Synthesis and photophysical properties of perylene bisimides from isoxazolines and isoxazoles.

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Introduction

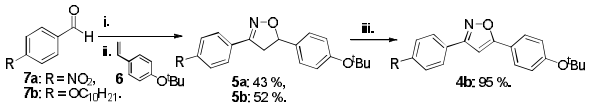
New materials synthesized from perylene bisimides bring a lot of interest in the field of photonic. Their compacted structure, allied with its π-staking interactions, show quite a unique optical property[1].

In this present work, we shall synthesize three new compounds with perylene bisimide as the central core and different lateral groups to intent increasing its solubility. Furthermore, spectroscopy tests, including photophysical study, absorbance and fluorescence, will be done in order to characterize these materials.

Results and Discussion

The first step on the synthesis for intermediates (scheme 1) starts with the cycloaddition [3+2] 1,3 dipolar from *p*-substituted benzaldehyde **7a-b** and *p*-*tert*-butyloxystyrene (**6**), following the oxidation of the heterocycle isoxazoline to isoxazole **4b**. In this step the heterocycles are formed preliminarily.

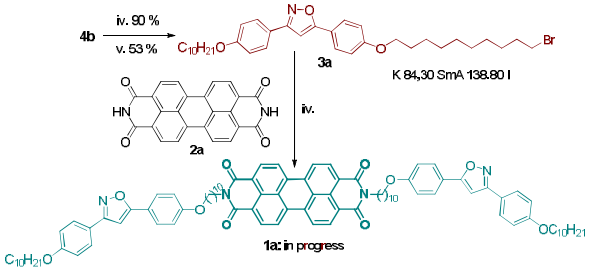
Scheme 1. Synthetic route for intermediates.



i. $NH_2OH.HCl$, AcONa, EtOH/H_2O (1:1), reflux, 3h; ii. CH_2Cl_2, NaClO (5 %), 30min; iii. MnO_2, MePh, reflux, 10h.

To synthesize the perylene bisimide derivative **1a**, the isoxazole **4b** is deprotected and alkylated with 1,10-dibromodecane in good yields (scheme 2). The advanced intermediate **3a** shows interesting mesomorphic properties[2]. Next step consist in the direct SN_2 reaction between **2a** and **3a**[3].

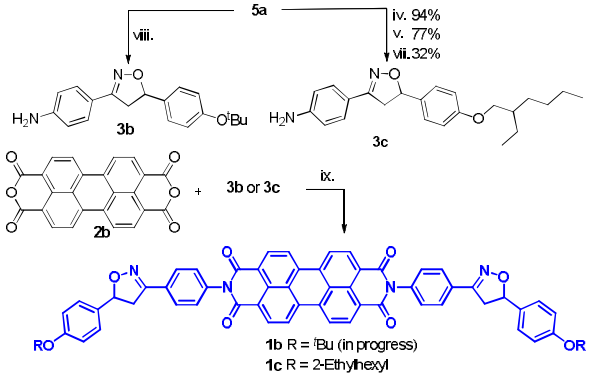
Scheme 2. Synthetic route for **1a**.



iv. MeOH, HBr, AcOH, reflux, 24h; v. K_2CO_3, CH_3CN, reflux, 72 h; vi. Cs_2CO_3, DMF, NaI, reflux.

To synthesize the other two target (scheme 3) molecules **1b-c**, the isoxazoline **5a** is reduced to give **3b** or deprotected, alkylated and then reduced to give **3c**. Finally, compound perylene-3,4,9,10-tetracarboxylic dianhydride **2b**, goes under imidation[4] with **3b** or **3c** to give **1b-c**, respectively.

Scheme 3. Synthetic route for compounds **1b-c**.



iv. MeOH, HBr, AcOH, reflux, 24h; v. K_2CO_3, CH_3CN, reflux, 24h; vii. H_2 (4bar), Pd/C, THF; viii. $SnCl_2.2H_2O$, EtOH, N_2, reflux, 4h; ix. $Zn(AcO)_2$, imidazole, 160°C, 2h.

Table 1. Photophysical properties of **1a** in CH_2Cl_2.

Entry	$\lambda_{max\ (abs)}$	$\Delta\lambda_{ST}$	ε
1c	526 nm	7 nm	$5{,}2.10^4$

Figure 1 shows the absorption and emission spectrum of **1c** and Table 1 shows the photophysical data.

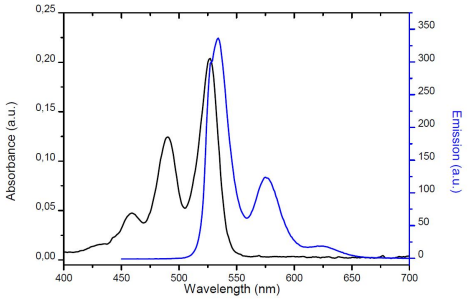


Figure 1. Absorption (black) and Fluorescence (blue) spectrum of **1c**.

Conclusions

Our preliminary results for compound **1c** showed that the solubility was improved in most organic solvents and showed interesting photophysical properties as described in Figure 1. The synthesis of compound **1a-b** and full characterization are in progress.

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