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From textile coloring to light-emitting electrochemical devices: Upcycling of the Isoviolanthrone vat dye

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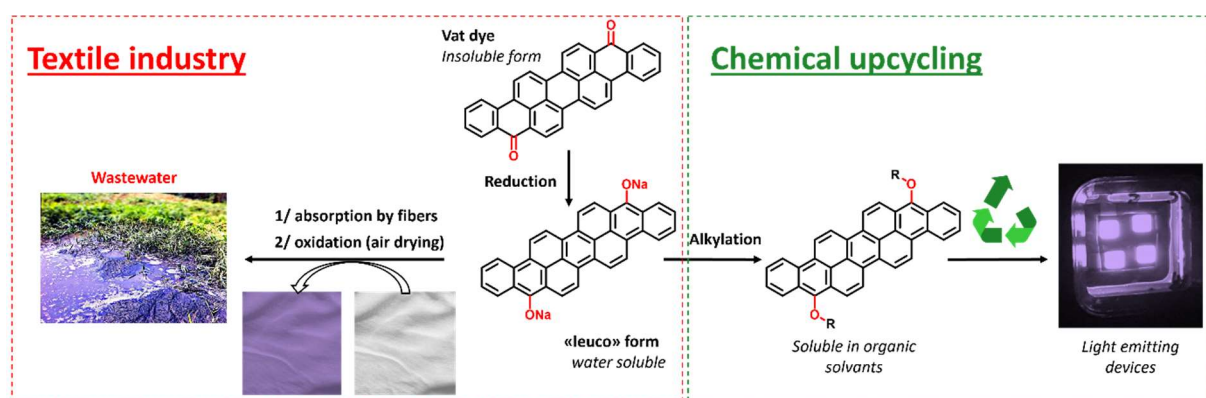
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Abstract: Produced at ton scale, vat dyes are major environmental pollutants generated by textile industry. However, they represent ideal and accessible candidates for chemical upcycling since usually composed of large π -conjugated scaffolds. Based on the valorization of “old” products, waste or even contaminant into high-added value goods, this concept can be easily transposed to the laboratories. As a contribution to the current environmental and ecological transition, we demonstrate herein the valorization/upcycling of wastewaters generated during the dyeing procedure. To do so, the reduced (*leuco*) form of vat violet 10, also known as isoviolanthrone, was functionalized to afford a readily soluble derivative that was subsequently and successfully used as active material in operating solution processed light emitting electrochemical cells, *ie*, from textile dyeing to high tech application.

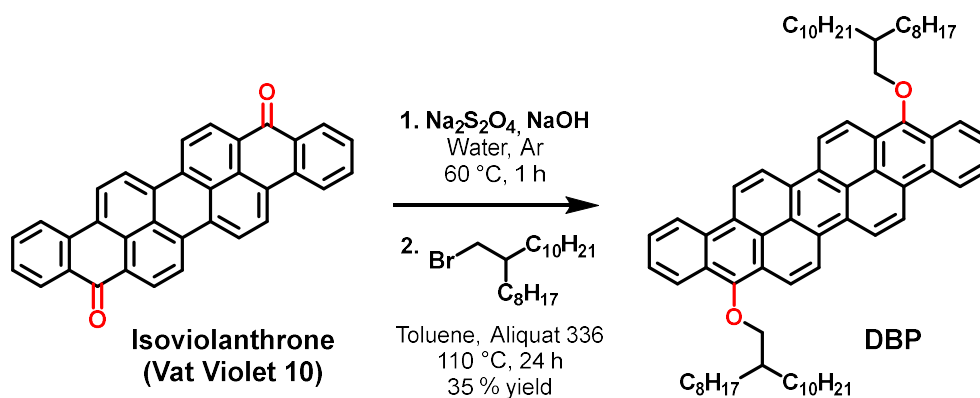
Introduction: Over the last century, organic synthesis evolved as a powerful and almost limitless tool to design and create functional molecules. The boundless imagination of chemists led to the preparation and use of myriad structures from the simplest to the most complicated. As a result, synthetic or “man-made” organic compounds are ubiquitous and intrinsic to our modern society. Prime example, vat dyes have been massively investigated and used for textile coloring.¹⁻³ Major contributors to the global economy, thousands of tonnes are indeed annually produced for fashion industries. Disastrous for the environment since mostly discharged without treatment into waterways (more than 200,000 tons per year),⁴⁻⁶ improvement of their recyclability has consequently attracted significant research attention.⁷

On the other hand, and from a molecular/structural point of view, these types of dyes usually possess, in addition to interesting optical properties, large π -conjugated scaffolds, making them appealing building blocks for optoelectronic applications. Hence, the functionalization of several vat dyes has already been reported as well as their use in organic field-effect transistors (**OFETs**), light-emitting devices (**OLEDs**) and battery applications.⁸⁻¹⁰

In this context and through a simple chemical transformation, we report herein the upcycling¹¹ of the isoviolanthrone, also known as vat violet 10, from textile dyeing agent to active compound in light-emitting electrochemical cells (**LECs**). Selected for their simplicity and compatibility with conventional cost-effective printing technics on lightweight and flexible substrates, these devices indeed appeared to be ideal candidates for this proof of concept based on the valorization of an abundant and cheap dye-based organic materials.^{12, 13}

Results and discussion:

The 9,18-dialkoxylated 1.2,8.9-dibenzoperopyrene (**DBP**) was prepared according to the one-pot sequential reaction depicted in scheme 1.



*Scheme 1. Synthesis of the target compound entitled **DBP***

The carbonyl groups of the commercially available isoviolanthrone were first reduced to give the soluble “*leuco*” form using the industrially applied pathway of sodium dithionite under basic conditions. Once textile fibers soaked into these water-based solutions, the later are generally thrown away, even if still full of unreacted phenolates derivatives. Hence, through the simple addition of an organic solvent and a phase transfer catalyst, these reactive species can be, for instance, engaged in a nucleophilic substitution reaction with 9-(bromomethyl)nonadecane to afford, in our case, the alkylated **DBP**.¹⁰

Once isolated and fully characterized by nuclear magnetic resonance spectroscopy (¹H and ¹³C) and high-resolution mass spectrometry (see SI), the impact of the *O*-alkylation on the optoelectronic properties was then investigated but significantly limited due to the insoluble nature of the starting **isoviolanthrone**. Hence, the highest occupied molecular orbital (HOMO) energy levels were first probed by photoemission yield spectroscopy in air (PYSA) measurements performed on each molecule in their powder form (Figure 1-a). While a HOMO level lying at -5.26 eV was determined for **DBP**, a significantly lower value was obtained for **isoviolanthrone** (HOMO = -5.70 eV). This feature, investigated by quantum chemical simulations, was correlated to i) an improved delocalization of both frontier energy levels beyond the central pyrene core (Figure 1-b), inducing a better conjugation and electronic communication along the π -conjugated backbone (Figure S7-a) and ii) the

replacement of electron-withdrawing ketones (inductive and resonance effects) by mesomeric donor methoxy groups (Figure 7-b).^{14, 15}

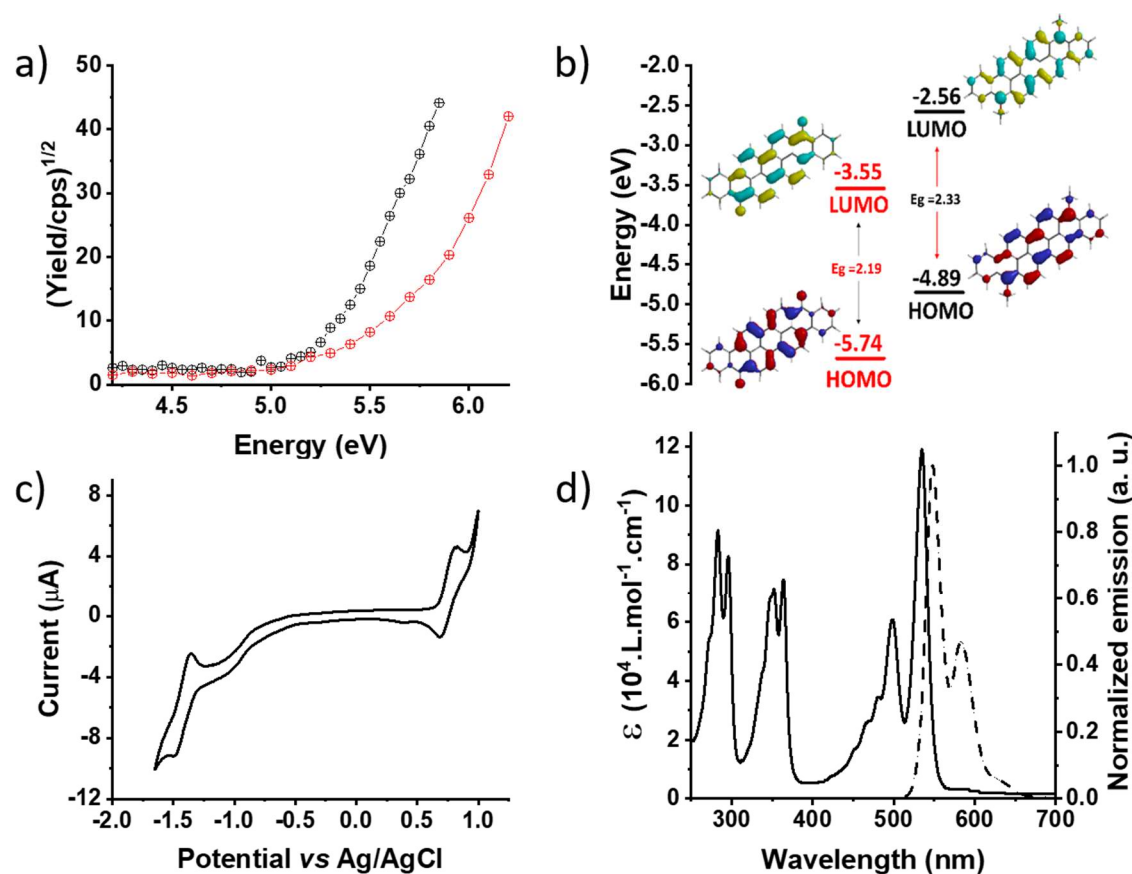


Figure 1. a) PYSA spectra recorded on **isoviolanthrone** (red) and **DBP** (black) powders. b) Optimized geometries and computed energy diagram (methods described in the SI) for **isoviolanthrone** (red) and **DBP** (black). c) Cyclic voltammograms of **DBP** (1 mM) in degassed THF solutions using tetrabutylammonium perchlorate as the electrolyte (0.1 M), glassy carbon as the working electrode, platinum as the counter electrode, Ag/AgCl as the reference electrode and a scan rate of 100 mV s⁻¹. d) Absorbance (solid line) and normalized fluorescence (dashed line) of **DBP** in CHCl₃ solution at 1x10⁻⁶ M.

Soluble in most common solvents, such as toluene, chloroform, tetrahydrofuran, etc.), the cyclic voltammetry of **DBP** was then carried out, revealing a reversible wave in both anodic and cathodic regions peaking at E_{PA}=+0.80 V and E_{PC}=-1.49V respectively (vs. Ag/AgCl, Figure 1-a). Frontier orbital energy levels were then estimated from the onset potential of these redox processes using the equation $E_{(HOMO/LUMO)} = -(E_{REDOX}^{onset} + 4.62) \text{ eV}$.^{16, 17} Values of -5.28 eV and - 3.31 eV were thus calculated for the HOMO and the lowest unoccupied molecular orbital (LUMO) energy levels, respectively, resulting in an electrochemical gap of

1.97 eV. In consistency with this value, **DBP** shows a significant absorption in the visible region with the two prominent and well-defined bands. Located at *ca.* 536 nm and 500 nm, the peaks are attributed to the allowed π - π^* transitions and characterized by impressive extinction coefficients of 120000 and 62000 $\text{M}^{-1}\cdot\text{cm}^{-1}$, respectively (figure 1-d). In addition to these high extinction coefficients, **DBP** also shows a significant greenish-yellow emission at 542 nm (and a shoulder at 582 nm) associated to a photoluminescent quantum yield (PLQY) of *ca.* 80%.

To capitalize on these optoelectronic properties and to demonstrate the upcycling potential of **DBP**, thin film-based light emitting devices were fabricated. In coherence with the synthetic accessibility of the dye, light-emitting electrochemical cells (LECs) were selected herein for their simplicity and ease of fabrication.¹⁸ Compared to their conventional multi stacks-based parent OLEDs, LECs usually consist of an active layer, constituted of an emitter (guest), a matrix (host), and the electrolyte, simply sandwiched between a transparent anode and a reflective metallic cathode.¹⁹ In this configuration, application of an external bias induces a redistribution of the ions followed by the electrochemical doping of the active layer by injected charges leading to the *in situ* generation of a p-n junction within the emitting layer. Electroluminescence finally results from the radiative recombination of the electrically injected holes and electrons. Compatible air-stable electrode materials, thus reducing the need for rigorous encapsulation and thick active layers, these more “default tolerant” devices hence appear particularly attractive for large-scale and cost-efficient industrial processing. Herein, active layers consisting of **DBP**, 4'-bis(*N*-carbazolyl)-1,1'-biphenyl (**CBP**), and **THAB** as an ionic liquid, used as guest (emitter), host, and supporting electrolyte, respectively, were processed on **PEDOT-PSS** pre-coated indium tin oxide (ITO) substrates before being covered by a thermally evaporated aluminum back electrode.

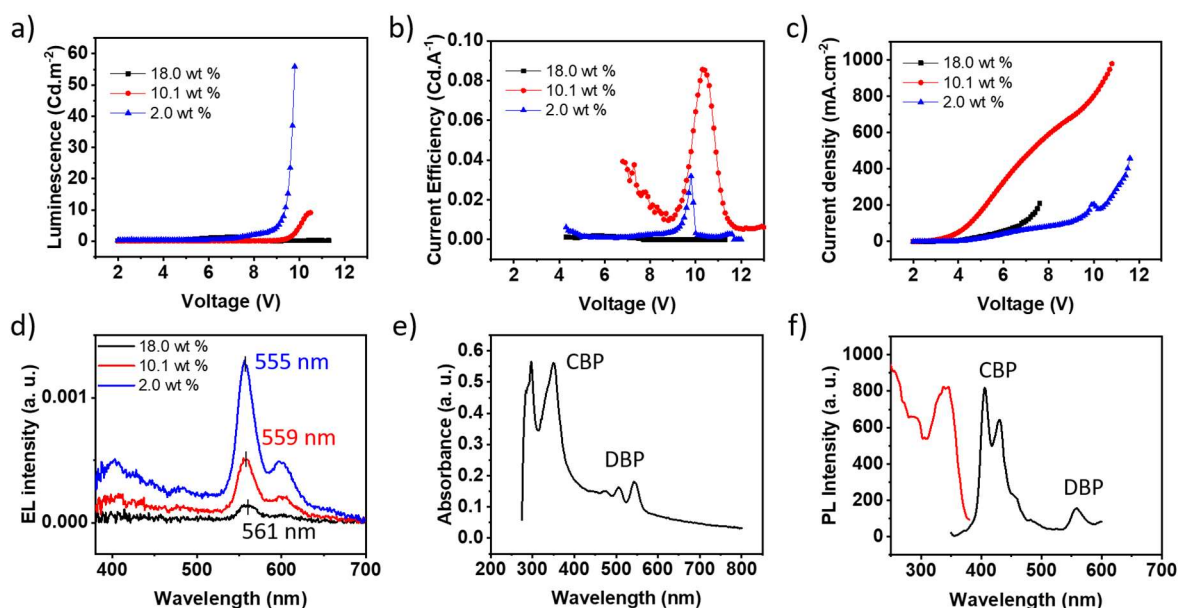


Figure 2. Luminescence (a), current efficiency (b), current density (c), and d) electroluminescence of the **DBP/CBP** device at different concentrations (18, 10.1, and 2.0 wt % of **DBP**). Absorbance (e) and photoluminescence intensity (f) of the best performing LEC (2.0 wt %).

First attempts were carried out on the active layer incorporating 18% by weight of **DBP**. While operating devices were demonstrated with promising turn-on voltages of *ca* 6.1 V under direct current-voltage-luminance (IVL) mode (increased of 0.1 V per second), a very low luminescence was nonetheless recorded (*ca* 1.2 cd m⁻² @ 561 nm). Even if functionalized by long and bulky alkyl chains, these modest emission values might have originated from the aggregation-caused quenching (ACQ) effect induced by the large π -conjugated scaffold of **DBP**. Consequently, the guest weight percentage was therefore reduced to limit this ACQ effect to 10.1 and then 2 weight % resulting in a significant increase of luminescence from 9.1 cd m⁻² to 55.9 cd m⁻² respectively (figure 2-a) along with a shift of the **DBP** characteristic EL peak from 559 nm (10.1 wt %) to 555 nm (2.0 wt %, Figure 2-d). Moreover, while quite intense luminescence of the **DBP** was monitored from the EL spectra, PL experiments, performed on the best operating device, showed a strong and major contribution at 406 nm attributed to the **CBP**, thus emphasizing a good transfer from the host to the guest under EL conditions.

Finally, to improve the device performance, the driving method was changed from IVL mode to pulsed current-voltage mode (Table 1, Figure 3-a).²⁰⁻²² As expected, both the turn-on and peak voltage were reduced (Table 1) while the luminescence was significantly increased (+36%) with maximum intensity reached at 557 nm (Figure 3-b).

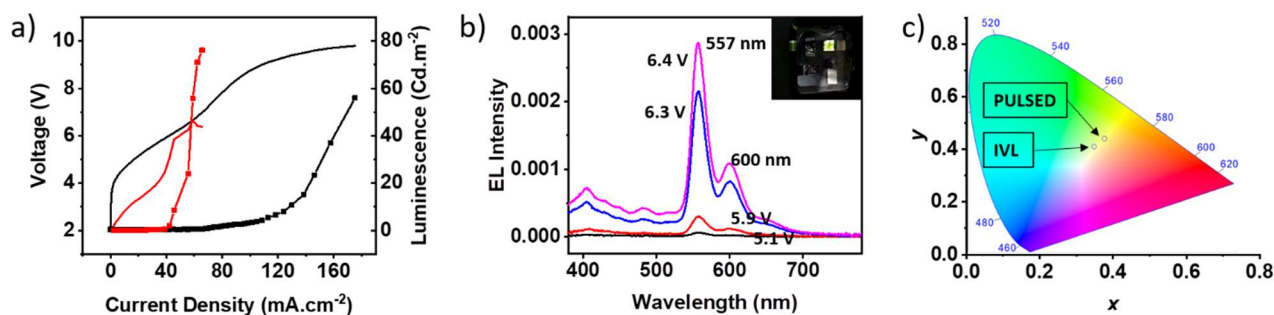


Figure 3. a) The luminescence (square) and voltage (solid line) change with increasing current density under different driving conditions of IVL (black) and pulse current mode (red) (b). EL spectra for pulse current-driven **DBP/CEC** LEC devices. c) 1931 CIE chromaticity diagram of the **DBP** LEC device under IVL and pulse current mode.

Moreover, almost negligible, the *ca* 2-nm redshift of the maximum EL peak recorded under pulsed conditions (vs. 555 nm for direct IVL) yet still has a noticeable effect on the respective *Commission Internationale de l'Eclairage* (CIE) coordinates (Figure 3-c). Choice of driving conditions hence appears to be a method of choice to fine-tune the emitting and thus perceived color of the device.

Table 1. Comparison of the best device performances recorded under ILV and pulse current mode ^aTurn-on voltage above 1Cd m^{-2} . ^bVoltage at peak luminescence.

Driving current	Turn-on Voltage ^a (V)	Peak Luminescence (Cd m ⁻²)	Peak Voltage ^b (V)	Current Efficiency (Cd A ⁻¹)	Current Density (mA cm ⁻²)
IVL	7.3	55.9	9.8	0.0027	175.2
Pulse	5.1	76.1	6.4	0.11	65.6

Conclusion

Initially synthesized for textile coloring, we report a successful example of upcycling through a one-pot sequential functionalization of the vat violet 10's *leuco* form and embedment, for the first time, in light-emitting electrochemical cells. Considering *i*) the simplicity of the reaction carried out in this contribution, *ii*) the large amount of wastewater still full of reactive anionic precursors generated and discarded by the textile industry, *iii*) the successful fabrication/demonstration of low-cost operating devices, and *iv*) the tremendous variety of ton-scale-produced and commercially available vat dyes, this contribution highlights the huge potential of upcycling such building blocks for both value-added applications and environmental purposes. Even if conversion yields are somehow moderates, as well as devices performances in term of pure efficiencies,^{12, 23} we therefore demonstrate that dye contaminated wastewaters can still be valorized with a minor effort. In a current context of ecological transition, it is indeed vital to develop simple research guidelines aiming at transposing our recycling/upcycling household routines to laboratories, and above all, industries.

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Contributions

Synthesis and characterization: T.G. and P.J. Device fabrications and testing: K. K. L. & H. J.

Computational Chemistry: D.L. Supervision. P.B., E.K. and C.C. Conception and writing:

D.L. and C.C. All authors discussed the results and contributed to the final manuscript.

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