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Impact of non-symmetric 2,9,10-aryl substitution on charge transport and optical properties of anthracene derivatives

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ABSTRACT

A new methodology for the synthesis of non-symmetric 2,9,10-arylanthracenes is proposed. The anthracenes were intentionally decorated with non-symmetric aryls to improve charge transport properties. The impact of non-symmetric aryl substituents on optical and electrical properties was thoroughly studied. Non-symmetric 9,10-aryl substituents ensured blue emission in the range of 422–436 nm and fluorescence quantum efficiency of ca. 0.45, while the type of substituents had a minor impact on excited state deactivation due to their twisted configuration. Optical properties of the compounds obtained in dilute solution and in a rigid polymer matrix revealed the dominating non-radiative decay mechanism to be due to the intersystem crossing (ISC), which was mainly governed by 2-phenyl substitution. Favourable alignment of the singlet and triplet energy levels for efficient ISC was confirmed by density functional theory calculations. Some of the non-symmetrically substituted anthracene derivatives showed very high hole drift mobilities reaching 10^{-2} cm^2/Vs in solution-processed neat films.

1. Introduction

Anthracene is well-known aromatic compound used for drugs [1], anticancer agents [2], chemosensors [3], and as scintillators for high energy particle detection [4]. Owing to the extended π-electron system anthracene derivatives find a large variety of applications in organic optoelectronic devices including thin-film transistors [5,6], solar cells [7,8], and light emitting diodes (OLEDs) [9–14]. Easy modification, deep-blue emission and high photostability make them particularly attractive for manufacture of blue emitters. Moreover, the unique feature of anthracene compounds is its perfect energy level alignment for triplet–triplet annihilation (TTA) enhanced emission, when fusion of two triplet excitons results in energy up-conversion and boosting the fluorescent OLEDs efficiency with additional 37.5% [15]. Anthracene OLEDs employing TTA overcome the theoretical 5% limit of quantum efficiency for conventional OLEDs (with extraction efficiency of 0.2) and reaches values up to 11% [9,14,16–18]. Anthracene derivatives were also applied for engineering of thermally-activated delayed fluorescence emitters [19]. Low-power colour-tunable and light upconversion devices is another important example of the application of TTA, when the low energy photons are converted to high energy ones applying various anthracene derivatives [20].

Owing to their flat and rigid backbone, unsubstituted anthracene, suffers from crystallization induced fluorescence quenching and low fluorescence quantum yield ($\Phi_F = 0.3$) [21]. Substitution at the 9th and 10th position with phenyl groups (or other aryl groups [22–24]) remarkably decreases ISC rate and enhances fluorescence quantum yield up to the unity [24,25]. However the structural modifications with phenyl moieties at 9th and 10th positions are insufficient to eliminate unwanted crystallization and fluorescence quenching in the films [10,26]. Further modifications with more bulky aryl groups at 9th and 10th positions [17,26–29] greatly reduce the intermolecular interactions and enable to achieve amorphous thin films. The additional substitution at the 2nd position also helps to ensure amorphous state and improves charge transport properties of the films [10,30]. However the additional π-conjugation extension towards the long axis of the molecule results in the reorganization of singlet and triplet energy levels when the T_n level emerges below S_1 leading to the efficient ISC recombination

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and low Φ_F [26]. Despite the importance of the intersystem crossing, recent studies have suggested that the vibrational relaxation may also be the important pathway for the non-radiative decay in anthracene derivatives [31,32]. Modification of anthracene core with various alkyl groups allows to obtain amorphous thin films, however those anthracene derivatives like 9,10-di(2-naphthyl)anthracene possess low hole drift mobility (μ_h) [33–35] of about 10^{-7} – 10^{-5} cm^2/Vs. Nevertheless, observations of remarkably higher μ_h, exceeding 10^{-3} cm^2/Vs were also reported for a few anthracene compounds when symmetrically functionalized with arylamino [36] or pyridine [37] moieties. However, the presence of highly-polar substituents resulted in the undesirable redshift of the compound's emission wavelength.

Thus non-symmetric modification of anthracene derivatives by aryl substituents seems to be a promising way of chemical engineering to improve the film-forming, charge-transfer and emissive properties of the functional layers, however the impact of such modification on charge transport and energy level alignment should be thoroughly addressed.

In this work the new synthesis methodology and properties of a series of 2-phenylanthracene derivatives non-symmetrically modified at 9th and 10th positions are presented. The impact of the non-symmetric substitution was evaluated by estimating thermal, electrochemical, optical and charge-transport properties of the compounds. Remarkable improvement of the charge transport properties for some of the non-symmetric 2,9,10-anthracenes is validated. Disclosed energy level scheme, supplemented by analysis of excitation relaxation pathways, enables us to distinguish the dominant role of intersystem crossing and the impact of the introduced substituents on ISC rate variation.

2. Experimental methods

2.1. Instrumentation

Solvents were purified using standard procedure. Reactions were carried out under dry argon atmosphere at magnetic stirring. All reactions and the purity of the synthesized compounds were monitored by gas chromatography using *Agilent Technologies* 7890A GC System with triple axis detector 5975C inert XL MSD and *Agilent Technologies* 6890N Network GC System, and thin layer chromatography using Silica gel 60 F_{254} aluminium plates (*Merck*). Purification of synthesized compounds was performed by preparative column chromatography using silica gel Kieselgel 60 0.06–0.2 mm ^{1}H and ^{13}C NMR spectra were recorded with a *Varian Unity* INOVA spectrometer (300 MHz) or *Brucker* ASCEND 400 (400 MHz) in chloroform-d_3 or benzene-d_6, using residual solvent signal as an internal standard. HRMS spectra were obtained on a mass spectrometer Dual-ESI Q-TOF 6520 (*Agilent Technologies*). All melting points were determined using *Digital Melting Point Apparatus* IA9000 Series. Differential scanning calorimetry (DSC) measurements were carried out using DSC 8500 (*PerkinElmer*) thermal analysis system at a heating/cooling rate of 10 C/min under nitrogen flow. Optical properties of the 2,9,10-arylanthracene derivatives were assessed in dilute 10^{-6} M tetrahydrofuran (THF) solutions and wet-casted thin films prepared from 5×10^{-3} M THF solutions. Absorption spectra were recorded on a UV–Vis–NIR spectrophotometer Lambda 950 (*Perkin–Elmer*). Fluorescence of the investigated compounds was excited by a 365 nm wavelength light from Xe lamp (FWHM<10 meV) and measured using a back-thinned CCD spectrometer PMA-11 (*Hamamatsu*). 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 (Φ_F) of the solutions were estimated using the integrated sphere method [38]. An integrating sphere (*Sphere Optics*) coupled to the CCD spectrometer via optical fibre was also employed to measure Φ_F of the thin films. Cyclic voltammetry (CV) experiments were performed on the *Edaq* ER466 Integrated Potentiostat System. Pt/Ti wire, glassy carbon disk [Ø 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 of wet-casted neat films was measured by xerographic time of flight (XTOF) method [39–41]. The samples for the charge carrier mobility measurements were prepared as described earlier [42]. The film thickness was in the range of 2–6 μm. The ionization potentials (I_p) of the compound films were measured by electron photoemission in air method as described elsewhere [43].

2.2. Synthesis

Non-symmetric 2-phenylanthracene based derivatives with different type of aryl-substituents at 9th and 10th positions are showed in Fig. 1.

2.2.1. 10-bromo-2-phenylanthracene (M8)

N-bromosuccinimide (4.2 g, 0.0236 mol) was slowly added to a solution of 2-phenylanthracene (**M7**) (6.0 g, 0.0236 mol) in dry *N,N*-dimethylformamide (200 ml) at 30 °C and the mixture was stirred for 30 min. The reaction mixture was diluted with water (250 ml); a yellow solid was obtained and collected by filtration. The solid was washed with hot water and crystallized from mixture of isopropanol and toluene (1:3) to provide fine yellow crystals of **M8** (6.3 g, 80%): mp 144–146 °C; ^{1}H NMR (400 MHz, C_6D_6) δ: 8.89 (t, *J* = 8.8 Hz, 1H), 8.57 (dd, *J* = 8.8, 0.8 Hz, 1H), 8.00 (s, 1H), 7.72–7.62 (m, 4H), 7.55 (dd, *J* = 8.7 Hz, 1.6 Hz, 1H), 7.32–7.22 (m, 3H), 7.22–7.17 (m, 1H), 7.14 (t, *J* = 1.6 Hz, 1H).^{13}C NMR (101 MHz, C_6D_6) δ: 140.94, 139.94, 132.28, 131.44, 131.11, 130.95, 129.25, 128.98, 128.53, 127.62, 127.59, 127.58, 127.19, 126.95, 125.73, 125.42, 125.29, 122.72. ppm. HRMS (ES): M + H$^+$, found 333.0283. $C_{20}H_{13}Br$ requires 333.028.

2.2.2. 10-Aryl-2-phenylanthracenes (1a and 1b)

92 mg of 1 mol% $Pd(PPh_3)_2Cl_2$ was added to the solution of 4.0 g (0.012 mol) of 10-bromo-2phenylantracene in 250 ml toluene in argon atmosphere. Then boronic acid (0.0138 mol) was added to the heated mixture, after that 100 ml of 2 M K_2CO_3 solvent in water was poured to the mixture and then boiled. After the reaction completion, which was monitored by the gas chromatography, reaction mixture was quenched with 200 ml of water extracted and water layer was washed with toluene (3 × 100 ml). Combined organic layers were dried with Na_2SO_4, filtrated through silica gel. After the evaporation of solvent under reduced pressure, the material was purified by recrystallization from isopropanol and toluene mixture (1:5).

2.2.3. 10-(Naphthalen-2-yl)-2-phenylanthracene (1a)

(3.8 g 85%): ^{1}H NMR (400 MHz, C_6D_6) δ 8.36 (s, 1H), 8.22 (t, *J* = 1.2 Hz, 1H), 7.99 (d, *J* = 8.8 Hz, 1H), 7.94 (d, *J* = 8.5 Hz, 1H), 7.81–7.75 (m, 2H), 7.74–7.66 (m, 4H), 7.62–7.56 (m, 1H), 7.50–7.41 (m, 4H), 7.29–7.26 (m, 3H), 7.15–7.10 (m, 1H), 7.04–6.98 (d, 2H). ^{13}C NMR (101 MHz, C_6D_6) δ 141.58, 138.65, 137.81, 136.69, 134.02, 133.30, 132.16, 131.56, 131.28, 131.25, 130.66, 129.79, 129.59, 129.12, 128.82, 128.54, 128.42, 127.94, 127.60, 127.47, 127.43, 127.04, 126.65, 126.45, 126.01, 125.78, 125.53, 124.86. ppm. MS (EI) (*m*/*z*): 380.2