reveal the major component (see Table 4).



Fig. 7 Fluorescence transients of DPA derivatives in THF solutions and neat films. Lines indicate single or double exponential fits to the experimental data. (a) Compounds **1–3**. (b) Compounds **4–6**. The excitation wavelength is 375 nm (repetition rate 1 MHz, pulse duration 70 ps).

The fractional intensity of each component, which signifies the actual contribution of the component to the overall excitedstate decay, is indicated in the brackets next to the $\tau_{\rm F}$ value. A considerably faster excited state decay of the compound neat films as compared to that of solutions indicated enhanced excitation migration and migration-assisted non-radiative relaxation at the quenching sites.

To evaluate the contribution of radiative and non-radiative relaxation rates and to reveal the dominant mechanisms determining differences in the optical properties of the compounds 1–3 and 4–6, radiative (τ_r) and non-radiative (τ_{nr}) decay time constants were calculated (see Table 4). The time constants were calculated using the following relations:

$$\tau_{\rm r} = \tau_{\rm F} / \Phi_{\rm F}, \ \tau_{\rm nr} = \tau_{\rm F} / (1 - \Phi_{\rm F}),$$
 (1)

where the term τ_{nr} takes into account all the possible nonradiative decay pathways including intersystem crossing to triplet states, which is considered to be very important in the anthracene-based compounds.^{1,48}

Alteration of the intersystem crossing rate

Despite the similar fluorescence lifetimes of the two series of DPA derivatives **1–3** and **4–6** in solution, the series show different behavior of the radiative and non-radiative relaxation processes. Radiative decay times of the compounds are

rather similar, *i.e.* the average τ_r is 10.8 ns and 8.5 ns for the compound series 1-3 and 4-6, respectively, whereas nonradiative time constants of these series differ by a factor of 2. τ_{nr} is found to be significantly shorter, and so the non-radiative relaxation rates are faster, for the 2-phenyl-substituted DPA compounds 1–3 ($\tau_{\rm nr} \approx 9.7$ ns) as compared to those bearing the 2-pentyl moiety, compounds **4–6** ($\tau_{\rm nr} \approx 18.9$ ns). The 2-fold enhancement of non-radiative decay rates in the compounds 1-3 can be associated with the intensified intramolecular torsions induced by the twisted phenyl group attached at the 2nd position of the DPA core, although $\tau_{\rm nr}$ enhancement may also be promoted by the enhanced intersystem crossing rate due to the 2-phenyl substituent, which can invoke better triplet and singlet energy alignment. To differentiate between the two possible mechanisms, the DPA compounds were dispersed in a rigid polystyrene (PS) matrix at a low mass percentage (0.1 wt%). Such low molecular concentration in the matrix prevented the DPA molecules from interacting while simultaneously inhibiting their intramolecular motions. Estimated fluorescence lifetimes, quantum yields, radiative and non-radiative decay time constants for the DPA derivatives 1-6 as well as for the unsubstituted DPA in PS matrices are summarized in Table 3 for comparison. Fluorescence decay transients of the DPA derivatives 1-6 dispersed in the polystyrene (PS) matrix are provided in Fig. S5 in the ESI.†

It is worth noting that the fluorescence quantum yield of the unsubstituted DPA in solution and the rigid PS matrix is nearly the same and approaches 100%. This unambiguously indicates that phenyl moieties at the 9,10-positions of the DPA core are not involved in torsional motions, and thus, do not contribute to the non-radiative deactivation of the excited state. This is explained by the perpendicular orientation of the 9,10-phenyls with respect to the core, which ensures their stiffness and resistance to twisting. Consequently, only the phenyl group linked to the DPA core at the 2nd position could invoke nonradiative deactivation via the intramolecular torsions. A comparison of the $\Phi_{\rm F}$ of the compounds 1–3 with the 2-phenyl moieties in dilute solution and the PS matrix shows a slight increase of the $\Phi_{\rm F}$ in the rigid matrix (from ~0.47 in solution to ~ 0.60 in the PS matrix) mainly due to the decreased nonradiative decay time. However a similar increase of $\Phi_{\rm F}$ is also observed for 4-6 derivatives without these moieties (from ~ 0.69 in solution to ~ 0.84 in the PS matrix), where torsional motions are absent. This result clearly rules out the intramolecular torsions as the key-mechanism responsible for enhanced non-radiative relaxation of the compounds 1-3 and suggests enhanced intersystem crossing to triplet states to play the decisive role. As in the case of solutions, τ_r values of the DPA derivatives 1-3 and 4-6 in the PS matrix are estimated to be rather similar, 12 ns and 10.7 ns, respectively, whereas τ_{nr} values of the compounds 1-3 are found to be up to 4 times shorter than those of the compounds 4-6. Similarly to the compound solutions, enhanced non-radiative relaxation in PS matrices for compounds 1-3 can be attributed to the 2-phenyl moieties induced enhanced intersystem crossing to triplet states. In the case of 2-pentyl groups, most likely the misalignment of the first singlet and higher-lying triplet states is larger making the intersystem crossing rate not so efficient. This results in longer $\tau_{\rm nr}$ and thus higher $\Phi_{\rm F}$.

The importance of the non-symmetric substitution at the 2nd position of the DPA derivatives to the optical properties can be confirmed by comparing their radiative and non-radiative decay rates (or time constants) with those of the reference compound, the unsubstituted DPA. The radiative decay time of the solutions of DPA derivatives bearing either 2-phenyl or 2-pentyl moieties differs by less than twice as compared to that of the reference DPA. Meanwhile the difference in the nonradiative decay time of all the derivatives with respect to the reference is dramatic, *i.e.* τ_{nr} is one order of magnitude shorter for the compounds with 2-phenyl moieties (1-3) and 5 times shorter for those with 2-pentyl moieties (4-6). An analogous behavior of τ_r and τ_{nr} with respect to those of the reference DPA is also observed for the DPA derivatives in the PS matrix. This result again verifies the importance of the type of substituent linked to the 2nd position of the DPA in governing the nonradiative relaxation processes via the intersystem crossing to triplet states.

The influence of the alkyl group length attached at the *para* position of 9,10-phenyls on the optical properties of the DPA derivatives in a dilute solution or the polymer matrix is insignificant. The alkyl groups become by far important in the film formation, fluorescence concentration quenching and carrier transport properties as will be discussed below.

Fluorescence concentration quenching

Fluorescence concentration quenching is a key factor, which determines the applicability of a compound for OLED application.49,50 Utilization of an emissive material at high concentrations (typically of more than a few percent) in a host material is limited by the enhanced molecule interaction, and in severe cases, physical molecule agglomeration activating exciton migration and migration-induced exciton quenching, and therefore is detrimental to the device performance.51,52 Concentration quenching in the DPA derivatives was evaluated by dispersing DPA molecules in a rigid and transparent polystyrene (PS) host while measuring fluorescence quantum yield changes vs. concentration in the broad range of concentrations 0.1-100 wt% (see Fig. 8). All the DPA derivatives 1-6 demonstrated negligible fluorescence concentration quenching up to 8 wt% in PS. The rate of concentration quenching for the compounds 1-3 featuring the 2-phenyl substituent is very similar (Fig. 8a). $\Phi_{\rm F}$ quenches just slightly faster as compared to that of the unsubstituted DPA. Conversely, concentration quenching of the compounds 4-6 possessing the 2-pentyl substituent is found to be dependent on the alkyl group length (Fig. 8b). The shorter alkyl groups attached at the 9,10-phenyls of the DPA result in more rapid quenching as compared to the longer groups. This is evidently caused by the reduced intermolecular separation, and thus enhanced intermolecular interaction, due to the smaller alkyl spacers. Importantly, the quenching with increasing the concentration of 2-pentyl-substituted DPA compounds 4-6 in the PS matrix is slower as compared to that of the



Fig. 8 The normalized fluorescence quantum yield of the DPA compounds **1–3** (a) and **4–6** (b) as a function of their concentration in the PS matrix. Lines are guides to the eye. Absolute values of fluorescence quantum yields are displayed in insets.

reference DPA, and moreover, slower than that of the 2-phenyl substituted DPA **1–3**. The obtained results highlight a significance of the 2-pentyl moieties in more effective suppression of intermolecular interaction resulting from looser molecular packing than that caused by the 2-phenyl groups.

Electrochemical properties

Cyclic voltammetry was employed to elucidate the energies of HOMO and LUMO of the DPA derivatives **1–6** (see Fig. 9 and Table 5). All the compounds demonstrated non-reversible oxidation–reduction processes by applying a low scan rate (50 mV s⁻¹) in the range of positive potentials. For the compounds **2** and **3**,

 Table 5
 Electrochemical properties (oxidation and reduction potentials, energies of HOMO and LUMO levels, electrochemical and optical band-gaps) of the DPA derivatives 1–6

Comp.	$\begin{array}{c}E_{\rm FC}^{1/2\ a}\\ {\rm (eV)}\end{array}$	$E_{\rm ox} {\rm onset}^b$ (eV)	$\frac{E_{\rm red}}{(\rm eV)}^c$	$\frac{E_{\rm HOMO}}{\rm (eV)}^d$	E_{LUMO}^{e} (eV)	E_{g}^{elf} (eV)	$E_{g}^{\text{opt.}g}$ (eV)
1 2 3 4 5 6	0.52	1.03 0.98 0.99 1.11 1 1.03	-1.71 -1.73 -1.73 -1.84 -1.88 -1.88	-5.31 -5.26 -5.27 -5.39 -5.28 -5.31	$\begin{array}{r} -2.58 \\ -2.55 \\ -2.56 \\ -2.45 \\ -2.4 \\ -2.41 \end{array}$	2.72 2.74 2.72 2.94 2.88 2.91	2.94 2.94 2.93 3.07 3.04 3.04

^{*a*} Half-wave potential *vs.* Ag/AgCl for reversible oxidation reduction of ferrocene. ^{*b*} Onset of oxidation potential for the HOMO level. ^{*c*} Half-wave potential *vs.* Ag/AgCl for the LUMO level. ^{*d*} HOMO and LUMO energy, $E_{\rm HOMO}/E_{\rm LUMO} = -(4,8 + E_{\rm ox}^{1/2}/E_{\rm red}^{1/2} - E_{\rm FC}^{1/2})$. ^{*e*} HOMO and LUMO energy, $E_{\rm HOMO}/E_{\rm LUMO} = -(4,8 + E_{\rm ox}^{1/2}/E_{\rm red}^{1/2} - E_{\rm FC}^{1/2})$. ^{*f*} Electrochemical bandgap, $|E_{\rm g}^{\rm cl}| = |E_{\rm LUMO}| - |E_{\rm HOMO}|$. ^{*g*} Optical bandgap, estimated from the onset of the absorption band.

a quasi-reversible oxidation–reduction potential was observed after the scan rate was increased to 200 mV s⁻¹, whereas in the range of negative potentials quasi-reversible oxidation–reduction potentials were observed for all the DPA compounds independent of the scan rate.

1–3 and 4–6 series of the derivatives exhibited rather similar HOMO energies, ~5.28 eV and ~5.32 eV, respectively, whereas somewhat greater variation in LUMO energies between the series was obtained. The compounds 1–3 showed lower LUMO levels (~2.56 eV) as compared to the levels (~2.42 eV) estimated for the compounds 4–6 (see Table 5). The decreased LUMO energy observed for the compounds bearing the more conjugated 2-phenyl substituent is likely a cause of the lower $\Phi_{\rm F}$ due to the enhanced intersystem crossing rate.

Charge transport properties and ionization potential

Achieving high carrier mobility in the amorphous films requires a good balance of the film forming properties and charge carrier transfer rate. The impact of alkyl group length (C0, C1 and C6) on the charge transport properties of the two non-symmetricallysubstituted DPA compound series bearing 2-phenyl (compounds 1, 2, 3) and 2-pentyl moieties (compounds 4, 5, 6) was investigated. The wet-casted amorphous films of the DPA derivatives



Fig. 9 Cyclic voltammograms of the dilute solutions of compounds 1-3 (a) and 4-6 (b) in *N*,*N*-dimethylformamide at 50 mV s⁻¹ scan rate. Compound concentration was 0.002 M with tetrabutylammonium perchlorate (0.1 M) used as the electrolyte.

were investigated by using the XTOF method. The reference DPA was found to form polycrystalline neat films with low photosensitivity, which made XTOF measurements practically impossible. Introduction of the additional phenyl or pentyl moieties at the 2nd position and the methyl groups at the para positions of 9,10-phenyls (compounds 1, 2, 4, 5) completely suppressed DPA crystallization and ensured formation of amorphous neat films. It is worth emphasizing that these modified non-symmetric DPA derivatives expressed very high hole drift mobilities (μ_h) well exceeding 10⁻³ cm² V⁻¹ s⁻¹ at 1 MV cm⁻¹ electric field. The obtained drift mobility values varied from 4.6 \times 10⁻³ cm² V⁻¹ s⁻¹ in the compound 1 up to almost $1 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in the compound 4 at an electric field of 1 MV cm⁻¹ (see Fig. 10 and Table 6). XTOF transients measured at different voltages are displayed in Fig. S6 in the ESI.[†] Although alkyl groups at the para positions of 9,10-phenyls negligibly affected optical properties of the DPA compounds, their length severely altered the molecular packing, and thus charge carrier transport properties. Introduction of the methyl group (compound 2) slightly enhanced the hole drift mobility and increased the glass transition temperature, whereas analogous substitution for the compounds possessing the 2-pentyl moiety, worsened the drift mobility and the glass transition temperature. This can be attributed to the better steric hindrance effect of the twisted 2-phenyl substituent. Further extension of the alkyl group length up to C6 atoms (compounds 3 and 6) strongly impaired film forming properties and made XTOF



Fig. 10 Hole drift mobility as a function of the applied electric field in the neat films of the DPA compounds **1–6**. Lines are guides to the eye. The average film thickness is indicated.

Table 6Hole drift mobilities and ionization potentials of the amorphousneat films of DPA derivatives **1–6**

Comp.	${\mu_{\rm h}}^a ({ m cm}^2 { m V}^{-1} { m s}^{-1})$ @ 1 MV ${ m cm}^{-1}$	$I_{\rm p}^{\ b}$ (eV)	
1	$4.6 imes10^{-3}$	5.82	
2	$6.5 imes10^{-3}$	5.74	
3	_	5.77	
4	9.9×10^{-3}	5.9	
5	$6.5 imes10^{-3}$	5.83	
6	_	5.81	

^a Hole drift mobility of ambient atmosphere processed neat films.
 ^b Ionization potential of ambient atmosphere processed neat films.

measurements impossible. Samples 3 and 6 were not suitable for XTOF measurements because of high plasticity of their neat film. The injected carriers were found to distribute unevenly causing film deformation by electrostatic forces in the sites with high carrier density, and thus making carrier drift mobility unattainable. The continuous increase of $\mu_{\rm h}$ with the applied electric field for all the DPA derivatives implies the governing role of energetic disorder⁵³ in the charge carrier transport of the wet-casted amorphous films. The high drift mobilities obtained for the non-symmetric DPA derivatives 1, 2, 4, 5 are well above usually reported values estimated in other DPA compounds.^{26,27} However remarkably high $\mu_{\rm h}$ values (up to 10^{-2} cm² V⁻¹ s⁻¹) have also been achieved by introducing electron donating 9,10-arylamino units into the anthracene core.²⁹ However, the arylamino substitution enlarged conjugation of the DPA compound resulted in an undesirable shift of the emission color to longer wavelengths (>450 nm).

Ionization potentials (I_p) of the DPA derivatives **1–6** showed very similar values 5.74–5.9 eV comparable to those reported for 2-phenyl-substituted anthracene.³⁹

Conclusions

Realization of anthracene-based deep-blue emitters exhibiting fluorescence efficiency close to that of 9,10-diphenylanthracene (DPA), though, in contrast to DPA, demonstrating good film forming properties and high carrier drift mobilities was attempted. To this end, a series of structurally modified nonsymmetric DPA derivatives with the phenyl and pentyl moieties at the 2nd position and the alkyl groups at the 9,10-phenyls were synthesized and investigated. Relatively small and poorly conjugated phenyl and pentyl substituents enabled to improve film forming properties by resulting in glass transition temperatures of up to 92 °C (for the 2-phenyl moiety), meanwhile only up to -1 °C (the for 2-pentyl moiety). The poorly conjugated 2-phenyl and 2-pentyl substituents weakly impacted the transition energy with respect to the unsubstituted DPA resulting in the deep-blue emission with emission maxima below 450 nm. Absorption and fluorescence measurements supported by DFT calculations revealed relatively small shifts in singlet and triplet transition energies (<100 meV), which however, caused drastic changes in the intersystem crossing rate. Fluorescence measurements in dilute solution and the rigid polymer matrix enabled to distinguish between the two possible pathways of non-radiative recombination, i.e. intramolecular torsions and intersystem crossing, and demonstrated the dominant role of the latter process. Roughly a 10-fold and 5-fold increase in the intersystem crossing rate was obtained in the 2-phenyl- and 2-pentyl-substituted DPA compounds, respectively. Despite the large enhancement of the intersystem crossing rate the DPA compounds showed relatively high fluorescence quantum yields, up to 0.7 in a solution and up to 0.9 in a polymer host. The DPA derivatives exhibited almost no concentration quenching of fluorescence up to 8 wt% in the PS matrix. Substitution at the 2nd position by the pentyl moiety resulted in less pronounced concentration

quenching as compared to the substitution by the 2-phenyl group and also with respect to the unsubstituted DPA. The influence of the alkyl groups attached at the *para* position of 9,10-phenyls on the optical properties was found to be insignificant, whereas they strongly affected film forming and charge transport properties. It is worth noting that the non-symmetric DPA derivatives expressed very high hole drift mobilities of up to 4.6×10^{-3} cm² V⁻¹ s⁻¹ for 2-phenyl-substituted compounds and up to almost 1×10^{-2} cm² V⁻¹ s⁻¹ for 2-pentyl-substituted analogues at an electric field of 1 MV cm⁻¹.

Further optimization of the DPA at the 2nd position by introducing non-conjugated and more branched or bulky substituents should enable to achieve an even higher glass transition temperature and carrier drift mobility while preserving the high fluorescence efficiency.

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