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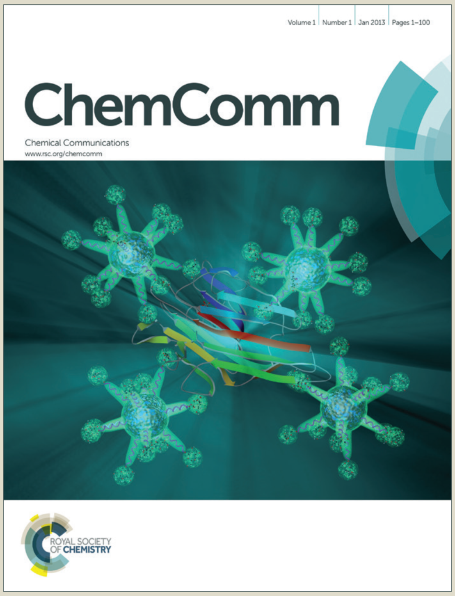

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ARTICLE TYPE

Indanthrone dye revisited after sixty years

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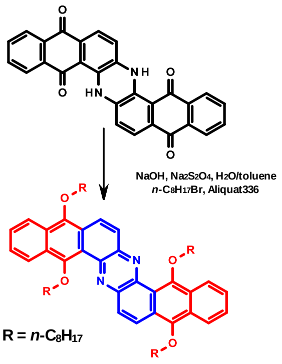
Indanthrone, an old, insoluble dye can be converted into a solution processable, self-assembling and electroluminescent organic semiconductor, namely tetraoctyloxydinaptho[2,3-a:2’,3’-h]phenazine (P-C8), in a simple one-pot process consisting of the carbonyl group reduction with sodium dithionite followed by the substitution with solubility inducing groups under the phase transfer catalysis conditions.

An impressive development of organic electronics in the past decade was inherently associated with the elaboration of new synthetic strategies leading to low and high molecular weight organic semiconductors, mainly of fused aromatic and heterocyclic nature.[1] Among many promising approaches in the synthesis of semiconductors with tunable redox, spectroscopic and electronic properties, functionalization of oligoacenes with pyridine- or pyrazine-type moieties deserves a special attention.[1c] Replacement of some methine-type carbons with nitrogen radically changes the properties of the resulting semiconductors. As indicated by Winkler and Houk[2] N-substituted oligoacenes should be considered as potential n-type semiconductors because of their high electron affinity[3] in contrast to oligoacenes not containing nitrogene atoms which are widely used in organic electronic devices as p-type semiconductors.[1a,4] Moreover, N-substituted oligoacenes are less sensitive to oxidative degradation or to dimerization processes as compared to their all carbon counterparts.[5] Finally, by controlling the N to C ratio, as well as the positions of nitrogen atoms in the molecule, it is possible to prepare derivatives strongly differing in their physical properties, adapting them to a given application.[2,6]

Initially developed methods for the preparation of N-substituted acenes consist of the condensation reaction between *o*-diaminoacenes with *o*-diketones (or hydroxyketones).[5a,c,7] Other synthetic strategies towards spatially expanded azaacenes involve Buchwald-type coupling between *o*-diaminoacenes with *o*-dichloroacenes.[5b,8] More recently, a „zig-zag”- type azaacene molecule, namely dinaphtho[2,3-a:2’,3’-h]phenazine substituted with solubilizing triisopropylosilylethynyl groups was obtained by oxidative coupling of two 2-aminoanthracene molecules.[9]

Popular alizarin-type dyes such as indanthrone or flavanthrone are structurally strikingly similar to several azaacene semiconductors presently tested as components of organic electronic devices.[1c,3a,10] In the past six decades the research interest in these compounds was very limited, scarce publications described liquid crystallinity of indanthrone derivatives,[11] their nonlinear optical properties,[12] or their possible use of as a low molecular weight Bcl2 inhibitors.[13] Meanwhile several new semiconductors have been obtained by functionalization of well known dyes (including natural ones). The use of isoindigo ((E)-1H,1H’-[3,3’]bindolylidene-2,2’-dione)[14] or diketopyrrolopyrrole or diketopyrrolopyrrole-derived azaacenes[15] as a building block in the synthesis of solution processable organic semiconductors must be quoted here as an instructive example.

In this communication we describe the preparation and detailed characterization of a new, solution processable, electroactive conjugated molecule, namely tetraoctyloxydinaptho[2,3-a:2’,3’-h]phenazine **(P-C8)** – tetraalkoxy-substituted indanthrone (scheme 1). This tetraoctyloxy derivative of diazaacene, containing a phenazine-type central unit was synthesized from a well known blue dye - indanthrone - commercially available, insoluble in organic solvents reagent which can be obtained from 1-aminoanthraquinone (see *Supplementary Information*). Indanthrone is readily transformed into **P-C8** in a one-pot system by carrying out the carbonyl group reduction with sodium dithionite followed by the substitution reaction under the phase transfer catalysis conditions. This is a well known method, previously used for the synthesis of alkoxy derivatives of quinone moieties containing compounds,[16] here modified by replacing zinc with sodium dithionite.



Scheme 1. Synthetic route to **P-C8**

^{1}H and ^{13}C NMR spectra of **P-C8** are fully consistent with the condensed *zig-zag* dinaphtho[2,3-a:2’,3’-h]phenazine structure of C_{2h} symmetry (see *Supplementary Information*). In particular two doublets can be observed in the aromatic part of the ^{1}H NMR spectrum with the coupling constant of J = 9.5 Hz which unambiguously originate from four protons of the phenazine ring. The presence of the pyrazine ring was further corroborated by Field Desorption (FD$^+$) and Electron Ionization (EI$^+$) mass spectra which gave molecular peaks of 893,6 and 892,7, respectively (calcd for $(C_{60}H_{80}N_2O_4)^+$ = 892,6).

P-C8 readily crystallizes in THF solutions yielding good-quality single crystals suitable for crystal structure determination. There are two almost planar molecules in the triclinic unit cell (space group: $P\bar{1}$) (see Figure 1). For details concerning crystal structure determination and the crystallographic parameters see *Supplementary Information*.

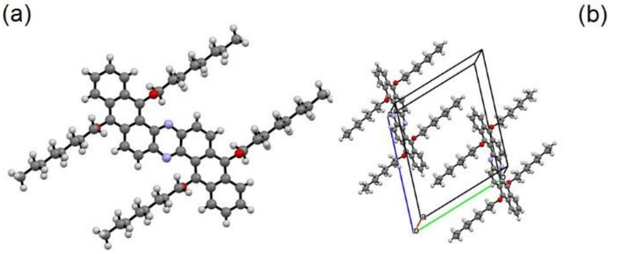


Figure 1. (a) X-Ray crystallographic structure of **P-C8**. (b) Crystal structure packing of **P-C8** in the unit cell (a = 9.93781(14) Å, b = 15.1528(2) Å, c = 17.8125(2) Å, α = 69.7564 °(13), β = 88.9555 °(11), γ = 87.1772 °(12)).

P-C8 shows a strong tendency to form self-assembled monolayers on surfaces of appropriate substrates as, for example, HOPG. Figure 2 shows a representative STM image of a monolayer deposited from hexane solution. The unit cell parameters determined from this image are: a = 20.5 Å, b = 18.5 Å, α = 87° yielding a nearly rectangular 2D unit cell. This shape of the unit cell is in contrast with three fold symmetry of the graphite surface and clearly indicates that adsorbate-adsorbate interactions are a dominant factor determining the supramolecular organization of **P-C8** in the monolayer. Both 2D and 3D supramolecular structures are governed by mode of the substituents interdigitation. The main difference between these organizations has its origin in a different spatial orientation of the alkoxy substituents with respect to the conjugated core. In the monolayer both parts form the same plane whereas in the single crystals they are nearly orthogonal. As a consequence the 2D cell parameters are increased.

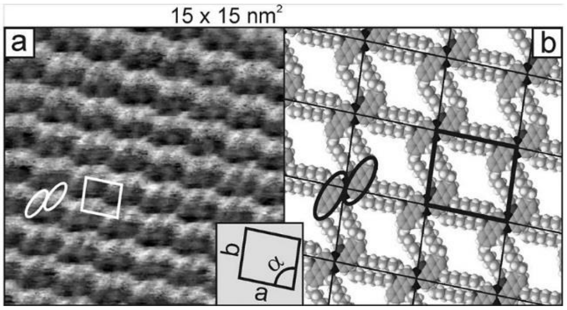
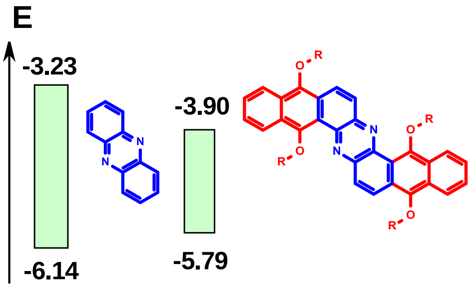


Figure 2. (a) STM image and (b) corresponding model of adsorption geometry of a monolayer of **P-C8** deposited from hexane on HOPG graphite (15x15 nm^2, I_t = 1 nA, V_{tip} = -1V).

Redox properties of **P-C8** were studied by cyclic voltammetry. Its cyclic voltammogram yields two irreversible oxidation peaks and one reduction peak (see Figure S5 in *Supplementary Information*). The HOMO and LUMO positions, determined from the electrochemical studies[17] are significantly altered as compared to the case of the corresponding levels in phenazine (see Scheme 2).[7g] **P-C8** can be considered as a DAD molecule with a central electroaccepting phenazine unit connected to two dialkoxynaphthalene donors. This chemical constitution results in significant lowering of the electrochemical band gap from 2.91 in phenazine to 1.89 eV in **P-C8.**



Scheme 2. Comparison of HOMO and LUMO energy levels of phenazine and **P-C8** (phenazine data are taken from [7g]).

It is instructive to confront the electrochemical data with the plots of frontier molecular orbitals and spin densities of the radical cation and radical anion formed, respectively, upon the oxidation and reduction **P-C8,** obtained from quantum chemical calculations. They were performed using Gaussian09 Revision D.01[18] package and employing hybrid B3LYP[19] exchange correlation potential combined with 6-31G(d,p) basis set. The HOMO is extended over the aromatic rings avoiding the central nitrogen atoms whereas LUMO is preferentially located on the central phenazine unit. Upon the formation of a radical cation through oxidation the spin density preferentially concentrates on the dialkoksynaphthalene D segment. Reduction of **P-C8** to a radical anion moves the spin density towards the central phenazine part. (see Fig. S6 in Supplementary Information). This finding supports the DAD nature of the studied compound and explains its electrochemical properties.

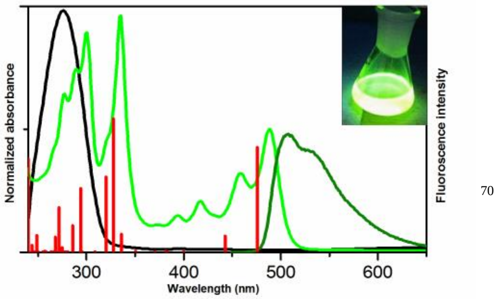


Figure 3. Absorption spectra of indanthrone and P-C8 solutions in chloroform together with with its emission spectrum. The calculated positions and relative oscillator strengths of the electronic transitions of this compound are depicted as red bars for comparison. The inset is the photograph of P-C8 solution under UV light.

In Figure 3 absorption spectra of indanthrone and **P-C8** are shown, the latter being compared with the calculated one. In the spectrum of indanthrone one unresolved band peaked at 278 nm is observed. For **P-C8** three bathochromically shifted peaks at 300, 333 and 489 nm with a pronounced vibrational structure are registered. The spectrum is similar to those reported for other azaacenes[7g,9,20] and consistent with the calculated transition. (see Figure 3 and Table S3 in *Supplementary Information*). The lowest energetic band (at 489 nm) is an intramolecular CT band associated with DA interactions involving charge transfer between the HOMO localized on the anthracene parts of the molecule and the LUMO located on the phenazine central part. It is worth noting that the HOMO-LUMO transition is highly privileged due to the symmetry of the molecule being restricted to the centrosymmetric (C_i) point group. Since HOMO and LUMO belong to A_g and A_u irreducible representations, respectively, the transition between them is highly privileged according to the Laporte selection rule. For full analysis of the electronic transitions natural transition orbitals analysis was performed and included to *Supplementary Information*.

Finally, a difference of 0.41 eV between the optical and electrochemical band gaps should be pointed out. This is mainly associated with the exciton binding energy which in some organic compounds may reach values up to 0.5 eV.[21]

P-C8 is photoluminescent, emitting green light with a relatively low Stokes shift of 881 cm^{-1} (22 nm) (see Figure 3). The measured high photoluminescence quantum yield (56%) together with its short lifetime (3.9 ns) prompted us to apply this derivative as an active component of "guest – host" type organic light emitting diodes. In Figure 4 the electroluminescence spectrum of 1 wt.% molecular dispersion of **P-C8** in a two component matrix consisting of hole transporting poly(9-vinylcarbazole) (PVK) and electron transporting 2-(4-biphenylyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD) is compared with the spectrum of the pure matrix. It is clear that the Förster energy transfer is efficient and complete since the spectrum is characteristic of **P-C8** with no features originating from the matrix (PVK + PBD). This is assured by a strong overlap the **P-C8** absorption spectrum with the emission spectrum of the matrix.

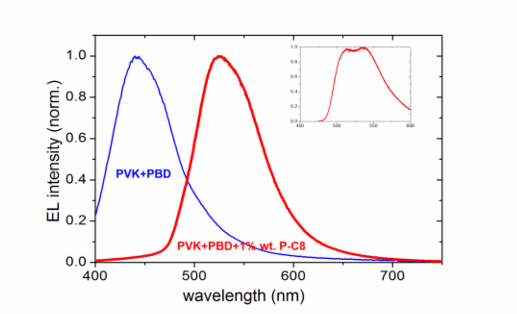


Figure 4. Electroluminescence spectra of: 1 wt% dispersion of **P-C8** in PVK+PBD matrix (red line) and pure PVK+PBD matrix (blue line). The inset shows the zoom of the **P-C8** electroluminescence spectrum over narrower spectral range.

Preliminary tests carried out on non-optimized devices of the following structure ITO/PEDOT:PSS/PVK+1wt% **P-C8**+PBD/LiF/Al yield luminance exceeding 250 cd/m^2 and luminous efficiency of 1.0 cd/A (for details see *supplementary information*).

To summarize, we have demonstrated that indanthrone, an old insoluble dye, can be transformed into an interesting, solution processable semiconductor through a one-step, one pot process involving its reduction and substitution with alkoxy solubilizing groups. Self-assembling capabilities of **P-C8** and its interesting luminescent and optoelectronic properties should be pointed out.

This research was carried out in the framework of the project entitled "New solution processable organic and hybrid (organic/inorganic) functional materials for electronics, optoelectronics and spintronics" (Contract No. TEAM/2011-8/6), which is operated within the Foundation for the Polish Science Team Programme cofinanced by the EU European Regional Development Fund. The Gaussian 09 calculations were carried out in the Wroclaw Centre for Networking and Supercomputing, WSCC, Wroclaw, Poland, http://www.wcss.wroc.pl, under calculational Grant No. 283.

Notes and references

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†Electronic Supplementary Information (ESI) available: Experimental procedures, characterization data of **P-C8**, organic light emitting diode fabrication. CCDC 1006274. For ESI and crystallographic data in CIF see DOI: 10.1039/b000000x/

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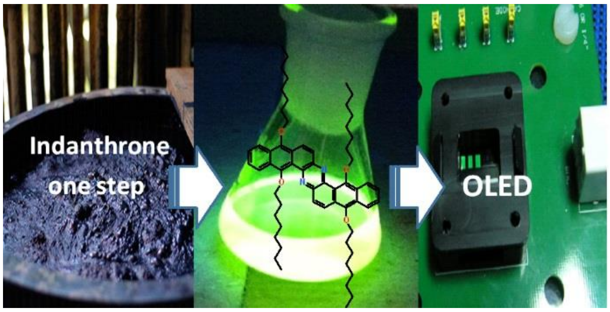

Text:

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