Synthesis and characterization of novel phthalazine based push-pull heterocyclic systems for DSSCs

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Abstract: Research on renewable energy sources have been expanding considerably in order to decrease the consumption of fossil fuels and therefore reduce global warming and environmental pollution. Solar cells based on organic dye sensitizers (DSSCs) is a photovoltaic device that have been extensively studied due to their high incident solar light-to-electricity conversion efficiency and low cost of production.

In the interest of achieving chromophores with high performance for DSSCs, wide-ranging research has been conducted on structural modifications of the sensitizing dyes. One of the approaches is the tuning the π-bridge with auxiliary electron donor/acceptor groups, such as electron-rich thiophene and furan heterocycles linked to the electron-deficient phthalazine ring substituted with appropriate acceptor groups, which are promising candidates among such push-pull systems.

As part of an on-going research to develop efficient donor – π-spacer – acceptor heterocyclic systems for several optoelectronic applications we report the synthesis and characterization of phthalazine derivatives functionalized with cyanoacetic or rhodanine-3-acetic acid as anchoring groups and (hetero)aryl groups as donor/π-spacers. The experimental results indicate that, these compounds could have potential application as NLO chromophores as well as sensitizers for DSSCs.

Keywords: Suzuki coupling, Knoevenagel condensation, Phthalazine, Cyanoacetic acid, Rhodanine-3-acetic acid, π-Conjugated heterocyclic systems, Push-pull molecules, Dye-sensitized solar cells (DSSC)

1. Introduction

Research on renewable energy sources and sustainable development have been expanding considerably in order to decrease the consumption of fossil fuels and therefore reduce global warming and environmental pollution[1]. Solar energy is an excellent source due to its inexhaustibility and cleanness, and can be directly transformed into electric energy through photovoltaics, namely the most promising organic solar cells[2].

Solar cells based on organic dye sensitizers (DSSCs) adsorbed on nanocrystalline TiO_2 electrodes have been extensively studied due to their high incident solar light-to-electricity conversion efficiency, colourful and decorative natures and low cost of production[3]. Wide-ranging research has been conducted on structural modifications of the sensitizing dyes in the interest of achieving chromophores with high performance for DSSCs[2, 4].

Dipolar chromophores, having an electron donor and electron acceptor groups linked through a π-conjugated bridge electronic arrangement are currently of great interest because of their applicability to optical and photovoltaic devices such as nonlinear optics (NLO) and dye-sensitized solar cells (DSSCs), as it assures efficient intramolecular charge transfer and generates a dipolar push-pull system featuring low energy and intense charge transfer absorption. These systems can be improved by modification of the electron donor, electron acceptor, or/and the π-bridge of the molecule. Recent approaches to the design of these compounds are based on the presence of a five-membered heterocyclic ring in a push-pull donor-acceptor chromophore. Another approach consists on adjusting the π-bridge with electron rich and/or electron deficient aromatic rings that can an auxiliary electron donor/acceptor group performance[2, 4a, 5]. Electron-rich thiophene and furan heterocycles linked to the electron-deficient phthalazine ring substituted with appropriate acceptor groups are promising candidates among such push-pull systems.

Having in mind these facts and also our recent work, in which we have used formyl heterocyclic systems, such as oligothiophenes, arylthiophenes, thienylpyrroles, arylfurans and thienylfurans[6] as precursors for the synthesis of more complex molecules (e.g. dicyanovinyl- and thiobarbituric derivatives, benzothiazoles, (benz)imidazoles, benzoxazoles, BODIPYs, Schiff-bases, imidazo-crown ethers, thiosemicarbazones etc.) for several optoelectronic applications (OLEDs, SHG, TPA, chemosensors)[7], we decided to synthesize the new formyl-phthalazines **3a** and **4a**. Further derivatization of these precursors with cyanoacetic acid or rhodamine-3-acetic yield the final push-pull systems **3b-c** and **4b-c**. Compounds **3-4** were prepared in order to study the influence of the electronic nature of the (hetero)aryl group linked to the diazine moiety, as well as the influence of the strength of the acceptor group on the optical properties of the novel push-pull systems.

2. Experimental

2.1. Instruments

NMR spectra were obtained on a Varian Unity Plus Spectrometer at an operating frequency of 300 MHz for ^{1}H NMR and 75.4 MHz for ^{13}C NMR or a Brucker Avance III 400 at an operating frequency of 400 MHz for ^{1}H NMR and 100.6 MHz for ^{13}C NMR using the solvent peak as internal reference at 25 ºC (δ relative to TMS). All chemical shifts are given in Hz. Assignments were made by comparison of chemical shifts, peak multiplicities and *J* values and were supported by spin decoupling-double resonance and bidimensional heteronuclear HMBC and HMQC correlation techniques. UV-visible absorption spectra (200-800 nm) were obtained using a Shimadzu UV/2501PC spectrophotometer.

2.2. Materials

Phosphorous (V) oxybromide, boronic acids, cyanoacetic acid and rhodamine-3-acetic acid were purchased from Aldrich, Acros Organics and Fluka and used as received. All commercially available reagents and solvents were used as received. TLC analyses were carried out on 0.25 mm thick precoated silica plates (Merck Fertigplatten Kieselgel $60F_{254}$) and spots were visualized under UV light. Chromatography on silica gel was carried out on Merck Kieselgel (200-300 mesh).

2.3. Synthesis

Procedure for the synthesis of 1-bromo-4-(thiophen-2-yl)phthalazine[8] **2**: A mixture of 4-(thiophen-2-yl)phthalazin-1(2H)-one **1** (2.2 mmol, 0.5 g) and $POBr_3$ (5.5 mmol, 1.6g) was heated for 6 h at 110-120 ºC. This mixture was cooled till room temperature and then poured onto ice-water, basified with a solution of ammonia (2 M) and stirred for 30 min. to give a brown solid which was filtered and washed with water and light petroleum to give the pure thienylphthalazine **2** as brown solid (96%). ^{1}H NMR ($CDCl_3$, 400MHz) δ 7.26 (dd, 1 H, H-4', *J* = 5.2 and 2.8 Hz), 7.63 (dd, 1 H, H-5', *J* = 1.2 and 0.8 Hz), 7.68 (dd, 1 H, H-3', *J* = 3.6 and 1.2 Hz), 8.00 (m, 2 H, H-7 and H-8, *J* = 3.6 and 1.2 Hz), 8.33 (dd, 1 H, H-6, *J* = 6.2 and 1.6 Hz), 8.46 (d, 1 H, H-9, *J* = 7.0 and 2.4 Hz) ppm.

General procedure for the synthesis of aldehydes **3a** and **4a** through Suzuki coupling: 1-bromo-4-(thiophen-2-yl)phthalazine **2** (0.7 mmol) was coupled to boronic acids (0.9 mmol) in a mixture of DME (6 mL), aqueous 2 M Na_2CO_3 (1 mL) and $Pd(PPh_3)_4$ (5%) at 80°C under nitrogen. The reactions were monitored by TLC which determined the different reaction times (24-48 h). The mixture was cooled to room temperature, and neutralized with a saturated solution of sodium

acetate. The organic layer was extracted with chloroform, dried with anhydrous $MgSO_4$ and the solvent was evaporated under reduced pressure. The product was purified by column chromatography on silica gel with increasing amounts of dichloromethane in light petroleum as solvent. The solvent was evaporated to give the coupled products as solids. Recrystallization from dichloromethane/hexane gave the pure compounds **3a** and **4a**.

4-(1'-(Thiophen-2''-yl)phthalazin-4'-yl)benzaldehyde **3a**. Yellow solid (56%). Pf. 161-163 ºC. UV (ethanol): λ_{max} nm (ε, $M^{-1}cm^{-1}$) 331 (9167). ^1H NMR ($CDCl_3$, 300 MHz) δ 7.29 (dd, 1 H, H-4'', *J*= 5.2 and 3.6 Hz), 7.65 (dd, 1 H, H-5'', *J*= 5.2 and 1.2 Hz), 7.79 (dd, 1 H, H-3'', *J*= 3.6 and 1.2 Hz), 7.93-8.03 (m, 4 H, H-7', H-6', H-3, H-5), 8.09-8.12 (m, 3H, H-2, H-6, H-8'), 8.62 (d, 1 H, H-5', *J*= 8.0 Hz), 10.18 (s, 1 H, CHO) ppm.

5-(1'-Thiophen-2''-yl)phthalazin-4'-yl)furan-2-carbaldehyde **4a**. Yellow solid (21%). UV (ethanol): λ_{max} nm (ε, $M^{-1}cm^{-1}$) 366, (12800). ^1H NMR ($CDCl_3$, 300 MHz) δ 7.30 (dd, 1 H, H-4'', *J*= 5.0 and 3.6 Hz), 7.47 (dd, 1 H, H-5'', *J*= 5.4 and 1.2 Hz), 7.67 (dd, 1H, H-3'', *J*= 5.2 and 1.2 Hz), 7.83-7.98 (m, 2 H, H-7', H-6'), 8.02-8.09 (m, 2 H, H-8', H-5'), 8.61 (d, 1 H, H-4, *J*= 7.6 Hz), 9.09 (d, 1 H, H-3, *J*= 7.2 Hz), 9.84 (s, 1 H, CHO) ppm.

General procedure for the synthesis of cyanoacetic acids **3b** and **4b** through Knoevenagel condensation: To a solution of aldehyde (0.3 mmol) and 2-cyanoacetic acid (54 mg, 0.6 mmol) in ethanol was added 4 drops of *N*-triethylamine. The mixture was refluxed for 6 h then cooled down to room temperature. The crude product was concentrated and ethyl ether was added to induce precipitation. The precipitate was filtered and washed with ethyl ether to give the pure product.

2-Cyano-3-(4'-(1''-(thiophen-2'''-yl)phthalazin-4''-yl)phenyl)acrylic acid **3b.** Yellow solid (70%). Pf. 170-172 ºC. UV (ethanol): λ_{max} nm (ε, $M^{-1}cm^{-1}$) 345 (4500). ^1H NMR ($CDCl_3$, 300 MHz) δ 7.31 (d, 1 H, H-4'', *J*= 3.9 Hz), 7.60 (d, 1 H, H-5'', *J*= 4.8 Hz), 7.76 (d, 1 H, H-3'', *J*= 3.9 Hz), 7.91-8,01 (m, 4 H, H-7', H-6', H-3, H-5), 8.12 (d, 2 H, H-2, H-6, *J*= 7.5 Hz), 8.18 (d, 1 H, H-8', *J*= 7.8 Hz), 8.36 (s, 1 H, =CH), 8.60 (d, 1 H, H-5', *J*= 8.4 Hz) ppm.

2-Cyano-3-(5'-(1''-(thiophen-2'''-yl)phthalazin-4''-yl)furan-2'-yl)acrylic acid **4b**. Yellow solid (8%). UV (ethanol): λ_{max} nm (ε, $M^{-1}cm^{-1}$) 392, (67500). ^1H NMR ($CDCl_3$, 400 MHz) δ 7.24 (dd, 1 H, H-4''', *J*= 5.0 and 4.0 Hz), 7.36 (d, 1 H, H-4', *J*= 4.0 Hz), 7.62 (dd, 1 H, H-5''', *J*= 5.0 and 1.2 Hz), 7.78 (dd, 1 H, H-3''', *J*= 3.6 Hz and 0.8 Hz), 7.83 (d, 1 H, H-3', *J*= 3.6 Hz), 7.96-8.08 (m, 3 H, =CH, H-7'', H-6''), 8.54 (d, 1 H, H-8'', *J*= 7.6 Hz), 9.30 (d, 1 H, H-5'', *J*= 8.8 Hz) ppm.

General procedure for the synthesis of rhodamine-3-acetic acids **3c** and **4c** through Knoevenagel condensation: To a solution of aldehyde (0.25 mmol) and rhodanine-3-acetic acid

(58 mg, 0.3 mmol) in ethanol was added 4 drops of *N*-triethylamine. The mixture was refluxed for 6 h then cooled down to room temperature. The crude product was concentrated and ethyl ether was added to induce precipitation. The precipitate was filtered and washed with ethyl ether to give the pure product.

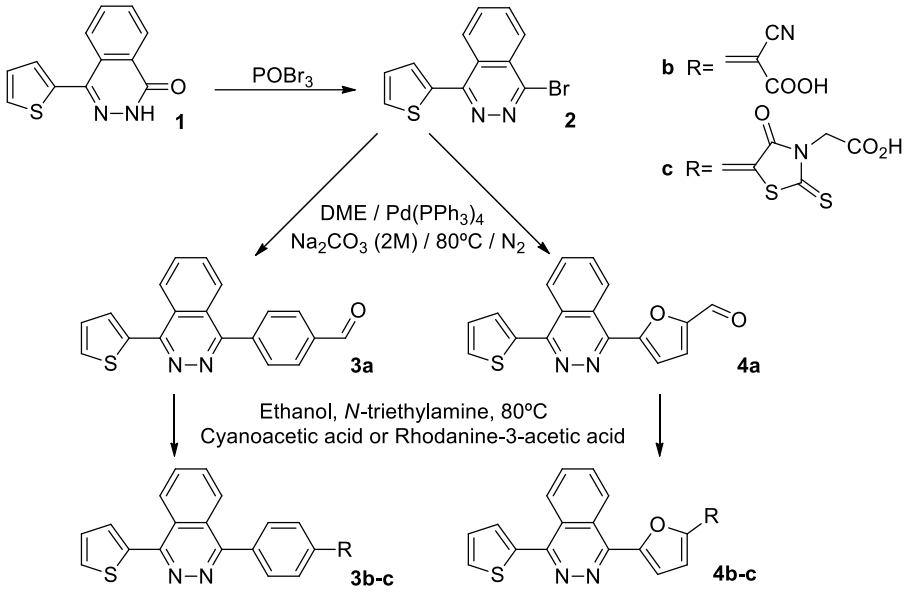
2-(4'-Oxo-5'-((4''-(1'''-(thiophen-2''''-yl)phthalazin-4'''-yl)phenyl)methylene)-2'-thioxothiazolidin-3'-yl)acetic acid **3c**. Yellow solid (76%). Pf. 189-191 ºC. UV (ethanol): λ_{max} nm (ε, $M^{-1}cm^{-1}$) 382, (23750). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.91 (s, 2 H, CH_2), 7.31 (dd, 1 H, H-4'''', *J*= 5.4 and 3.6 Hz), 7.66 (dd, 1 H, H-5'''', *J*= 4.9 and 1.2 Hz), 7.73-7.78 (m, 3 H, =CH, H-6'', H-2''), 7.90-8.03 (m, 5 H, H-3'''', H-6''', H-7''', H-3'', H-5''), 8.16 (d, 1 H, H-8''', *J*= 7.5 Hz), 8.62 (d, 1 H, H-5''', *J*= 7.8 Hz) ppm.

2-(4'-Oxo-(5'-((5''-(1'''-(thiophen-2''''-yl)phthalazin-4'''-yl)furan-2''-yl)methylene)-2'-thioxothiazolidin-3'-yl)acetic acid **4c**. Orange solid (41%). UV (ethanol): λ_{max} nm (ε, $M^{-1}cm^{-1}$) 436, (21500). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.63 (s, 2 H, CH_2), 7.27 (dd, 1 H, H-4'''', *J*= 4.9 and 6.9 Hz), 7.33 (d, 1 H, H-4'', *J*= 3.6 Hz), 7.58 (d, 1 H, H-3'', *J*= 3.6 Hz), 7.72 (dd, 1 H, H-5'''', *J*= 4.9 and 1.2 Hz), 7.78 (dd, 1 H, H-3'''', *J*= 3.6 and 1.2 Hz), 7.97 (s, 1 H, =CH), 8.07-8.10 (m, 2 H, H-7''', H-6'''), 8.55-8.59 (m, 1 H, H-8'''), 8.80-8.83 (m, 1 H, H-5''') ppm.

3. Results and Discussion

3.1. Synthesis

The precursor phthalazinone **1** was prepared by condensation of ethyl-2-(thiophene-2-carbonyl)benzoate with hydrazine hydrate in ethanol. On the other hand the bromo-thienylphthalazine **2** was prepared by reaction of thienylphthalazinone **1** with $POBr_3$. Formyl derivatives **3a** and **4a** were synthesized by Suzuki cross-coupling reaction of 3-bromo-6-(thiophen-2-yl)phthalazine **2** with commercially available (hetero)aryl-boronic acids in fair to good yields (21-56%) (Table 1, Scheme 1). Cyanoacetic acid derivatives **3b** and **4b** were obtained by Knoevenagel condensation of the formyl precursors with cyanoacetic acid in refluxing ethanol in fair to good yields (8-70%). On the other hand, rhodanine-acetic acid derivatives **3c** and **4c** were prepared by Knoevenagel condensation of the same formyl precursors with rhodanine-3-acetic acid in refluxing ethanol in moderate to good yields (41-76%). The new heterocyclic systems **3**-**4** were characterised by the usual spectroscopic techniques.



Scheme 1. Synthesis of compounds **2**, **3** and **4**.

Table 1. Yields, UV-visible absorption data of thienylphthalazine dyes **3**-**4** in ethanol solutions.

Cpd	Yield	λ_{max} (nm)			ε
	(%)	$CHCl_3$	EtOH	DMSO	($M^{-1}cm^{-1}$)
3a	56	-	331	-	9167
3b	70	338	345	339	4500
3c	76	388	382	387	23750
4a	21	-	366	-	12800
4a	8	388	392	397	67500
4b	41	450	436	445	21500

3.2. UV-Visible study

The electronic spectra of thienylphthalazine **3-4** were recorded in ethanol solutions (10^{-4} M) and exhibited an intense lowest energy charge-transfer absorption band in the UV-visible region (Table 1, Figure 1). The location of the aforementioned band depends not only on the electronic nature of the aryl or heterocycle group linked at position 4 of the phthalazine moiety, but also on the electronic nature of the acceptor moiety. Bathochromic shifts (35-54 nm) were detected upon substitution of the aryl group (**3**) with a furan heterocycle (**4**). This observation confirms previously obtained results[6b, 6e, 6g] showing that the incorporation of electron rich heterocycles such as thiophene, pyrrole or furan heterocycles in push-pull compounds enhances their

charge-transfer properties. Therefore, dyes **4a**-**c** in which the phenyl ring was substituted by the furan ring exhibit improved optical properties compared to the corresponding aryl derivatives **3a**-**c**, probably due to the auxiliary donor effect of the furan heterocycle. We also notice bathochromic shifts in the range of 14-70 nm upon substitution of the formyl group (**a**) by the cyanoacetic acid (**b**) or by the rhodanine-3-acetic acid moiety (**c**) due to the higher electronic delocalization as well as the stronger acceptor ability of the rhodanine-3-acetic acid group.

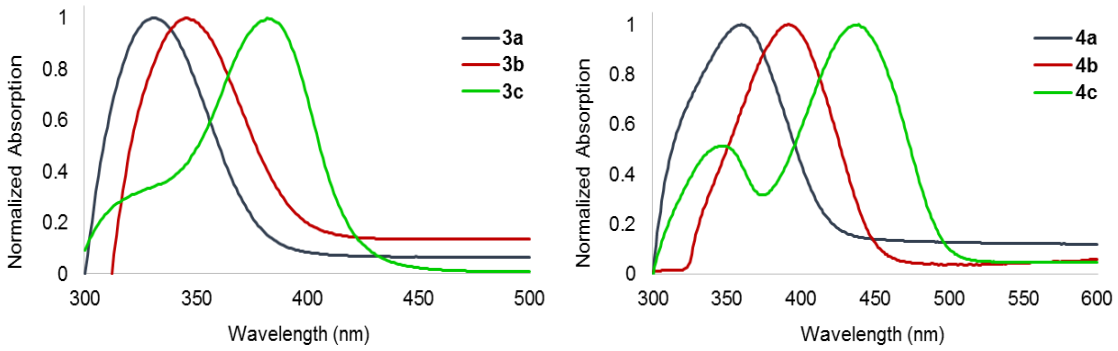


Figure 1. Normalized absorption spectra of thienylphthalazines **3**-**4** recorded in ethanol.

A preliminary solvatochromic study of the absorption spectra of compounds **3b-c** and **4b-c** in three selected solvents possessing different solvation character (ethanol, chloroform and DMSO) was performed (Table 1, Figure 2). For compounds **3c**, **4b**-**c** the highest-energy transitions are found in ethanol, more polar solvents such as DMSO result in lower energy transitions, thus indicating a positive solvatochromic response ($\Delta\nu_{max}$ = 1111-2000 cm^{-1}), being compound **4c** the most solvatochromic.

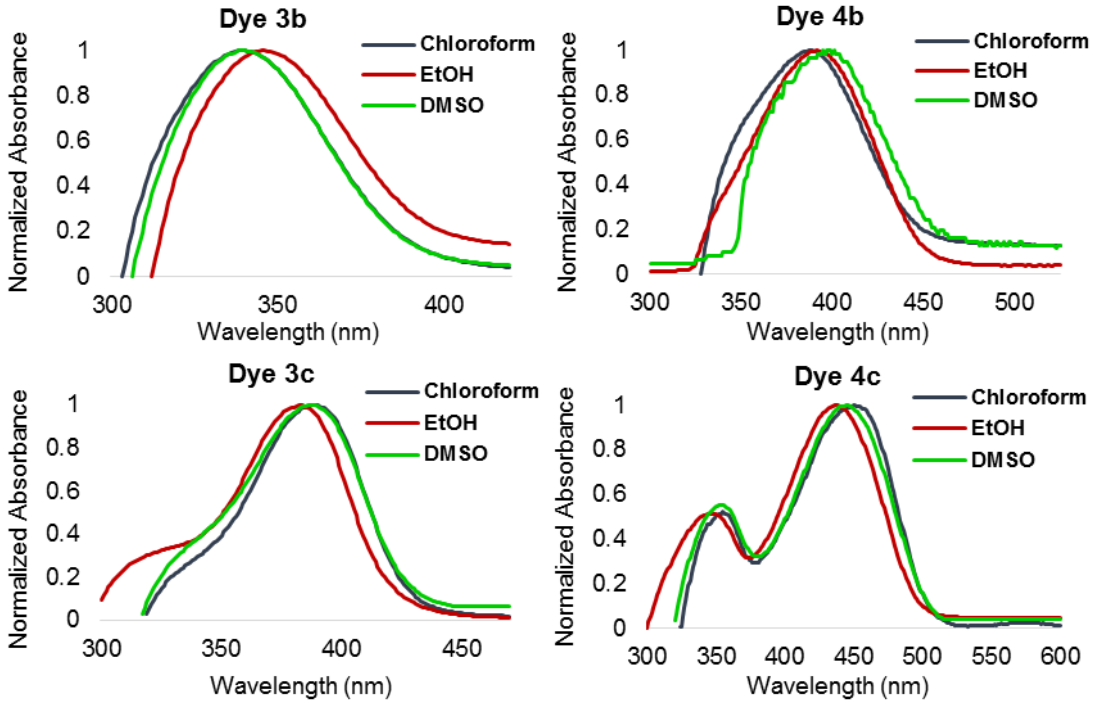


Figure 2. Normalized UV-Vis absorption spectra of thienylphthalazines **3b-c** and **4b-c** in chloroform, ethanol and dimethylsulfoxide.

4. Conclusions

Six novel thienyl-phthalazines **3a**-**c** and **4a**-**c** were synthesized in fair to good yields through several synthetic methodologies. Compounds **3-4** exhibit absorption bands in the UV-visible range influenced by the electronic nature of the (heteroaryl)aryl groups substituted on the thienyl-phthalazine conjugated bridge as well as by the different acceptor moieties. Due to their push-pull character and optical properties the synthesized thienylphthalazines **3b-c** and **4b-c** will be studied in the future for nonlinear optical applications as second-harmonic generation (SHG) chromophores. Additionally, and as a result of their functionalization with appropriate anchoring groups and their optical properties, compounds **3b**-**c** and **4b**-**c** could have also potential application as sensitizers for DSSCs, particularly dyes **4b** and **4c**. The studies concerning their application as NLO chromophores as well as sensitizers for DSSCs are currently underway.

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6. References

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