



Practical synthesis of bis-substituted tetrazines with two pendant 2-pyrrolyl or 2-thienyl groups, precursors of new conjugated polymers

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Abstract—Novel linear oligoheterocycles based on substituted tetrazines are described. The desired compounds have been accomplished by a variation of the original Pinner [Ann. Chem., 297 (1897) 221] synthesis in which the aromatic nitrile reacted with hydrazine in an aqueous solution to give bis(pyrrolyl)tetrazines or bis(phenyl)tetrazines. The bis(phenyl)tetrazines reacted with 3,4-ethylenedioxy-2-(trimethyltin)thiophene or 2-(trimethyltin)thiophene in the presence of Pd(PPh₃)₂Cl₂ or Pd(PPh₃)₄ as catalyst to give the desired compounds. Quantum-chemical calculations were performed to assess the usefulness of the synthesized compounds for electropolymerization. Studies have indicated qualitative difference between bis-pyrrole tetrazine and bis-phenyl tetrazines regarding the electronic density rearrangement due to the loss of an electron. © 2003 Elsevier Science Ltd. All rights reserved.

1. Introduction

During the past decades, the design and synthesis of novel conjugated polymers as low-cost materials with high potential for electronic and optoelectronic applications have received considerable attention.² A few years ago, we reported on the synthesis of a 1,4-bis(pyrrol-2-yl)arylenes.^{3–5} This new synthetic route opens up a number of opportunities for the synthesis of derivatized, potentially soluble and processable pyrrole containing polymers. With our ongoing interest in precursors of conducting polymers we report on the synthesis of novel symmetric bis-pyrrole-, and also bis-thiophene or bis-dioxanethiophene, derivatives based on tetrazines. By contrast, the interest in thiophene⁶ or 3,4-ethylenedioxythiophene⁷ is more recent. As is known from the literature, the resulting polymers exhibit high electroconductivity and improved electrochemical and thermal stability. We reasoned that the tetrazines with pyrrole, thiophene or 3,4-ethylenedioxythiophene rings would be good candidates for polymerization.

It has been established⁵ that the rearrangement of the electronic density distribution correlates with parameters important for the experimental electropolymerization. Theoretical studies of the structures and properties of

newly synthesized compounds are performed with the aim of assessing the usefulness of newly synthesized moieties for polymerization.

2. Results and discussion

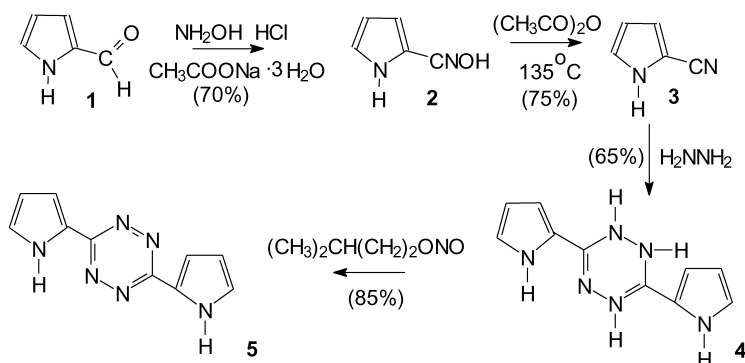
2.1. Synthesis of 3,6-bis-(pyrrol-2-yl)-1,2,4,5-tetrazine

Herein we present our synthesis of 3,6-bis(pyrrolyl)-1,2,4,5-tetrazine. The synthesis was carried out as outlined in Scheme 1. The 2-pyrrolealdehyde (**1**) was reacted with hydroxylamine hydrochloride and sodium acetate to give 2-pyrrolealdehyde oxime.⁸ Treatment of compound **2** with an excess of acetic anhydride produced the corresponding nitrile (**3**).⁸ 2-Pyrrolenitrile was reacted with tetrazine to give new 3,6-bis(pyrrolyl)-1,2-dihydro-1,2,4,5-tetrazine **4** (in a procedure similar to that used for the preparation of 3,6-bis(phenyl)-1,2-dihydro-1,2,4,5-tetrazine).⁹ Compound **4** after reaction with isoamyl nitrite, oxidized to the corresponding fully aromatic compound **5** (according to a literature procedure for the preparation of 3,6-bis-diphenyl-1,2,4,5-tetrazine).¹⁰

In this paper we also report a synthetic study of bis-thiophene- and bis-(dioxanethiophene)-tetrazines. This study has been inspired by a literature review^{6,7} and our previous experiences⁵ concerning conjugated oligomers

Keywords: precursors; tetrazines; bis-dioxanethiophene; bis-thiophene.

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Scheme 1.

based on various combinations of thiophene and 3,4-ethylenedioxythiophene.

2.2. Synthesis of 3,6-bis-(4-iodophenyl)-1,2,4,5-tetrazine

4-Aminobenzonitrile (7) prepared in 70% yield from 4-nitrobenzonitrile (6) as previously reported¹¹ (Scheme 2) was cyclized by heating with anhydrous hydrazine (98%)¹¹ into the previously unreported 3,6-bis-(4-aminophenyl)-1,2-dihydropyridazine (8) in 65% yield. Compound (8) was oxidized to the corresponding tetrazine 9 by treatment with

hydrogen peroxide (6%) following a literature procedure.¹¹ 3,6-Bis-(4-aminophenyl)-tetrazine (9) was isolated after purification by column chromatography. Under the conditions shown in Scheme 2, diamine 9 was converted by a Sandmeyer reaction (in a procedure similar to that used for the iodination of 2-bromo-3,6-dimethoxyaniline)¹² into 3,6-bis-(4-iodophenyl)-tetrazine 10.

2.3. Synthesis of 3,6-bis-(4-bromophenyl)-1,2,4,5-tetrazine

An analogous Sandmeyer reaction¹² was used to prepare bromide 11 (as was used to synthesize tetrazine 10). 3,6-Bis-(4-aminophenyl)-1,2,4,5-tetrazine (9) was reacted with NaNO₂/HBr/CuBr in methanolic acetic acid at 0 °C to give 11 in 80% yield (Scheme 2).

2.4. Synthesis of 3,6-bis-(4-phenyl-4-thiophene)-1,2,4,5-tetrazine

The synthesis of bis(thienyl)tetrazines was accomplished by the reaction of 3,6-bis(4-halogenophenyl)tetrazines with 2-metallated thiophene (12).¹³

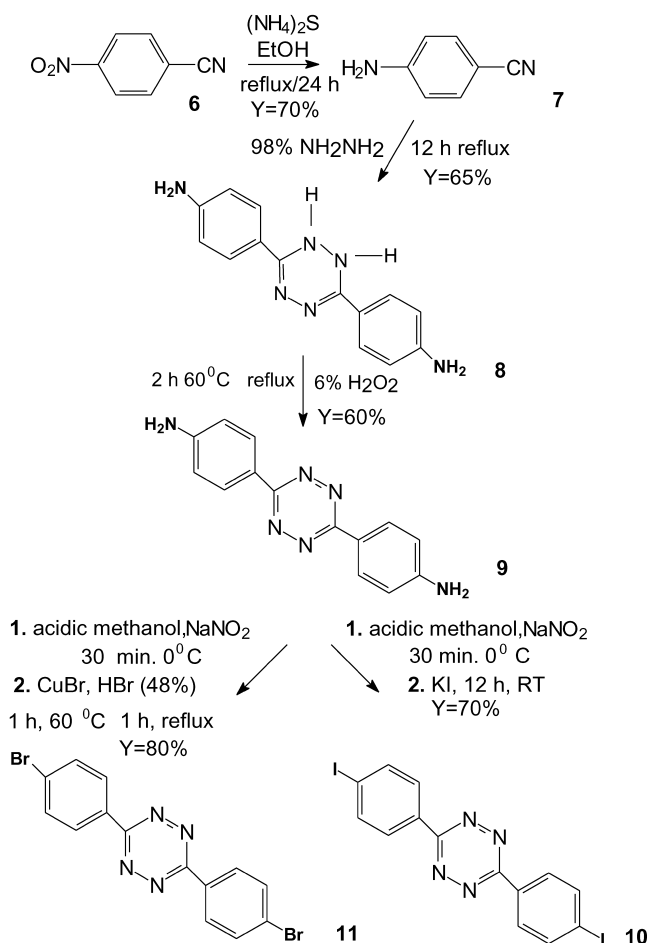
Compound 13 was synthesized through the coupling reaction between 12 and 3,6-bis(4-iodophenyl)- or 3,6-bis(4-bromophenyl)-1,2,4,5-tetrazine (10, 11, Scheme 3) according to the literature procedure for the preparation of bis(thienyl)fluorene derivatives.¹⁴

2.5. Synthesis of 3,6-bis{(4-phenyl-4-[3,4-ethylenedioxythiophene])}-1,2,4,5-tetrazine

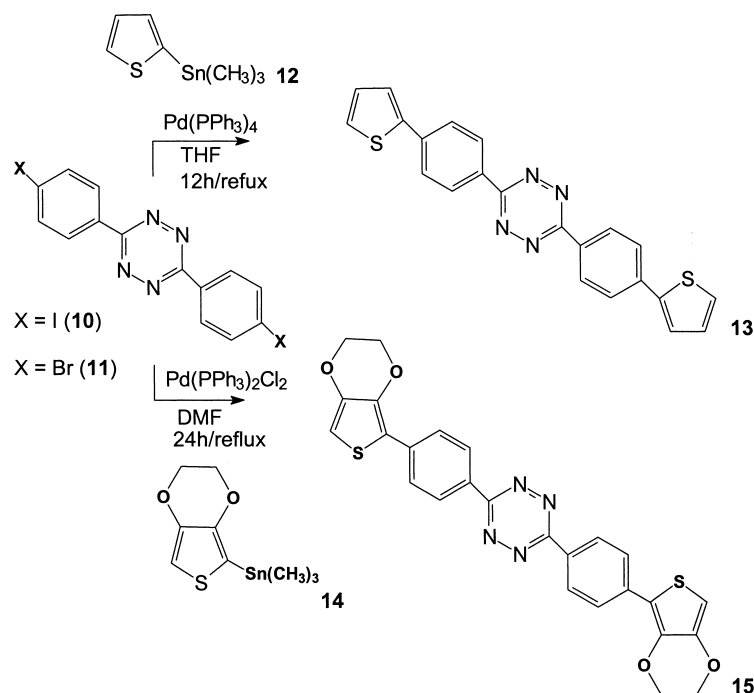
The synthesis was carried out as outlined in Scheme 3 where a Stille coupling was employed to couple 3,4-ethylenedioxy-2-(trimethyltin)thiophene⁷ (14, Scheme 3) with 3,6-bis(4-bromophenyl)- or 3,6-bis(4-iodophenyl)-1,2,4,5-tetrazine (Scheme 3) to give 3,6-bis{(4-phenyl-4-1,4-dioxane-[2,3-*c*]-thiophene)}-1,2,4,5-tetrazine (15).

2.6. Molecular modelling results

The properties of polymers are related to properties of monomers. It has been shown⁵ that the electronic charge distribution as well as an ionization potential correlate with experimental parameters describing the polymerization process. The optimization of tetrazine derivatives



Scheme 2.



Scheme 3.

(**5**,**10**,**11**,**13**,**15**) leads to structures with the planar conjugated three ring fragment (Fig. 1). All the molecules studied possess C_n symmetry resulting in the lack of a dipole moment. The thiophene rings in 3,6-bis-(4-phenyl-4-thiophene)-1,2,4,5-tetrazine (**13**) and 3,6-bis(4-[3,4-ethylenedioxythiophene])-4,4'-bis(phenyl)-1,2,4,5-tetrazine (**15**) derivatives are out of plane by 24° and 17° , respectively. Substitution has little impact on the central tetrazine fragment regarding structural changes as well as electronic charge distributions.

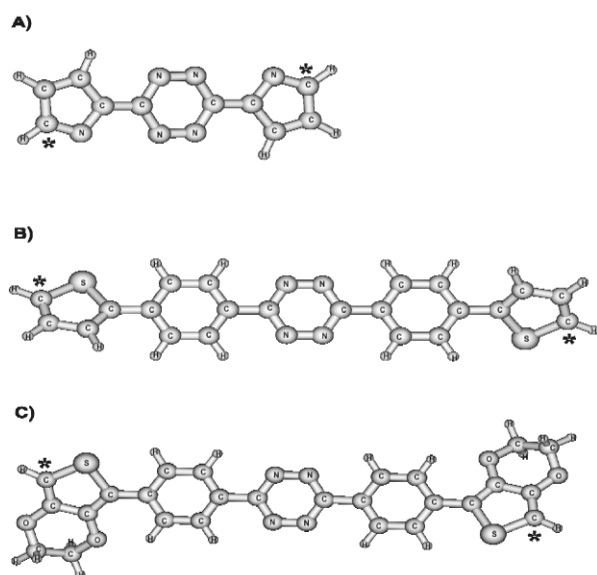


Figure 1. The optimized structure of (a) 3,6-bis-(pyrrol-2-yl)-1,2,4,5-tetrazine (**5**), (b) 3,6-bis-(4-phenyl-4-thiophene)-1,2,4,5-tetrazine (**13**), and (c) 3,6-bis-[(4-phenyl-4-[3,4-ethylenedioxythiophene])]-1,2,4,5-tetrazine (**15**). The asterisk (*) indicates the potential sites of the polymerization.

The loss of an electron due to ionization leads to a change in electronic density distribution, which is qualitatively different in 3,6-bis(pyrrol-2-yl)-1,2,4,5-tetrazine (**5**) and phenyl containing (**13**,**15**) moieties. The ionization potential of bis-pyrrolyl-tetrazine amounts to 8.06 eV and the main change of electronic density takes place on the tetrazine ring. The calculated electronic population loss from this fragment is 0.49 electron. The population change on the possible site of polarization (Fig. 1) only amounts to 0.04 electron. The derivatives of bis-phenyl-tetrazine are ionized at lower energies (6.86 and 6.41 eV for **13** and **15**, respectively). The electronic population change due to the ionization is below 0.1 electron on the tetrazine ring. The main loss of density is observed on thiophene in 3,6-bis-(4-phenyl-4-thiophene)-1,2,4,5-tetrazine (**13**, 0.260 electron) and on dioxanethiophene in 3,6-bis(4-[3,4-ethylenedioxythiophene])-4,4'-bis(phenyl)-1,2,4,5-tetrazine (**15**, 0.283 electron) rings. More importantly, the potential sites of the polymerization (Fig. 1) are characterized by a large electronic population change of 0.49 electron in **13** and 0.49 electron in **15**.

3. Conclusions

We have successfully developed a new strategy for preparation of 3,6-bis(pyrrolyl)-bis(thiophene)- or bis(dioxanethiophene)-tetrazines: a potential bifunctional building block for the synthesis of linear oligoheterocycles. The desired compounds have been accomplished by a variation of the original Pinner synthesis¹ to give bis(pyrrolyl)tetrazines or diphenyltetrazines. The diphenyltetrazines reacted with 3,4-ethylenedioxy-2-(trimethyltin)-thiophene in the presence of $\text{Pd}(\text{PPh}_3)_3\text{Cl}_2$ or $\text{Pd}(\text{PPh}_3)_4$ as catalysts to give the designed compounds. This methodology may also be applicable for the synthesis¹ of other tetrazine derivatives. Further work is in progress in order to

understand the role of tetrazine in these reactions and also in polymer results.

The structures and properties of synthesized molecules were determined theoretically. All examined molecules possess the planar three-ring fragment with negligibly different structural parameters. The main difference between bis-pyrrole tetrazine and substituted bis-phenyl tetrazines concerns the change in charge distribution due to ionization. The main change in bis-pyrrole is observed on the central pyrazine ring with the little impact on the potential polarization sites. The situation in substituted bis-phenyl moieties is qualitatively different. The electron loss due to the ionization takes place on thiophene in 3,6-bis-(4-phenyl-4-thiophene)-1,2,4,5-tetrazine (**15**) and on dioxane-thiophene in 3,6-bis-(4-[3,4-ethylenedioxythiophene])-4,4'-bis(phenyl)-1,2,4,5-tetrazine (**19**) rings. More important, the concentration on the electron loss is observed on atoms being potential centers for the polarization.

4. Experimental

4.1. General comments

Melting points are uncorrected. All NMR spectra were performed using a Varian VXR-300 spectrometer operating at 300 MHz (^1H) and 75 MHz (^{13}C) in DMSO and CDCl_3 . Chromatography column was carried out on Merck Keisel gel 60 (5386) silica gel. THF was used immediately after distilling from a solution containing benzophenone/sodium. Other starting materials, reagents and solvents were used as received from suppliers.

4.1.1. 2-Pyrrolaldoxime (2). A solution of hydroxylamine hydrochloride (7.5 g, 0.11 mol) and sodium trihydrate (15 g, 0.11 mol) in 40 mL water was shaken vigorously with 2-pyrrolaldehyde **1** (9.0 g, 0.095 mol) for 10 min, then refrigerated overnight. The crude product was recrystallized from benzene. Yield 70% (7.29 g), mp 164–166°C (lit. 164–164.5°C).

4.1.2. 2-Pyrrolenitrile (3). 2-Pyrrolealdoxime (9.2 g, 0.084 mol) in acetic anhydride was warmed slowly and then refluxed gently for 30 min. The cooled reaction products were poured into 200 mL water, extracted three times 20 mL portion of ether, and dried over sodium sulfate. After removal of the residue they were vacuum-distilled and the fraction bp 89–91°C was collected. Yield 75% (5.76 g).

4.1.3. 3,6-Bis-(pyrrol-2-yl)-1,2-dihydro-1,2,4,5-tetrazine (4). Anhydrous hydrazine (98%, 5 mL) was added to pyrrolyl-2-nitrile (**3**) (1.0 g, 8.4 mmol). The solution was heated on a steam bath for 18 h. After cooling, the resulting orange-yellow precipitate was filtered, washed with water and immediately used in the next step without purification. Red plates, yield (1.55 g, 65%), mp 205°C. ^1H NMR δ (DMSO- d_6) 6.11 (s, 2H, pyrrole H), 6.53 (s, 2H, pyrrole H), 6.67 (s, 2H, pyrrole H), 8.50 (s, 2H, –NH–NH), 11.11 (s, 2H, NH); ^{13}C NMR δ (DMSO- d_6) 108.7, 109.3, 118.39, 120.5, 148.5.

4.1.4. 3,6-Bis-(pyrrol-2-yl)-1,2,4,5-tetrazine (5). To a solution of isoamyl nitrite (5 g in 95% ethanol, 100 mL) was added 3,6-bis(pyrrol-2-yl)-1,2-dihydro-1,2,4,5-tetrazine (6 g, 28.0 mmol) (**4**). The mixture was refluxed for 4 h, cooled to room temperature, and filtered. The product was recrystallized from toluene to yield 85% (red product, 5.05 g), mp 285°C. ^1H NMR δ (DMSO- d_6) 6.12 (s, 2H, pyrrole H), 6.55 (s, 2H, pyrrole H), 6.68 (s, pyrrole H), 11.14, (s, 2H, NH); ^{13}C NMR δ (DMSO- d_6) 108.7, 109.3, 118.39, 120.5, 148.5. Anal. calcd for $\text{C}_{10}\text{H}_8\text{N}_6$: C, 76.89; H, 5.16; N, 17.94. Found: C, 76.71; H, 5.03; N, 17.90.

4.1.5. 3,6-Bis-(4-aminophenyl)-1,2-dihydro-1,2,4,5-tetrazine (8). A solution of 4-nitrobenzotrile (**6**) (2.0 g, 13.5 mmol) and ammonium sulfide in ethanol (20 mL) was heated on a steam bath for 24 h. The precipitate was removed by filtration, and the solvent concentrated under reduced pressure. The residue was heated with a small amount of water and filtered.

Anhydrous hydrazine (98%, 5 mL) was added to crude 4-aminobenzotrile (**7**) (1.0 g, 8.4 mmol). The solution was heated on a steam bath for 18 h. After cooling, the resulting orange-yellow precipitate was filtered, washed with water and immediately used in the next step without purification. Yield 51% (2.29 g, red product), mp 261°C; ^1H NMR δ (DMSO- d_6) 5.47 (s, 4H, NH_2), 6.53 (d, 4H, $J=8.3$ Hz, arom. H), 7.47 (d, 4H, $J=8.3$ Hz, arom. H), 8.51 (s, 2H, NH); ^{13}C NMR δ (DMSO- d_6) 113.0, 117.3, 126.9, 148.6, 150.4. HRMS calcd for $\text{C}_{14}\text{H}_{14}\text{N}_6$ 267.1371 (M^-+1). Found: 267.1371.

4.1.6. 3,6-Bis-(4-aminophenyl)-1,2,4,5-tetrazine (9). A solution of 3,6-bis-(4-aminophenyl)-1,2-dihydro-1,2,4,5-tetrazine (**8**) (0.5 g, 1.8 mmol) and aqueous hydrogen peroxide (6%, 50 mL) was warmed at 60°C for 2 h, to yield a red solid, which was collected by filtration and air-dried. The crude product was purified by column chromatography on silica gel using acetone and hexane (2:1) as eluent. Yield 60% (0.3 g), brown-red product, mp 288–289°C; ^1H NMR δ (DMSO- d_6) 6.01 (s, 4H, NH_2), 6.73 (d, 4H, $J=8.7$ Hz, arom. H), 8.15 (d, 4H, $J=8.7$ Hz, arom. H); ^{13}C NMR δ (DMSO- d_6) 113.8, 118.3, 128.5, 152.8, 162.3; HRMS calcd for $\text{C}_{14}\text{H}_{12}\text{N}_6$ 265.1201 [$M+1$]. Found: 265.1207.

4.1.7. 3,6-Bis-(4-iodophenyl)-1,2,4,5-tetrazine (10). Sodium nitrate (0.10 g, 4.8 mmol) in water (0.8 mL) was added during 5 min to a solution of 3,6-bis-(4-aminophenyl)-1,2,4,5-tetrazine (0.1 g, 0.37 mmol) in concentrated hydrochloric acid (1 mL) and ice (1.0 g) at 0°C while stirring. The mixture was stirred at 0°C for a further 20 min, then was placed into a jacketed addition funnel at 0°C, and was added over 20 min to a stirred solution of potassium iodide (2.45 g, 0.015 mol) in water (3 mL) at rt. The mixture was left to stand at rt overnight and then extracted with ether (2×30 mL). The combined organic extracts were washed successively with 10% aqueous NaOH (30 mL), 5% NaHCO_3 (30 mL), and H_2O (50 mL) and dried over anhydrous MgSO_4 . Concentration *in vacuo* and flash chromatography of the residue (hexane/ethyl acetate, 2:1) gave 3,6-bis-(4-iodophenyl)-1,2,4,5-tetrazine (**5**). Yield

70% (0.13 g, pink prism), mp 278°C; ^1H NMR δ (DMSO- d_6) 7.84 (d, 4H, $J=8.4$ Hz, arom. H), 7.91 (d, 4H, $J=8.1$ Hz, arom. H); ^{13}C NMR δ (DMSO- d_6) 96.3, 105.9, 127.9, 137.7. Anal. calcd for $\text{C}_{14}\text{H}_8\text{N}_4\text{J}_2$: C, 35.59; H, 1.66; N, 11.52. Found: C, 35.58; H, 2.06.

4.1.8. 3,6-Bis-(4-bromophenyl)-1,2,4,5-tetrazine (11). Sodium nitrate (3.14 g, 0.045 mol) in water (9.1 mL) was added with stirring over 10 min to a cold (0°C) solution of 3,6-bis-(4-aminophenyl)-1,2,4,5-tetrazine (0.5 g, 0.019 mol) in mixture of concentrated sulfuric acid (4.5 mL), methanol (2.3 mL), and water (6.7 mL). The mixture was stirred at 0°C for further 30 min and then added over 45 min to a stirred, warm (60°C) solution of copper(I) bromide (0.4 g, 2.8 mmol), hydrobromic acid (48%, 1.2 mL), and water (6.7 mL). At the end of the addition the mixture was refluxed for 1 h, cooled, and filtered. The precipitate was washed with water (15 mL), and air-dried. Purification by flash chromatography (hexane/ethyl acetate, 2:1) gave 3,6-bis-(4-bromophenyl)-1,2,4,5-tetrazine (**6**). Yield 80% (0.60 g, red needles), mp 198°C; ^1H NMR δ (DMSO- d_6) 7.69 (d, 4H, $J=8.3$ Hz, arom. H), 8.00 (d, 4H, $J=8.5$ Hz, arom. H); ^{13}C NMR δ 122.7, 126.6, 128.3, 132.5, 164.0. Anal. calcd for $\text{C}_{14}\text{H}_8\text{N}_4\text{Br}_2$: C, 42.88; H, 2.05. Found: C, 42.88; H, 2.15.

4.1.9. 2-(Trimethyltin)-thiophene (12). Compound **12** was prepared according the standard procedure.¹³ Yield 70%. ^1H NMR (CDCl_3): 0.35 (s, 9H, CH_3); 6.05 (s, 1H, CH); 6.20 (s, 1H, CH), 6.45 (s, 1H, CH).

4.1.10. 3,6-Bis-(4-phenyl-4-thiophene)-1,2,4,5-tetrazine (13). Compound **12** (0.52 g, 2.1 mmol), 3,6-Bis-(4-bromophenyl)-1,2,4,5-tetrazine (0.4 g, 1.0 mmol), and $\text{Pd}(\text{PPh}_3)_4$ (0.6 g, 0.8 mmol) were added to THF (100 mL). The mixture was stirred at 65°C overnight under nitrogen atmosphere. The THF was evaporated to give solid. The residue was purified by column chromatography (eluent: hexane/ethyl acetate, 2:1). Yield 85% (0.34 g, yellow-green plates), mp 199–201°C. ^1H NMR (CDCl_3): 6.15 (s, 2H, CH, thiophene); 6.25 (s, 2H, CH, thiophene), 6.35 (s, 2H, CH), 7.15 (d, 4H, $J=7.05$ Hz, arom. H), 7.45 (d, 4H, $J=7.42$ Hz, arom. H); ^{13}C NMR δ 60.5, 61.4, 67.2, 69.7, 122.7, 126.6, 128.3, 132.5, 164.0. Anal. calcd for $\text{C}_{22}\text{H}_{14}\text{N}_4\text{S}_2$: C, 63.33; H, 3.54; N, 14.07. Found, C, 63.1; H, 3.45; N, 14.00.

4.1.11. 3,4-Ethylenedioxy-2-(trimethyltin)thiophene (14). Compound **14** was prepared from 3,4-ethylenedioxythiophene according the literature procedure.⁷ Yield 70%. ^1H NMR (CDCl_3): 0.45 (s, 9H, CH_3); 4.25 (m, 4H, $\text{OCH}_2\text{CH}_2\text{O}$); 6.02 (s, 1H, CH).

4.1.12. 3,6-Bis-(4-[3,4-ethylenedioxythiophene])-4,4'-bis(phenyl)-1,2,4,5-tetrazine (15). Compound **14** (0.64 g, 2.1 mmol), 3,6-bis-(4-bromophenyl)-1,2,4,5-tetrazine (0.4 g, 1.0 mmol), and $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.6 g, 0.8 mmol) were added to DMF (100 mL). The mixture was stirred at 100°C overnight under a nitrogen atmosphere. The DMF was evaporated to give solid, which was purified by column chromatography (eluent: hexane/ethyl acetate, 2:1). Yield 87% (0.45 g, yellow-green plates), mp 212°C. ^1H NMR (CDCl_3) 4.27, 4.35 (s, 4H, $\text{OCH}_2\text{CH}_2\text{O}$); 6.35 (s, 1H, CH, thiophene); 6.60 (s, 1H, CH, thiophene); 7.05 (d, 4H, $J=7.05$ Hz, arom. H), 7.34 (d, 4H, $J=7.42$ Hz, arom. H); ^{13}C NMR δ 25.7, 28.8, 60.4, 61.3, 67.4,

69.8, 122.7, 126.6, 128.3, 132.5, 164.0. Anal. calcd for $\text{C}_{26}\text{H}_{18}\text{N}_4\text{O}_4\text{S}_2$: C, 60.71; H, 3.53; N, 10.90. Found, C, 60.3; H, 3.48; N, 10.6.

4.2. Theoretical methods

The calculations presented here were performed applying the density functional theory (DFT) method. The DFT approach utilized Becke's three-parameter functional¹⁵ with the local correlation part of Vosco et al.¹⁶ and the nonlocal part of Lee et al.¹⁷ (abbreviated as B3LYP). The calculations were performed in the standard 6-31G* atomic basis set.¹⁸ The geometry of molecules were optimized and later used for calculations of vertical ionization energies. The electronic density distribution is based on the Mulliken population scheme utilizing the DFT/B3LYP function. The results reported here were obtained using the GAUSSIAN-98 code.¹⁹

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