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Triphenylamine/Tetrazine based π-Conjugated Systems as Molecular Donors for Organic Solar Cells

Cassandre Quinton, Valérie Alain-Rizzo, Cécile Dumas-Verdes, Gilles Clavier, Laurence Vignau and Pierre Audebert

Conjugated systems built by connecting one electron-donor triphenylamine to an electron-withdrawing tetrazine have been prepared using various linkers. We describe here the synthesis, the electrochemical properties and some photophysical properties of these molecules, emphasizing the dependence upon the type of linker between the groups and an organic photovoltaic solar cell was prepared with one derivative.

Introduction

s-Tetrazine (Tz) is a strong electron-withdrawing molecule which finds many fields of applications such as retro Diels-Alder cyclisation, electrofluorochromism, coordination chemistry, and energetic compounds. Very recently, polymers containing s-tetrazine have been used in organic photovoltaic (OPV) cells and there is one example of transistor based on a tetrazine-naphthalene diimide system. Triphenylamine (TPA) is a well-known electron-donor unit, extensively investigated in diverse fields including electrochromism, organic electronics or two-photon absorption. Recently we showed interest in the study of covalently linked tetrazine-triphenylamine derivatives where the fluorescence of the tetrazine unit could be switched on upon oxidation of the triphenylamine unit. However it is interesting to notice, that although these compounds can be regarded in principle as donor–acceptor (D–A) systems, no intramolecular charge transfer (ICT) bands were detected in the UV-vis spectra. In fact, TPA and Tz units have never been covalently combined in a conjugated linked D–A system, in which an ICT band from the donor TPA moiety towards the accepting Tz ring is expected to occur, with the aim of using such an assembly as donor in an OPV cell. Indeed, the structure of efficient molecular donors generally involves a combination of donor and acceptor blocks. The goal is to create an ICT which produces at the same time an extension of the absorption spectrum towards longer wavelengths and a lowering of the HOMO level leading to an increase in the open-circuit voltage (Voc) of the OPV cell. In recent years, this approach has led to the synthesis of different classes of active molecules.

Results and discussions

Synthesis

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Design of tetrazine molecules 1-6 was rationalized in order to get mono or di-substitutions of the tetrazine core. First we were interested in introducing a phenyl group as a bridge between the tetrazine unit and the triphenylamine moiety and in studying the influence of the position of the substituents on the phenyl bridge. Thus we targeted bichromophores 1-4 (Figure 1). In order to synthesize the four chromophores, organometallic coupling reactions between bis-((dibromophenyl)-s-tetrazine and functionalized TPA were realized. First of all the dihydroterazinones 11 and 12 were successfully obtained using the Pinner type reaction which involves sulphur addition on monohydrate hydrazine and then reaction with an aromatic nitrile (Scheme 1). Compounds 11 and 12 were then directly oxidized with nitrogen dioxide produced in situ to give the tetrazines 13 and 14. Purification of 14 appeared to be difficult as it is an insoluble product, so this explains its lower yield.

Scheme 1. Synthesis of bis(bromophenyl)-s-tetrazines 13 and 14

Then triphenylamine stannane derivative 15 was obtained by using described methods and was used without further purification (Scheme 2). Modest yield is due to the formation of triphenylamine and tetrabutylnannane during the reaction. Then triphenylamine stannane derivative 15 and tetrazine compounds were bounded by a Stille cross coupling reaction, using conditions which are efficient and compatible with the tetrazine moiety. Because of the weak solubility of 14 in toluene (usual solvent for Stille reaction), we used tetrahydrofuran (THF) as solvent.

We were also interested in the synthesis of bichromophores linked with thiophene between triphenylamine and tetrazine moieties. In order to increase the solubility, we chose to add an alkyl chain on the thiophene moiety. The synthetic pathway leading to 3,6-bis(5-bromo-4-decylthiophen-2-yl)-s-tetrazine 16 is outlined in Scheme 3.

Scheme 3. 3-decylthiophene 17 was obtained in good yield by Kumada-Corriu coupling between 3-bromothiophene and decylmagnesium bromide synthesized in situ, using a literature procedure. Then 3-decylthiophene 17 was brominated to give 2-bromo-3-decylthiophene 18. Treatment of 2-bromo-3-decylthiophene 18 with Et3N Li in THF at -78°C for 30 minutes, followed by the addition of dimethylformamide gave the expected aldehyde 19 with 70% yield. 5-bromo-4-decylthiophen-2-carboxaldehyde 19 was then oxidized in the presence of diode and ammonical solution to give the corresponding nitrile 20 in 75% yield. The desired 3,6-bis(5-bromo-4-decylthiophen-2-yl)-s-tetrazine 16 was obtained from 5-bromo-4-decylthiophen-2-carbonitrile 20 with 20% yield using the Pinner reaction type described previously following by an oxidation.

Optimized Suzuki-Miyaura coupling conditions (compatible with tetrazine moiety) were used with 3,6-bis(5-bromo-4-decylthiophen-2-yl)-s-tetrazine 16. Indeed solution of 3,6-bis(5-bromo-4-decylthiophen-2-yl)-s-tetrazine 16 and tetrakis(triphenylphosphine) Pd(PPh3)4 in toluene was mixed with triphenylamineboronic acid solution in methanol and aqueous sodium carbonate solution. The expected bichromophores 5 and 6 were then isolated in 40% and 55% yields respectively (Scheme 4).

To get the new compounds 7-10, we used different strategies for the synthesis of the tetrazine systems: Pinner-type condensation of aromatic nitriles, nucleophilic substitution of particularly electrodedeficient tetrazine synths or Suzuki-Miyaura cross-coupling with specific tetrazine precursors. The electrodedeficient 3-chloro-6-morpholino-s-tetrazine 21 (Figure 2) was then chosen as starting material for the synthesis of 7 as it can undergo nucleophilic substitution in very mild conditions. On the other hand, 3,6-bis(3-bromophenyl)-s-tetrazine 13 and methylthiotetrazines 22 and 23 were selected to be functionalized according to cross-coupling reactions, in order to lead respectively to 8, 9 and 10.

Fig. 2 Tetrazine derivatives used as starting materials
To provide the alkylnyl spacer between the TPA and Tz substructures of compound 7, we used aromatic nucleophilic substitution of an alkyne on a chlorotetrazine (Scheme 5), a method which has only once been briefly reported. First, 4-(diphenylamino)-benzaldehyde 24 was obtained from triphenylamine through a Vilsmeier-Haack reaction with a reasonable yield (77%). The action of the Bestmann-Ohira reagent 25 (previously synthesized using a literature procedure) led to 4-ethynyl-N,N-diphenylaniline 26 in 73% yield. Finally, treatment of ethynyl compound 26 with BuLi in THF at -78°C for 3h30, followed by addition of chlorotetrazine 21 (obtained by an aromatic nucleophilic substitution of 3,6-dichloro-s-tetrazine with morpholine), led to compound 7 in 12% yield. It must be noted that the low yield for this last step, was however mainly due to a low conversion of the starting material since 48% of 26 was recovered at the end of the reaction.

![Scheme 5. Synthesis of 7](image)

Synthesis of compound 8 where TPA and Tz are directly linked was achieved using Hartwig-Buchwald coupling on synthon 13 (previously prepared with Pinner reaction on 3-bromophenylnitrile) (Scheme 6). A first coupling between 3,6-bis(3-bromophenyl)-s-tetrazine 13 and excess of anisidine gave 3,3’-(s-tetrazine-3,6-diyl)bis(N-(4-methoxyphenyl)aniline) 27 (40% yield). A second Hartwig-Buchwald coupling between 27 and bromoanisole gave the expected 3,3’-(s-tetrazine-3,6-diyl)bis(N,N-bis-(4-methoxyphenyl)aniline) 8 in 47% yield. To the best of our knowledge, this is the first time that Hartwig-Buchwald conditions on dibromoaryltetrazine are reported. The same synthesis from 3,6-bis(4-bromophenyl)-s-tetrazine isomer did not give the expected product because of insolubility of the starting tetrazine.

![Scheme 6. Synthesis of 8](image)

In order to link directly the tetrazine unit with the para position of triphenylamine, we decided to use the Suzuki-Miyaura cross-coupling. Again, we were aware of only one report where Suzuki-Miyaura conditions were used for the direct functionalization of a tetrazine ring, as 3-methylthio-6-morpholino-s-tetrazine 22 and 3-methoxy-6-methylthio-s-
The absorption spectra of 6, 8 and 10 in dichloromethane solutions are displayed in Figure 4 and the absorption data are collected in Table 2. These bichromophores display several bands, the number depending on the delocalization between the tetrazine moiety and the triphenylamine unit. For all compounds, there are one or two intense bands in the UV region in agreement with transitions located both on the tetrazine moiety and the triphenylamine unit. For all compounds, the variation of the localization of the band is weak (around 7 nm) because the electron-withdrawing tetrazine moiety and the triphenylamine unit are directly linked.

The molar absorption coefficient of 8, where tetrazine is linked to the triphenazine via the meta position, reaches 49 000 L.mol$^{-1}$.cm$^{-1}$ whereas the one of 6, where the tetrazine and triphenylamine moieties are linked through a thiophene, reaches 49 000 L.mol$^{-1}$.cm$^{-1}$.

The absorption solvatochromism of this third band (between 360 and 440 nm) for compounds 3, 4, 6, 7, 9 and 10 has been studied in seven different solvents: cyclohexane (cy), dichloromethane (DCM), tetrahydrofurane (THF), ethyl acetate (AcOEt), acetonitrile (ACN), dimethylsulfoxide (DMSO) and ethanol (EtOH) and the results are gathered in Table 3. The variation of the localization of the band is weak (around 7 nm) in the case of the compounds 9 and 10 where the tetrazine and triphenylamine units are directly linked and in the case of 7 which has an alkyne link. This is probably due to the fact that

![Cyclic voltammetry diagram](image)

**Fig. 3** Cyclic voltammetry of compounds 8 (cis 5 10$^{-3}$ mol.dm$^{-3}$) in dichloromethane + 0.1 mol.dm$^{-3}$ BuNPF$_6$. Potentials are referenced to Ag$^{+}$/Ag. Scan rate: 50 mV.s$^{-1}$.

![Absorption spectra](image)

**Fig. 4** Molar absorption coefficient of compounds 6, 8 and 10 in dichloromethane. Conc of 10$^{-3}$ M.

**Table 2.** Photophysical properties for compounds 1-10 in dichloromethane: absorption wavelength ($\lambda$, nm), molar absorption coefficient ($\varepsilon$, L.mol$^{-1}$.cm$^{-1}$)

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda_1$</th>
<th>$\varepsilon_1$</th>
<th>$\lambda_2$</th>
<th>$\varepsilon_2$</th>
<th>$\lambda_3$</th>
<th>$\varepsilon_3$</th>
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<tr>
<td>1</td>
<td>304</td>
<td>64000</td>
<td>-</td>
<td>-</td>
<td>546</td>
<td>539</td>
</tr>
<tr>
<td>2</td>
<td>300</td>
<td>59000</td>
<td>-</td>
<td>-</td>
<td>547</td>
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<td>3</td>
<td>303</td>
<td>68000</td>
<td>412</td>
<td>59000</td>
<td>sh</td>
<td>sh</td>
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<tr>
<td>4</td>
<td>307</td>
<td>47000</td>
<td>401</td>
<td>23000</td>
<td>545</td>
<td>460</td>
</tr>
<tr>
<td>5</td>
<td>305</td>
<td>35000</td>
<td>441</td>
<td>25000</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>6</td>
<td>306; 354</td>
<td>49000; 34000</td>
<td>441</td>
<td>49000</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>7</td>
<td>295</td>
<td>24000</td>
<td>373</td>
<td>33000</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>8</td>
<td>307</td>
<td>76000</td>
<td>424</td>
<td>3300</td>
<td>sh</td>
<td>sh</td>
</tr>
<tr>
<td>10</td>
<td>289</td>
<td>13000</td>
<td>360</td>
<td>24000</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

sh: shoulder, n.d.: non-determined
the different solvents have similar effects on the two orbitals implied in this transition. However, the variation is, as expected, more important (around 14 nm) in the case of the compounds 3, 4 and 6 which have an extended conjugated pathway. A general trend for all the compounds can be observed from the values given in Table 3. When increasing the polarity of the solvent from cyclohexane (apolar solvent) to dichloromethane (a little more polar one), one can see a bathochromic shift. Then, when the polarity further increases (from DCM to ACN), a hypochromic shift occurs. It shows that the polarity influences the localization of the intramolecular charge transfer band. A similar change has been reported on the donor-acceptor compound 3-chloro-6-tetrafluorovalene-6-tetrazine.\textsuperscript{18} Behaviors in DMSO or ethanol (high polar solvents) are difficult to understand because there is no general trend for all compounds.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>(\lambda^0) (nm)</th>
<th>DCM</th>
<th>THF</th>
<th>AcOEt</th>
<th>ACN</th>
<th>DMSO</th>
<th>EtOH</th>
</tr>
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<tbody>
<tr>
<td>3</td>
<td>410</td>
<td>412</td>
<td>407</td>
<td>403</td>
<td>400</td>
<td>410</td>
<td>400</td>
</tr>
<tr>
<td>4</td>
<td>394</td>
<td>401</td>
<td>396</td>
<td>389</td>
<td>385</td>
<td>396</td>
<td>391</td>
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<tr>
<td>6</td>
<td>427</td>
<td>441</td>
<td>437</td>
<td>432</td>
<td>430</td>
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<td>437</td>
</tr>
<tr>
<td>7</td>
<td>368</td>
<td>373</td>
<td>369</td>
<td>n.d.</td>
<td>366</td>
<td>369</td>
<td>368</td>
</tr>
<tr>
<td>9</td>
<td>358</td>
<td>360</td>
<td>355</td>
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<td>352</td>
<td>355</td>
<td>356</td>
</tr>
<tr>
<td>10</td>
<td>358</td>
<td>360</td>
<td>356</td>
<td>356</td>
<td>354</td>
<td>355</td>
<td>354</td>
</tr>
</tbody>
</table>

A more detailed study has been realized in the case of compound 3 using a general and multiparameter scale developed by Catalán\textsuperscript{18} based on four empirical scales: the solvent polarizability (SP), dipolarity (SdP), acidity (SA) and basicity (SB). The absorption wavenumber \(\nu\) is fitted with these solvent parameters according to the equation:

\[
\nu = \nu^0 + aSP + bSdP + cSA + dSB
\]

Where \(\nu^0\) is the gas phase wavenumber, and \(a, b, c \) and \(d\) are the regression coefficients describing the sensitivity of \(\nu\) to the different parameters. From this treatment, it appears that this chromophore presents a solvatochromism dominated by non-specific interactions as seen by the predominance of de solvent polarizability parameter \((a=\approx3715, b=118, c=91, d=157, \ r^2=0.87)\), as already observed for charge transfer molecules.\textsuperscript{9,100}

Finally, these compounds have a high absorbance and solvatochromic intramolecular charge transfer band, which is an important property for various applications such as organic solar cell or two-photon absorption.

**Molecular modelling**

Quantum chemical calculations were carried out on the ten compounds. Geometry optimizations were first performed at the B3LYP level of theory and with the 3-21g basis set. Time-dependent density functional theory (TD-DFT) calculations at the PBE0 level of theory with the 6-31+g(d) basis set were subsequently performed. Note that a C\(_8\) chain was used instead of a C\(_6\) chain in the case of 5 and 6 in order to shorten the calculations.

All these compounds have a central planar part (Figure 5). In the case of 7, this plane surface is constituted by the tetrazine moiety and the phenyl ring which is linked to the alkyn. In the other cases, the planar surface is constituted by the tetrazine moiety and the adjacent aromatic part(s). In the case of the phenyl or thiophene links, the linker forms an angle with the first adjacent phenyl of the triphenylamine: 40° for 3 and 4, 41° for 1 and 2 and 50° for 5 and 6. The angle is more important for the thiophene linker because of the sterically hindered alkyl chain. In all cases, the two phenyl groups at the end of triphenylamine are out of the plane.
higher than the ones of the corresponding molecules with only one triphenylamine moiety 2, 4 and 5. Indeed, the replacement of an inductive attractor bromine atom with a donating triphenylamine core induces a destabilization of the orbitals. In the case of 7, the orbitals are higher because the electron-donating morpholine moiety is directly linked to the tetrazine ring.

A weak transition is found at around 550 nm. This is the classical band localized on the tetrazine ring (n-π*, Figure 7a), usually responsible for the colors of the tetrazine molecules, and the difference of symmetry of these orbitals explains the weak molar absorption coefficient found experimentally and also confirmed by calculations. For some compounds, this band is hidden by a very intense band located close to it. As with other tetrazine compounds, the localization of this band does not vary since the energy difference between the pair of orbital stays constant (from 3.52 to 4.09 eV, Figure 7b).

The compounds 3-10 also exhibit a third band which does not exist in the case of the compounds 1 and 2. The localization and the intensity of this absorption band are strongly dependent on the compounds (360 nm<λ<441 nm and 3300 L.mol⁻¹.cm⁻¹<ε<59000 L.mol⁻¹.cm⁻³, Table 2). Molecular modelling shows that this band is due to a transition from a π- orbital centered on the triphenylamine unit to a π*-orbital centered on the tetrazine ring and the link (Figure 8a). This is an intramolecular charge transfer band. The energetic gap between these latter orbitals is higher in the case of 7, 9 and 10, compared to the other compounds (Figure 8b). It fits well with the experimental observations since these three molecules show the weakest absorption wavelength. The energy of the π-orbital remains mainly constant whereas the π*-orbital is destabilized in the case of 7, 9 and 10. It is probably due to the donating effect of the methoxy or morpholine groups which are directly linked to the tetrazine ring. The experimental and calculated wavelengths do not fit very well because intramolecular charge transfer bands can be difficult to calculate precisely with standard programs.¹⁰¹

Organic solar cells

Knowing that the creation of an intramolecular charge transfer in the donor considerably improves the power conversion efficiency of the solar cell,¹⁰² we selected the compound 3 – which displays the highest intramolecular charge transfer band- to be tested as donor in an organic solar cell. Since donor 3 is weakly soluble in most common organic solvents, a donor/acceptor bilayer heterojunction solar cell structure was chosen. Donor 3 was first thermally evaporated (20 to 30 nm) on ITO substrates precoated with a 30 nm-PEDOT-PSS layer. Then fullerene C60 was evaporated on top on donor 3 (25 to 40 nm) to achieve a donor/acceptor planar heterojunction. The photovoltaic parameters have been measured under simulated solar illumination in AM 1.5 conditions at 100 mW/cm². The influence of thermal annealing and of the donor and the C60 layers thicknesses on the photovoltaic performance has been investigated. The best results were obtained with a 20 nm-thick layer of 3 annealed at 150 °C and a 40 nm-thick layer of C60 (Fig. S18 and Table S12, Supporting Information). This device exhibits a short-circuit current density JSC of 2.0 mA.cm⁻² and an open-circuit voltage VOC of 0.26 V. This low voltage is quite far from the expected theoretical value of 1.2 V obtained by the formula:¹⁰³

\[ V_{OC} = E_{LUMO(acceptor)} - E_{HOMO(Donor)} - 0.3 \]
where 0.3 V is an empirical factor corresponding to the voltage loss due to the presence of ohmic contacts at both interfaces. \( \text{E}_{\text{LUMO}} \) and \( \text{E}_{\text{HOMO}} \) were estimated from the cyclovoltammograms according to the formula:

\[
\begin{align*}
\text{E}_{\text{LUMO}} & = (E_{\text{onset}}^-/(0.05 V)) + 4.8 \\
\text{E}_{\text{HOMO}} & = (E_{\text{onset}}^+/(0.05 V)) + 4.8
\end{align*}
\]

Some voltage loss at interfaces can explain this value of 0.26 V. Moreover, the high dark saturation current observed in the devices also reduces \( V_{\text{OC}} \).

A short-circuit current density of 2 mA cm\(^{-2}\) shows that excitons are actually generated and separated even if the energy difference \( \Delta E \) of 0.1 eV between the LUMO of the donor and the LUMO of the acceptor C60 is not sufficient for efficient charge separation. Furthermore, donor absorbs at too low wavelengths to enable the collection of a large ratio of the solar spectrum, which results in a rather low \( J_{\text{sc}} \). However, this value is close to the 2.4 mA cm\(^{-2}\) obtained for a triphenylamine/tetracyanobutadiene-based D-A-D system. Combined with a fill-factor FF=0.42, these results led to a PCE of 0.21%.

**Experimental part**

**Spectroscopic measurements**

UV-visible absorption spectra were recorded on a Cary 5000 spectrophotometer in 1 cm optical length quartz cuvettes. Cyclohexane, dichloromethane, tetrahydrofuran, ethyl acetate, acetonitrile, dimethylsulfoxide and ethanol (SDS, spectrometric grade) were used as solvents for absorption measurements.

**Electrochemistry**

Dichloromethane (SDS, HPLC grade) and electrolyte salts (tetrabutylammonium hexafluorophosphate from Fluka, puriss.) were used without further purification. Cyclic voltammetry was performed in a three-electrode cell with a potentiostat (VersaSTAT4, Princeton Applied Research) driven by a PC. Carbon electrode disk (1 mm diameter) was used as the working electrode, whereas platinum wire and Ag\(^+\) (0.01 M in acetonitrile)/Ag were used, respectively, as the counter and reference electrodes. All the investigated solutions were deaerated by argon-bubbling for at least 2 min before performing the electrochemical measurements. The reference electrode was checked versus ferrocene as recommended by IUPAC.

**Quantum Chemical Calculations**

Calculations were performed at the MESO calculation centre of the ENS Cachan (Nec TX7 with 32 processors of type Itanium 2). Molecules were drawn with the Gaussview 03 software using included templates and their geometry optimized at the B3LYP/3-21g level of theory. Infrared spectra were calculated on the final geometry to ascertain that a minimum was obtained (no negative frequencies). Time-dependant density functional theory (TD-DFT) calculations at the PBE0 level of theory with the 6-31+g(d) basis set were subsequently performed.

**Synthesis**

Reagents were commercially available from Aldrich and used without further purification. Column chromatography was performed with SDS 0.040-0.063 mm silica gel. All compounds were characterized by the usual analytical methods: \(^1\)H, \(^{13}\)C NMR spectra were recorded with a JEOL ECS (400 MHz) spectrometer. All chemical shifts are referenced to solvent peak (J values are given in Hz). Melting points were measured with a Kofer melting-point apparatus. IR spectra were recorded with a Nicolet Avatar 330 FT-IR spectrometer.
The compounds $^{22,25}$, $^{25}$,$^{25}$,$^{25}$ and $^{27}$ were synthesized as already described.

**General procedure for Stille cross-coupling.**

Dibromophenyltetrazine compound (1.0 eq, 0.1 M) and N,N-diphenyl-4-trityltetramine (1.1 eq for monosubstitution and 3.0 eq for disubstitution) were dissolved in toluene (for 1 or 2) or THF (for 3 and 4). [Pd(PPh$_3$)$_4$] (5 mol% for each substitution) was added and the reaction mixture was refluxed for 10 hours (for 1 and 2) or 100 hours (for 3 and 4) under argon. 30 mL of a solution of potassium fluoride was added and the precipitate was removed by filtration on celite. The filtrate was extracted with diethyl ether (2x50mL), the organic layers were washed with water (100 mL) and dried over anhydrous sodium sulfate Na$_2$SO$_4$. The crude product was purified by a silicagel column chromatography to give an orange solid.

3,6-bis(N,N-diphenyl-3'-biphenylamine)-s-tetrazine 1

General procedure for Stille cross-coupling with 3,6-bis(3'-bromophenyl)-s-tetrazine (0.61 g, 1.6 mmol) Chromatography conditions: cyclohexane/toluene: 5/5; Yield: 19% (217 mg); mp: 92 °C; IR (ν$_{max}$/cm$^{-1}$): 2920, 1587, 1515, 1483, 1382, 1271, 918, 835; $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm): 89.1 (dd, J=1.8 and 1.8 Hz, 2H), 8.60 (ddd, J=7.8, 1.8 and 1.8 Hz, 2H), 7.85 (ddd, J=7.8, 1.8 and 0.9 Hz, 2H), 7.66 (ddd, J=7.8 and 7.8 Hz, 2H), 7.61 (d, J=8.7 Hz, 4H), 7.31 (dd, J=8.7 and 7.3 Hz, 8H), 7.21-7.17 (m, 12H), 7.08 (dt, J=3.7 and 1.4 Hz, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm): 161.4, 147.9, 147.7, 141.8, 133.8, 132.3, 130.8, 129.9, 129.5, 128.0, 126.1, 124.7, 123.8, 123.3; HRMS-ESI (m/z): (M+H)$_+$ calcd for C$_{52}$H$_{42}$N$_{8}$Br, 756.1131, found: 756.1140; UV-vis (CH$_2$Cl$_2$): $\lambda_{max}$ (c) = 307 nm (61000 L.mol$^{-1}$.cm$^{-1}$) and 401 (30100 L.mol$^{-1}$.cm$^{-1}$)

3-(4'-bromophenyl)-6-(N,N-diphenyl-4'-biphenylamine)-s-tetrazine 4

General procedure for Stille cross-coupling with 3,6-bis(4'-bromophenyl)-s-tetrazine (0.60 g, 1.5 mmol). Chromatography conditions: CH$_2$Cl$_2$/PE (5/5)-CH$_2$Cl$_2$; Yield: 19% (159 mg); mp: 258 °C; IR (ν$_{max}$/cm$^{-1}$): 3031-2917, 1604, 1584, 1496, 1433, 1355, 1317, 1274, 1174, 1155, 1060, 916, 819; $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm): 8.69 (d, J=8.7 Hz, 2H), 8.53 (d, J=8.2 Hz, 2H), 7.82 (d, J=8.2 Hz, 2H), 7.76 (d, J=8.2 Hz, 2H), 7.59 (d, J=8.2 Hz, 2H), 7.30 (d, J=7.8 and 7.3 Hz, 4H), 7.17 (d, J=8.7 Hz, 2H), 7.16 (d, J=8.7 Hz, 4H), 7.07 (dt, J=7.3 and 0.9 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm): 164.1, 163.4, 148.4, 147.5, 145.1, 133.2, 132.9, 132.8, 131.0, 129.5, 129.4, 128.7, 128.0, 127.9, 127.4, 125.0, 125.3, 123.4; HRMS-ESI (m/z): (M+H)$_+$ calcd for C$_{66}$H$_{59}$N$_{7}$Br, 556.1131, found: 556.1140; UV-vis (CH$_2$Cl$_2$): $\lambda_{max}$ (c) = 307 nm (61000 L.mol$^{-1}$.cm$^{-1}$) and 401 (30100 L.mol$^{-1}$.cm$^{-1}$)
3-(5-methoxyphenyl)aniline) 8 To a solution of 3,3’-(s-tetrazine-3,6-diyl)bis(N,N-bis-(4-methoxyphenyl)aniline) 8 (95 mg, 0.18 mmol, 1.0 eq) and cesium carbonate Cs₂CO₃ (190 mg, 0.58 mmol, 3 eq) in distilled toluene (10 mL) under argon were added 1-bromo-4-methoxybenzene (0.20 mL, 1.6 mmol, 0.58 mmol, 3.3 eq) in distilled toluene (10 mL) under argon for 2 hours with microwaves. Dichloromethane (10 mL) and saturated ammonium chloride solution (15 mL) were added. Organic compounds were extracted with dichloromethane (3×15 mL). The combined organic phases were dried over anhydrous sodium sulfate, filtrated and concentrated under reduced pressure. The crude product was solubilized in 2 mL of THF. 18 mL of argon was added butyllithium (2.5 M in hexane, 0.330 mL, 0.825 mmol, 1.25 eq) in distilled THF (2 mL). Mixture was then stirred at room temperature for 30 minutes. All volatile compounds were removed by concentration under reduced pressure. The crude product was purified by a silicagel column chromatography (PE/DCM (2/8)) to give a purple solid (29 mg, 47%).

To a solution of 3-methylthio-6-morpholino-1,3-(s-tetrazine-3,6-diyl)bis(N,N-bis-(4-methoxyphenyl)aniline) 8 (19 mg, 0.015 mmol, 5 mol%) in 1,2-dimethoxyethane (5 mL) were added copper thiophene-2-carboxylate (110 mg, 0.58 mmol, 2.0 eq) and tetrakis(triphenylphosphine) palladium(0) Pd(PPh₃)₄ (19 mg, 0.015 mmol, 5 mol%). Mixture was heated at 180 °C under argon for 30 min with microwaves. Dichloromethane (10 mL) and saturated ammonium chloride solution (15 mL) were added. Aqueous phase was extracted with dichloromethane (3×15 mL). The combined organic phases were dried over anhydrous sodium sulfate, filtrated and concentrated under reduced pressure. The crude product was purified by a silicagel column chromatography (DCM) to give a red solid (34 mg, 29%).

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(νmax/cm⁻¹): 1587, 1406, 1392, 1105, 1068, 1006, 915, 836, 825; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.87 (d, J=8.7 Hz, 4H); 7.64 (d, J=8.7 Hz, 4H); ³¹C NMR (100 MHz, CDCl₃) δ (ppm): 167.4: 132.7; 129.4: 129.0; 125.9; UV-vis (CH₂Cl₂): λmax=314 and 547 nm

Synthesis of N,N-diphenyl-4-tributyltinaniline

1.6 M solution of nBuLi in hexane (3.4 mL, 5.4 mmol, 1.0 eq) was added dropwise to a solution of 4-bromo-N,N-triphenylamine (1.8 g, 5.4 mmol, 1.0 eq) in THF (48 mL) at -78°C and stirred for 45 min at this temperature. Bu₃SnCl (1.6 mL, 5.7 mmol, 1.1 eq) was added and the reaction mixture was stirred for 4h30 at room temperature under argon. After removing all volatile materials under reduced pressure, N,N-diphenyl-4-tributyltinaniline was obtained as colorless oil (1.4 g, 2.7 mmol, 50%). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.32 (d, J=8.2 Hz, 2H); 7.25 (dd, J=8.7 and 7.3 Hz, 4H); 7.11 (dd, J=7.3 and 1.5 Hz, 4H); 7.04 (d, J=8.7 Hz, 2H); 7.01 (t, J=7.3 Hz, 2H); 6.90 (m, 2H); 2.60 (t, J=7.8 Hz, 2H); 1.60-1.2 (m, 14H); 0.88 (t, J=6.6 Hz, 3H); δ: 160.8, 144.8, 142.9, 132.7, 125.6, 108.4, 32.1, 29.9, 29.7, 29.6, 29.5, 29.4, 29.3, 22.8, 14.3; HRMS-ESI (m/z): (M)⁺ calcd for C₄₀H₃₁BrN₃S₂: 682.1374, found: 682.1379

3-decylphenidine 17

1-bromodecane (5.8 mL, 37 mmol, 1.7 eq) was added dropwise to a solution of iodine (60 mg, 0.24 mmol, 0.01 eq) and magnesium (0.92 g, 38 mmol, 1.7 eq) in diethyl ether (30 mL). The reaction mixture was refluxed for 2 hours under argon and then cooled down to room temperature. This solution was added at 0°C to a solution of 3-bromomethylenemethane (2.0 mL, 21 mmol, 1.0 eq) and dichloro[(diphenylphosphino)propane]nickel (135 mg, 0.75 mmol, 2.1 eq) in THF (8 mL). Iodine (1.3 g, 5.0 mmol, 2.0 eq) was then added. Mixture was stirred at room temperature for 3 hours. 5% Sodium thiosulfate solution (20 mL) was then added. Organic compounds were extracted with ethyl acetate (3x100 mL). The combined organic phases were washed with saturated sodium chloride solution (250 mL), dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. The crude product was purified by a silicagel column chromatography (DCM): gave a colorless liquid. Yield: 87% (0.72 g). IR (νmax/cm⁻¹): 2971, 2921, 2912, 2857, 2817, 1552, 1454, 1437, 1394, 1372, 1264, 1182, 1069, 910, 852, 837; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.30 (s, 1H); 7.48 (s, 1H); 7.25 (t, J=7.4 Hz, 2H); 1.56 (t, J=7.3 Hz, 2H); 1.32-1.2 (m, 14H); 0.88 (t, J=6.6 Hz, 3H); δ: 143.2, 138.0, 116.7, 113.4, 109.4, 31.8, 29.5, 29.4, 29.3, 29.2 (2C); 29.1, 29.0, 22.6, 14.1

5-bromo-4-decylthiophene-2-carboxaldehyde 18

A solution of 3-methylthio-6-morpholino-tetrazine 23 to a solution of 5-bromo-4-decylthiophene-2-carboxaldehyde (0.83 g, 2.5 mmol, 1.0 eq) in THF (8 mL). Iodine (1.3 g, 5.0 mmol, 2.0 eq) was then added. Mixture was stirred at room temperature for 3 hours. 5% Sodium thiosulfate solution (20 mL) was then added. Organic compounds were extracted with ethyl acetate (3x100 mL). The combined organic phases were washed with saturated sodium chloride solution (250 mL), dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. The crude product was purified by a silicagel column chromatography (CH₂Cl₂/PE: 3/7) to give a colorless oil. Yield: 87% (0.72 g). IR (νmax/cm⁻¹): 2970, 2910, 2857, 2817, 1552, 1454, 1437, 1394, 1182, 1069, 910, 852, 837; ¹H NMR (400 MHz, CDCl₃) δ: 7.30 (s, 1H); 2.55 (t, J=7.6 Hz, 2H); 1.56 (t, J=7.3 Hz, 2H); 1.32-1.2 (m, 14H); 0.81 (t, J=6.6 Hz, 3H); ¹C NMR (100 MHz, CDCl₃) δ: 181.7, 143.9, 142.9, 136.7, 121.9, 31.9, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 22.7, 14.1

5-bromo-4-decylthiophene-2-carboxaldehyde 19 At -78°C under argon, to THF (12 mL) was added first Et₃N (1.0 g, 13 mmol, 2.1 eq) and then 2-bromo-3-decylthiophene (1.9 g, 6.1 mmol, 1.0 eq). The reaction mixture was stirred at -78°C for 30 minutes before dimethylformamide (2.4 mL, 31 mmol, 5.1 eq) was added. The reaction mixture was stirred for 18 hours from -78°C to room temperature. 1 M hydrochloric acid (120 mL) was added and organic compounds were extracted with ethyl acetate (3x100 mL). The combined organic phases were washed with saturated sodium chloride solution (250 mL), dried over anhydrous magnesium sulfate, filtered and concentrated under reduced pressure. The crude product was purified by a silicagel column chromatography (CH₂Cl₂/PE) to give a colorless liquid. Yield: 70% (1.4 g). IR (νmax/cm⁻¹): 2971, 2921, 1669, 1427, 1409, 1377, 1233, 1150, 1066, 1057, 1028, 892, 879, 868; ¹H NMR (400 MHz, CDCl₃) δ: 9.75 (s, 1H); 7.48 (s, 1H); 2.59 (t, J=7.4 Hz, 2H); 1.61 (t, J=7.4 and 7.4 Hz, 2H); 1.5-1.2 (m, 14H); 0.88 (t, J=6.6 Hz, 3H); ¹C NMR (100 MHz, CDCl₃) δ: 181.7, 143.9, 142.9, 136.7, 121.9, 31.9, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 22.7, 14.1
reduced pressure. The crude product was purified by a silicagel column chromatography (PE/ethyl acetate (1/5)) to give a red solid (300 mg, 74%). 1H NMR (400 MHz, CDCl3) δ: 3.92 (t, J=4.6 Hz, 4H), 3.83 (t, J=4.6 Hz, 4H), 2.66 (s, 3H); 13C NMR (100 MHz, CDCl3) δ: 166.7, 160.5, 66.5, 43.8, 13.7; IR (νmax/cm−1): 2930, 2861, 1364, 1189, 1038, 942; mp: 138 °C (lit. 112-113). 4-(N,N-diphenylamino)benzaldehyde 24 To a solution of phosphorus oxychloride (1.85 mL, 20 mmol, 1.0 eq) in dimethylformamide (5.6 mL, 73 mmol, 3.7 eq) at 0°C under argon were added tert-butyllithium (4.22 g, 77%) as yellow solid. The reaction mixture was stirred at 70°C for 24 hours. Then it was poured onto the ice and neutralized with saturated sodium carbonate solution (20 mL). The aqueous layer was extracted with dichloromethane (3×20 mL). The combined organic layers were dried with anhydrous sodium sulfate, filtered and concentrated under reduced pressure. The crude product was purified by a silica gel flash chromatography (DCM) to give 257.2 mg, 64% yield as a white solid. IR (νmax/cm−1): 3317, 3278, 2921, 1667, 1594, 1467, 1394, 1372, 1285, 1263, 1063, 942; mp: 185 °C (lit. 146-148). 4-ethyl-N,N-diphenylaniline 26 To a solution of Ohira Bestmann reagent (377 mg, 1.96 mmol, 1.52 eq) in methanol (10 mL) and potassium carbonate K2CO3 (42 mg, 0.30 mmol, 0.081 mmol, 0.1 eq). Mixture was refluxed under argon for 19 hours. The reaction mixture was stirred at 70°C for 24 hours. Then it was poured onto the ice and neutralized with saturated sodium carbonate solution (20 mL). The aqueous layer was extracted with CH2Cl2 (3×20 mL). The combined organic layers were dried with anhydrous sodium sulfate, filtered and concentrated under reduced pressure. The crude product was purified by a silicagel column chromatography (PE to PE/DCM (9/1)) to give a red solid (146 mg, 40%). IR (νmax/cm−1): 2934, 2862, 1583, 1484, 1364, 1120, 1068, 1031, 967, 840; mp: 115 °C (lit. 110-111). 3,3’-(1-tetrazine-3,6-diyl)bis(N-(4-methoxyphenyl)aniline) 27 To a solution of 2H, NH), 8.13 (s, 2H), 7.89 (d, J=7.8 Hz, 2H), 7.48 (dd, J=7.8 and 7.8 Hz, 2H), 7.21 (dd, J=7.8 and 2.3 Hz, 2H), 7.18 (d, J=8.7 Hz, 4H), 6.97 (d, J=8.7 Hz, 4H), 3.78 (s, 6H); 13C NMR (100 MHz, DMSO) δ: 163.6, 154.7, 146.7, 135.4, 132.8, 130.4, 121.9, 117.3, 115.1, 114.9, 112.5, 55.4; IR (νmax/cm−1): 3384, 1598, 1504, 1452, 1381, 1292, 1236, 1226, 1033, 934, 841; mp: 185 °C; HRMS-ESI (m/z): [M+H]+ calcd for C24H25N5O4, 477.2039, found 477.203

Acknowledgements


Notes and references

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