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

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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[1,2] which finds many fields of applications such as retro Diels-Alder cyclisation,[3-9] energetic compounds,[10-16] coordination chemistry,[17-24] electrofluorochromism.[25-34] Very recently, polymers containing *s*-tetrazine have been used in organic photovoltaic (OPV) cells[35-39] and there is one example of transistor based on a tetrazine-naphthalene diimide system.[40]
Triphenylamine (TPA) is a well-known electron-donor unit, extensively investigated in diverse fields including electrochromism,[41-47] organic electronics[48-67] or two-photon absorption.[68-74]
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.[31,33] 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.[75] In recent years, this approach has led to the synthesis of different classes of active molecules.[60] In this context, the question of the choice of the link between the donor part and the acceptor part and its influence on the establishment of an ICT emerges as a quite interesting problem.
We report herein the synthesis, electrochemical and photophysical studies of new TPA-Tz systems, supported by theoretical calculations, together with the preliminary OPV results. Ten compounds including four different linkers have been thus investigated: compounds **1-4** with phenyl link, compounds **5-6** with thienyl link, compound **7** with alkynyl link and directly linked compounds **8-10** (Figure 1).

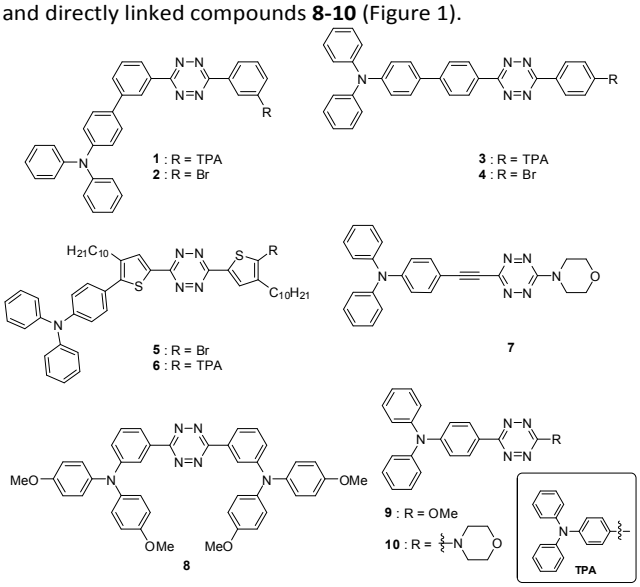

Fig. 1 Molecular structures of TPA-Tz systems **1**-**10**

Results and discussions

Synthesis

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† Electronic Supplementary Information (ESI) available: absorption spectra, results of TD-DFT calculations, representation of the main molecular orbitals involved in the electronic transitions, atomic coordinates of compounds after geometry optimization. See DOI: 10.1039/x0xx00000x

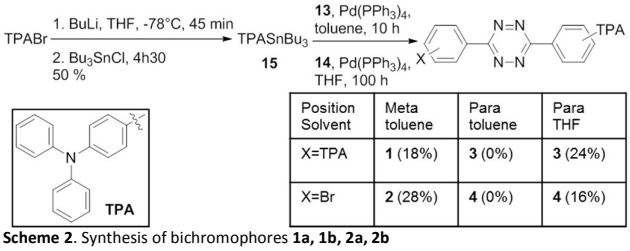
Design of tetrazine molecules **1-6** was rationalized in order to get mono or di-substitutions of the tetrazine core.

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 dihydrotetrazines **11** and **12** were successfully obtained using the Pinner type reaction[76-79] 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[80] 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[81] and was used without further purification (Scheme 2). Modest yield is due to the formation of triphenylamine and tetrabutylstannane during the reaction.

Then triphenylamine stannane derivative **15** and tetrazine compounds were bounded by a Stille cross coupling reaction,[82] using conditions which are efficient and compatible with the tetrazine moiety.[35,36,38,39,83] Because of the weak solubility of **14** in toluene (usual solvent for Stille reaction), we used tetrahydrofuran (THF) as solvent.

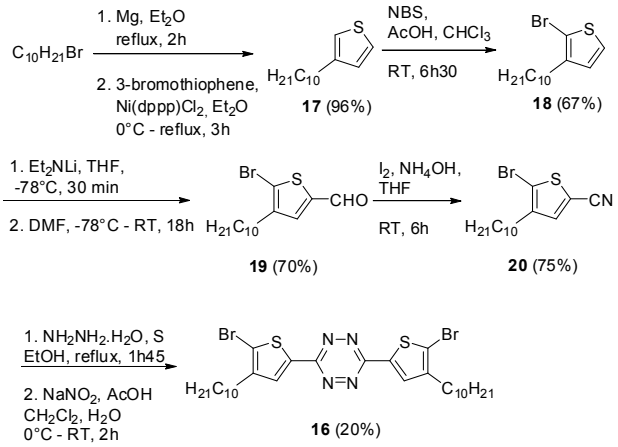


Position Solvent	Meta toluene	Para toluene	Para THF
X=TPA	**1** (18%)	**3** (0%)	**3** (24%)
X=Br	**2** (28%)	**4** (0%)	**4** (16%)

Scheme 2. Synthesis of bichromophores **1a, 1b, 2a, 2b**

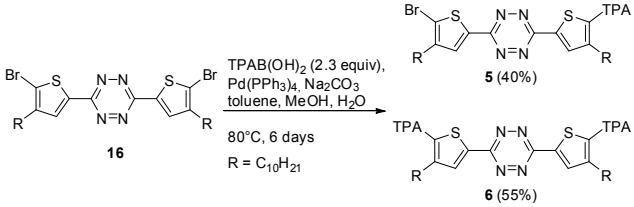
We were also interested in the synthesis of bichromophores linked with thiophene between triphenylamine and tetrazine moieties. In order to increase the solubility, we chose to add an alkyl chain on the thiophene moiety. The synthetic pathway leading to 3,6-bis(5-bromo-4-decylthiophen-2-yl)-*s*-tetrazine **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*,[84] using a literature procedure.[85,86] Then 3-decylthiophene **17** was brominated to give 2-bromo-3-decylthiophene **18**.[87] Treatment of 2-bromo-3-decylthiophene **18** with Et_2NLi in THF at -78°C for 30 minutes, followed by the addition of dimethylformamide,[88] gave the expected aldehyde **19** with 70% yield. 5-bromo-4-decylthiophene-2-carboxaldehyde **19** was then oxidized in the presence of diiode and ammoniacal solution[89] 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-decylthiophene-2-carbonitrile **20** with 20% yield using the Pinner reaction type described previously[76-79] followed by an oxidation.



Scheme 3. Synthesis of 3,6-bis(5-bromo-4-decylthiophen-2-yl)-*s*-tetrazine **16**

Optimized Suzuki-Miyaura coupling[90] 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 tetrakistriphenylphosphine $Pd(PPh_3)_4$ 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 (Sheme 4).



Scheme 4. Synthesis of bichromophores 5 and 6

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 electrodeficient tetrazine synthons or Suzuki-Miyaura cross-coupling with specific tetrazine precursors.

The electrodeficient 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**.

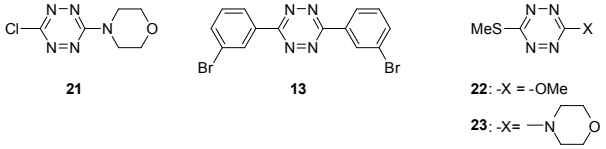
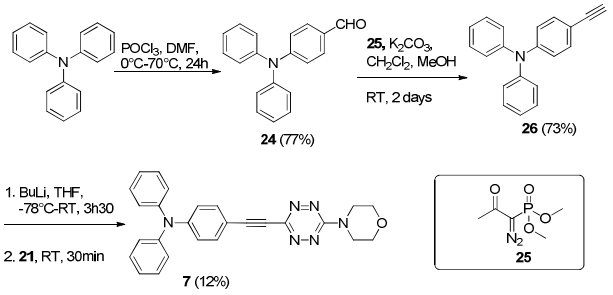


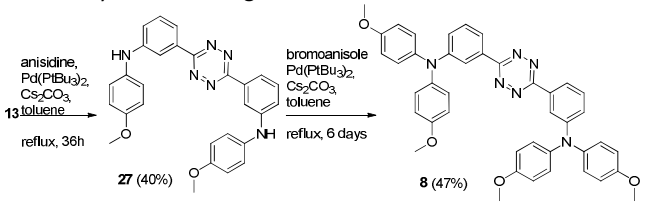
Fig. 2 Tetrazine derivatives used as starting materials

To provide the alkynyl spacer between the TPA and Tz substructures of compound **7**, we used aromatic nucleophilic substitution of an alkynide on a chlorotetrazine (Scheme 5), a method which has only once been briefly reported.[1] First, 4-(diphenylamino)-benzaldehyde **24** was obtained from triphenylamine through a Vilsmeier-Haack reaction with a reasonable yield (77%).[56] The action of the Bestmann-Ohira reagent **25**[91] (previously synthesized using a literature procedure)[92,93] 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**

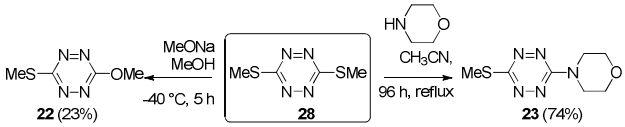
Synthesis of compound **8** where TPA and Tz are directly linked was achieved using Hartwig-Buchwald coupling[94,95] on synthon **13** (previously prepared with Pinner reaction[76,77] on 3-bromophenylnitrile) (Scheme 6). A first coupling between 3,6-bis(3-bromophenyl)-*s*-tetrazine **13** and excess 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**

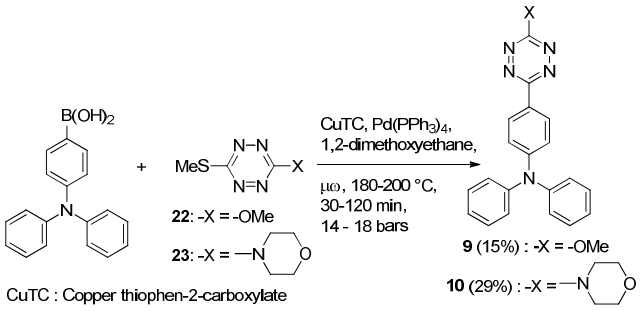
In order to link directly the tetrazine unit with the para position of triphenylamine, we decided to use to the Suzuki-Miyaura cross-coupling. Again, we were aware of only one report where Suzuki-Miyaura conditions were used for the direct functionalization of a tetrazine ring.[96] As 3-methylthio-6-morpholino-*s*-tetrazine **22** and 3-methoxy-6-methylthio-*s*-tetrazine **23** gave the best yields,[96] we decided to undergo the cross-coupling on these two synthons.

3,6-di-(thiomethyl)-*s*-tetrazine **28** was then obtained according to the method developed by Sandström.[97] Then this precursor underwent an aromatic nucleophilic substitution with sodium methanolate on the one hand and with morpholine on the other hand leading respectively to the expected thiomethyltetrazines **22** (23%) and **23** (74%) (Scheme 7).



Scheme 7. Synthesis of the tetrazine precursors **22** and **23**

A Suzuki-Miyaura cross-coupling between triphenylamine boronic acid and each precursor **22** and **23** gave the expected products **9** and **10** with respectively 15% and 29% yields (Scheme 8).



Scheme 8. Synthesis of compounds **9** and **10**

Finally we obtained ten new compounds **1-10**, centrosymmetrical or not, according to original synthetic ways in tetrazine chemistry. Thus, we can study the influence of the nature of the linker between the active subunits on the properties of our tetrazine-based compounds.

Electrochemical properties

The redox properties of all bichromophores were investigated by cyclic voltammetry (CV). Electrochemical data of all dyads are exemplified in Figure 3 for compound **8** and summarized in Table 1. Two well defined redox systems can be identified corresponding to the oxidation of the triphenylamine moiety into its cation radical and to the reduction of tetrazine moiety into its anion radical. The triphenylamine oxidation peaks of **8** and all the other compounds are reversible whereas the tetrazine electrochemistry is not entirely reversible. In the case of the compounds **1**, **3** and **4**, the reduction is totally irreversible and no standard potential could be determined. No clear explanation can be given but a similar behavior has been observed by J. Ding et al. in analogous compounds.[36]

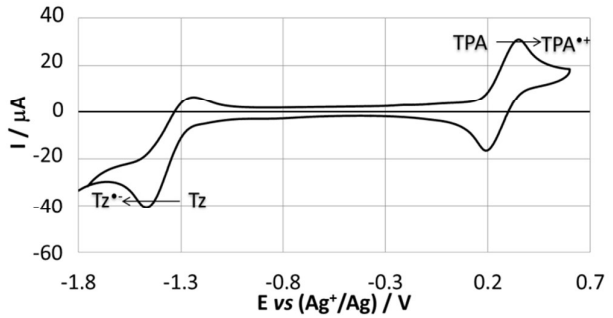


Fig. 3 Cyclic voltammetry of compounds **8** (C≈5 10^{-3}mol.dm^{-3}) in dichloromethane + 0.1 mol.dm^{-3} Bu_4NPF_6. Potentials are referenced to Ag^+/Ag. Scan rate: 50 mV.s^{-1}.

The reduction potential $E^{0/-1}$ has a very low variation and is around -1.45 V, except for the tetrazines **8**, **9** and **10**, where it is ca. 150 mV higher, but these ones have a quite different structure with much less donating substituents. The oxidation potential $E^{1/0}$ is around 0.45 V. It is slightly lower in the case of **8** because the triphenylamine is substituted with methoxy donor groups which stabilize the cation radical and facilitate its formation. Conversely, the oxidation potential is higher in the cases of **9** and **10** because the electron-withdrawing tetrazine is directly linked to the para position of the triphenylamine and thus makes the oxidation more difficult. To summarize, it seems, as previously observed with ferrocene-tetrazine compounds[5j] that the reduction potential of the tetrazine is weakly affected by the substituents, while on the other hand, the electron-withdrawing tetrazine induces a noticeable rise on the oxidation potential of the triphenylamine, when it is directly linked to it (compounds **9** and **10**). Since the oxidation process affects the HOMO and the reduction the LUMO, this tends to show that there is an efficient mixing of the HOMOs while the LUMO of the tetrazine is quite unaffected by the substituents besides purely inductive effects.

Table 1. Electrochemical data for compounds **1**-**10**. Potentials are referenced to Ferrocene. (The internal Ag wire reference electrode was checked *versus* ferrocene). All measurements in dichloromethane + $TBAPF_6$ on glassy carbon.

Compound	$E^{0/-1}$ (V)	$E^{1/0}$ (V)	Compound	$E^{0/-1}$ (V)	$E^{1/0}$ (V)
1	-1.67[a]	0.44	**6**	-1.43	0.46
2	-1.43	0.45	**7**	-1.46	0.42
3	-1.50[a]	0.45	**8**	-1.32	0.30
4	-1.53[a]	0.47	**9**	-1.31	0.65
5	-1.44	0.47	**10**	-1.34	0.57

[a] peak value, non-reversible reduction

Photophysical properties

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 π-π* transitions located both on tetrazine and triphenylamine units. The corresponding molar absorption coefficient varies between 13000 and 76000 L.mol^{-1}.cm^{-1} depending on the nature of the substituents on the tetrazine, which is reasonably high enough to be used in organic solar cells. Another band is located at around 545 nm and displays a weak molar absorption coefficient (around 500 L.mol^{-1}.cm^{-1}) due to a forbidden n-π* transition centered on the tetrazine unit. This band is not always well-defined because of its lower intensity. A last band appears around 400 nm for all the compounds where tetrazine moiety and triphenylamine unit are conjugated but not in the case of **1** and **2** because of the meta position of TPA on the phenyl link. This band is most probably an intramolecular charge transfer (ICT) band. Its molar absorption coefficient depends on the strength of the electronic delocalization. Indeed the molar absorption coefficient of **8**, where tetrazine is linked to the triphenylamine *via* the meta position, is only 3300 L.mol^{-1}.cm^{-1} whereas the one of **6**, where the tetrazine and triphenylamine moieties are linked through a thiophene, reaches 49000 L.mol^{-1}.cm^{-1}.

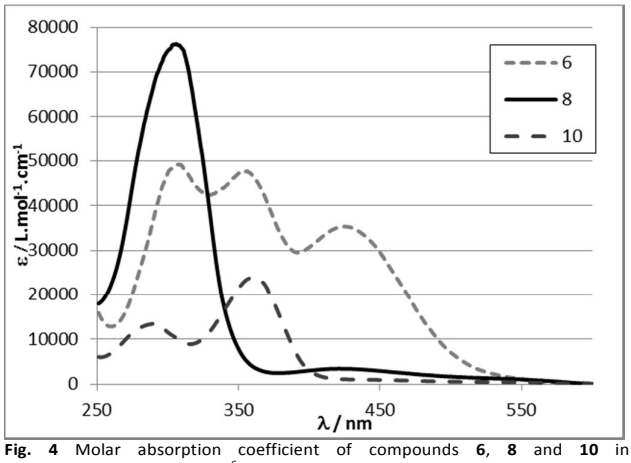


Fig. 4 Molar absorption coefficient of compounds **6**, **8** and **10** in dichloromethane. Conc of 10^{-6} M.

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

	λ_1	ε_1	λ_2	ε_2	λ_3	ε_3
1	304	64000	-	-	546	539
2	300	59000	-	-	547	572
3	303	68000	412	59000	sh	sh
4	307	47000	401	23000	545	460
5	305	35000	441	25000	n.d.	n.d.
6	306; 354	49000; 34000	441	49000	n.d.	n.d.
7	295	24000	373	33000	n.d.	n.d.
8	307	76000	424	3300	sh	sh
9	n.d.	n.d.	360	30000	n.d.	n.d.
10	289	13000	360	24000	n.d.	n.d.

sh: shoulder, n.d.: non-determined

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), dimethylsulfoxyde (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

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 hypsochromic 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-tetrathiafulvalene-*s*-tetrazine.[18] Behaviors in DMSO or ethanol (high polar solvents) are difficult to understand because there is no general trend for all compounds.

Table 3. Absorption wavelength (λ, nm) of the intramolecular charge transfer band in different solvents

Solvent	cy	DCM	THF	AcOEt	ACN	DMSO	EtOH
λ(3)	405	412	407	403	400	410	400
λ(4)	394	401	396	389	385	396	391
λ(6)	427	441	437	432	430	432	437
λ(7)	368	373	369	n.d.	366	369	368
λ(9)	358	360	355	353	352	355	356
λ(10)	358	360	356	356	354	355	354

A more detailed study has been realized in the case of compound **3** using a general and multiparameter scale developed by Catalán[98] based on four empirical scales: the solvent polarizability (SP), dipolarity (SdP), acidity (SA) and basicity (SB). The absorption wavenumber (ν) is fitted with these solvent parameters according to the equation:

$$\bar{\nu} = \bar{\nu}^{\circ} + aSP + bSdP + cSA + dSB$$

Where $\bar{\nu}^{\circ}$ is the gas phase wavenumber, and a, b, c and d are the regression coefficients describing the sensitivity of $\bar{\nu}$ 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 polarizabilty parameter (a=-3715, b=118, c=91, d=157, r^2=0.87), as already observed for charge transfer molecules.[99,100]

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_4 chain was used instead of a C_{10} 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 alkyne. 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.

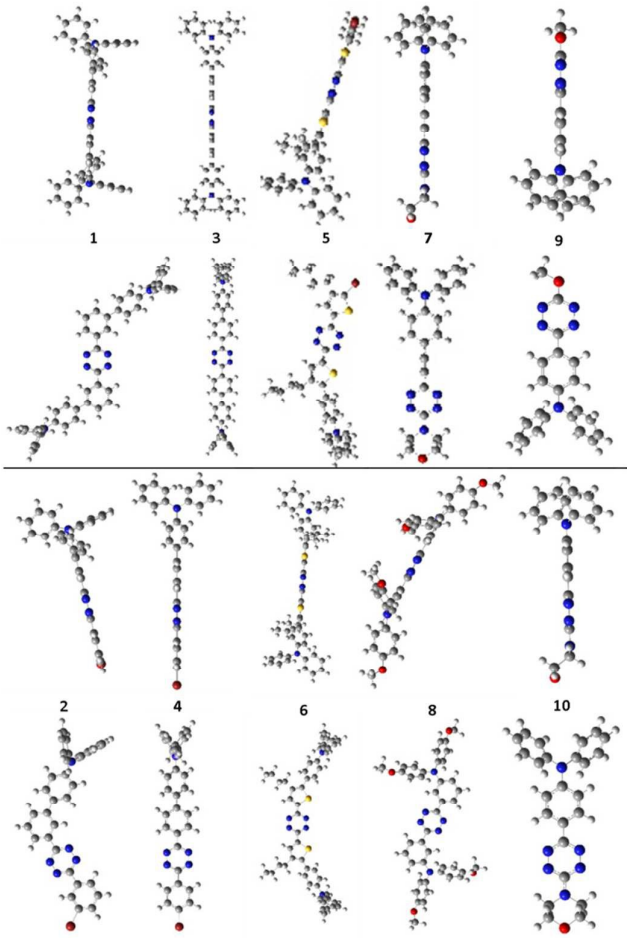


Fig. 5 Calculated geometries of compounds **1-10**

The lowest unoccupied molecular orbital (LUMO) is a π*-orbital centered on the tetrazine ring, which reflects its electron-withdrawing ability. Contrariwise, the highest occupied molecular orbital (HOMO) is always a π-orbital localized on the triphenylamine and the adjacent linker. The non-bounding orbital of the tetrazine is found at a lower energy.

All compounds show one absorption band around 300 nm. This absorption band is due to a transition from the π-orbital to π*-orbital both centered on the tetrazine unit and the adjacent link (Figure 6a). The important overlap between the orbitals of the latter transition explains the intense absorption. Molecular modelling shows that the energetic gap between these two orbitals varies slightly, depending on the molecules (between 3.75 and 3.92 eV, Figure 6b), which is in agreement with the experimental observation (maximal wavelength between 295 and 307 nm). The energies of the π and π* orbitals of the symmetrical compounds **1**, **3** and **6** are slightly

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.

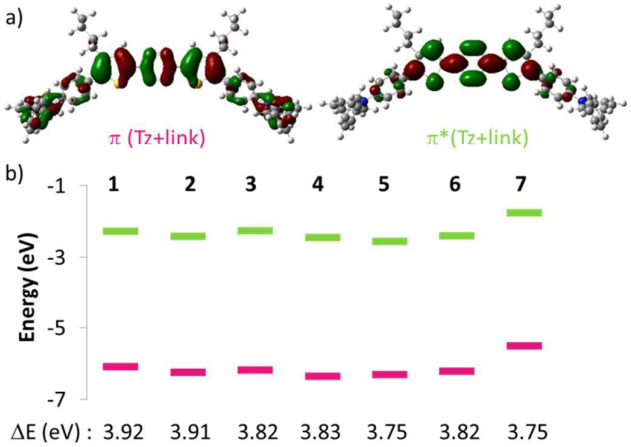


Fig. 6 a) Representation of the molecular orbitals involved in the absorption band at 306 nm of **6**; b) Energy levels of π (pink) and π*(green) orbitals involved in the transition at around 300 nm of **1-7**

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).

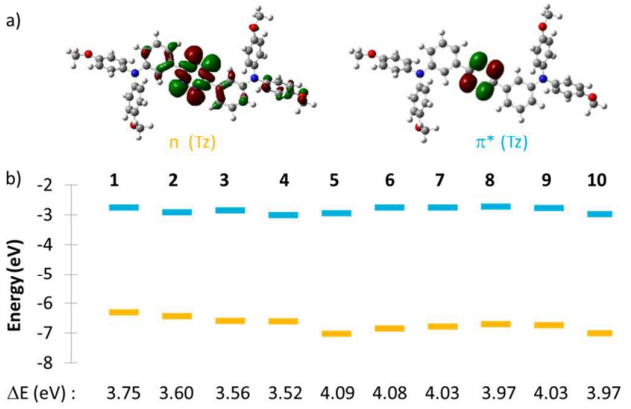


Fig. 7 a) Representation of the molecular orbitals involved in the absorption band at 550 nm of **8**; b) Energy levels of n (yellow) and π* (sky blue) orbitals involved in the transition at around 550 nm of **1-10**

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 $L.mol^{-1}.cm^{-1}$, 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]

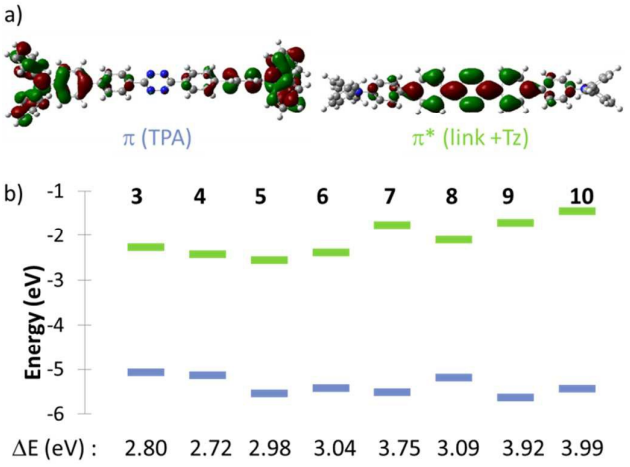


Fig. 8 a) Representation of the molecular orbitals involved in the absorption band at 412 nm of **3**; b) Energy levels of π (blue) and π* (green) orbitals involved in the intramolecular charge transfer transition of **3-10**

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/cm^2. 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 J_{SC} of 2.0 $mA.cm^{-2}$ and an open-circuit voltage V_{OC} of 0.26 V. This low voltage is quite far from the expected theoretical value of 1.2 V obtained by the formula:[103]

$V_{OC} \approx E_{LUMO(acceptor)}-E_{HOMO(Donor)}-0.3$

where 0.3 V is an empirical factor corresponding to the voltage loss due to the presence of ohmic contacts at both interfaces.[104] E_{LUMO} and E_{HOMO} were estimated from the cyclovoltammograms according to the formula.[105]

E_{LUMO}=-($E^{1/0}_{onset}$ (*vs* Fc/Fc^+)+4.8)

E_{HOMO}=-($E^{0/-1}_{onset}$ (vs Fc/Fc^+)+4.8)

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_{OC}.[106]

A short-circuit current density of 2 $mA.cm^{-2}$ shows that excitons are actually generated and separated even if the energy difference ΔE of 0.1 eV between the LUMO of the donor **3** and the LUMO of the acceptor C60 is not sufficient for efficient charge separation. Furthermore, donor **3** absorbs at too low wavelengths to enable the collection of a large ratio of the solar spectrum, which results in a rather low J_{SC}. However, this value is close to the 2.4 $mA.cm^{-2}$ obtained for a triphenylamine/tetracyanobutadiene-based D-A-D system.[60] Combined with a fill-factor FF=0.42, these results led to a PCE of 0.21%.

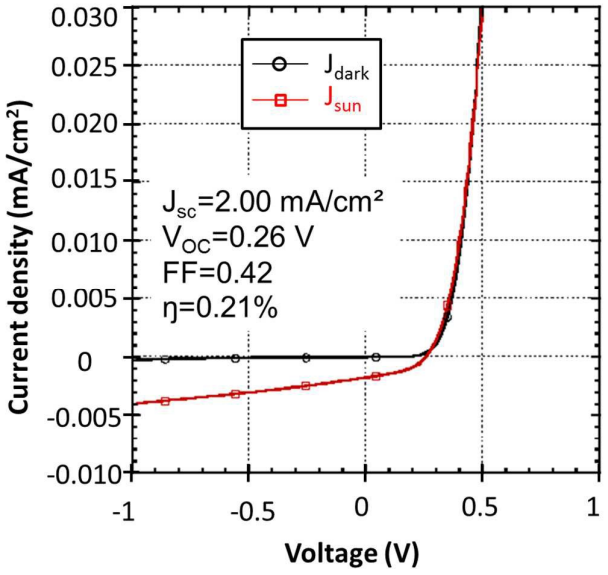


Fig. 9 Current *vs* voltage curves of a bilayer heterojunction **3**:C60. Black circles: in the dark. Red squares: under AM 1.5 white light illumination at 100 mW/cm^2.

While these first results are not as good as we could expect, some further improvement may be achieved through an optimization of the solar cell structure. For example the use of a bulk heterojunction may improve charge separation and the insertion of charge transport interlayers could improve V_{OC} through the lowering of the dark saturation current.

Conclusions

In summary, symmetrical and unsymmetrical D-A-D π-conjugated systems based on a tetrazine unit as acceptor and triphenylamine moiety as donor have been synthesized. Some of these compounds exhibit strong absorption in the visible range due to an intramolecular charge transfer (ICT) band. We have shown that the covalent bridging of the tetrazine acceptor group by a phenyl, a thiophene or an alkyne linker represents an efficient synthetic approach for engineering the ICT and the LUMO energy level of donor triphenylamine materials based on dipolar small donor-acceptor molecules. Taking into account the simplicity of the devices used for photovoltaic evaluation, these preliminary results suggest that the use of a more advanced technology for the devices fabrication can be expected to lead to higher performance. Also, bulk heterojunction solar cells could be fabricated using the soluble compound **6** as donor.

Experimental part

Spectroscopic measurements

UV-visible absorption spectra were recorded on a Cary 5000 spectrophotometer in 1 cm optical length quartz cuvettes. Cyclohexane, dichloromethane, tetrahydrofurane, ethyl acetate, acetonitrile, dimethylsulfoxyde 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: ^1H, ^{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 Kofler melting-point apparatus. IR spectra were recorded with a Nicolet Avatar 330 FT-IR spectrometer.

The compounds **22**[107] , **25**[92,93] and **28**[97] were synthesized as already described.

General procedure for Stille cross-coupling. Dibromophenyltetrazine compound (1.0 eq, 0.1 M) and *N,N*-diphenyl-4-tributyltinaniline (1.1 eq for monosubstitution and 3.0 eq for disubstitution) were dissolved in toluene (for **1** and **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 diethylether (2*50mL), the organic layer was washed with water (100 mL) and dried over anhydrous sodium sulfate Na_2SO_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): 8.91 (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 (dd, 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=7.3 and 1.4 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 164.1, 147.9, 147.7, 141.8, 133.8, 132.3, 130.8, 129.9, 129.5, 128.0, 126.3, 126.1, 124.7, 123.8, 123.3; HRMS-ESI (m/z): $(M+H)^+$ calcd for $C_{50}H_{36}N_6$, 721.3080, found: 721.3098; UV-vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ =304 nm (64000 L.mol^{-1}.cm^{-1}) and 546 nm (540 L.mol^{-1}.cm^{-1})

3-(3'-bromophenyl),6-(*N*,-diphenyl-3'-biphenylamine)-*s*-tetrazine 2 General procedure for Stille cross-coupling with 3,6-bis(3'-bromophenyl)-*s*-tetrazine (0.20 g, 0.51 mmol). Chromatography conditions: cyclohexane/toluene: 5/5; Yield: 28% (80 mg); mp: 205 °C; IR (ν_{max}/cm^{-1}): 3034-2917, 1586, 1495, 1485, 1438, 1383, 1356, 1317, 1273, 915, 820; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.87 (s, 1H), 8.81 (s, 1H), 8.59-8.56 (m, 2H), 7.84 (d, J=7.8 Hz, 1H), 7.76 (d, J=7.8 Hz, 1H), 7.65 (dd, J=7.8 and 7.8 Hz, 1H), 7,59 (d, J=8.7 Hz, 2H), 7,48 (dd, J=7.8 and 7.8 Hz, 1H), 7,31 (dd, J=8.2 and 7.3 Hz, 4H), 7.20-7.16 (m, 6H), 7.07 (t, J=7.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 164.3, 163.1, 147.9, 147.6, 141.9, 135.6, 133.9, 133.7, 132.1, 131.1, 130.9 (2C), 129.9, 129.5, 127.9, 126.5, 126.4, 126.2, 124.7, 123.7, 123.6, 123.3; HRMS-ESI (m/z): $(M+H)^+$ calcd for $C_{32}H_{22}N_5{}^{79}Br$, 556.1131, found: 556.1134; UV-vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$=300 nm (59000 L.mol^{-1}.cm^{-1}) and 547 nm (570 L.mol^{-1}.cm^{-1})

3,6-bis(*N*,*N*-diphenyl-4'-biphenylamine)-*s*-tetrazine 3 General procedure for Stille cross-coupling with 3,6-bis(4'-bromophenyl)-*s*-tetrazine (0.21 g, 0.53 mmol). Chromatography conditions: CH_2Cl_2/PE (9/1)-CH_2Cl_2; Yield: 24% (71 mg); mp: 102 °C; IR (ν_{max}/cm^{-1}): 1483, 1271; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.70 (d, J=8.2 Hz, 4H), 7.82 (d, J=8.2 Hz, 4H), 7,59 (d, J=8.7 Hz, 4H), 7,30 (dd, J=8.2 and 7.3 Hz, 8H), 7.19-7.15 (m, 12H), 7.07 (t, J=6.9 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 163.8; 148.3; 147.6; 144.9; 133.3; 131.7; 129.5; 128.5; 128.0; 127.4; 124.9; 123.5 (2C); HRMS-ESI (m/z): $(M+H)^+$ calcd for $C_{50}H_{36}N_6$, 721.3080, found: 721.3079; UV-vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$=304 nm (70700 L.mol^{-1}.cm^{-1}) and 412 nm (58600 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_2Cl_2/PE (5/5)-CH_2Cl_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; 123.5; 123.4; HRMS-ESI (m/z): $(M+H)^+$ calcd for $C_{32}H_{22}N_5{}^{79}Br$, 556.1131, found: 556.1140; UV-vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ =307 nm (61000 L.mol^{-1}.cm^{-1}) and 401 nm (30100 L.mol^{-1}.cm^{-1})

4-(5-(6-(5-bromo-4-decylthiophen-2-yl)-*s*-tetrazin-3-yl)-3-decylthiophen-2-yl)-*N*,*N*-diphenylaniline 5 and 4,4'-(5,5'-(*s*-tetrazine-3,6-diyl)bis(3-decylthiophene-5,2-diyl))bis(*N*,*N*-diphenylaniline) 6 To a solution of 3,6-bis(5-bromo-4-decylthiophen-2-yl)-*s*-tetrazine (0.25 g, 0.37 mmol, 1.0 eq) and tetrakis(triphenylphosphine) palladium(0) $Pd(PPh_3)_4$ (21 mg, 0.019 mmol, 5 mol%) in toluene (5 mL) were added first a solution of triphenylamine boronic acid (0.24 g, 0.84 mmol, 2.3 eq) in methanol (1.5 mL) and then a aqueous solution of sodium carbonate (2 M, 0.8 mL). The reaction mixture was stirred at 80 °C under argon for 48 hours. A solution of ammonium chloride (100 mL) was added and organic compounds were extracted with dichloromethane (2*100 mL). The combined organic phases were washed with a saturated solution of sodium chloride (250 mL), dried over anhydrous sodium sulfate, filtrated and concentrated under reduced pressure. The crude product was purified by a silicagel column chromatography (CH_2Cl_2/PE: 6.5/3.5) to give two orange solids **5** (Yield :42% (0.13 g)) and **6** (Yield: 57% (0.20 g)). Characterisations of **5**: mp: <50 °C; IR (ν_{max}/cm^{-1}): 2962, 2924, 2853, 1592, 1550, 1492, 1465, 1330, 1261, 1095, 1071, 1018, 800; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.12 (s, 1H), 8.08 (s, 1H), 7.37 (d, J=8.7 Hz, 2H), 7.30 (dd, J=8.2 and 7.3 Hz, 4H), 7.17 (dd, J=8.7 and 0.9 Hz, 4H), 7.12 (d, J=8.7 Hz, 2H), 7.08 (t, J=7.3 Hz, 2H), 2.74 (t, J=7.3 Hz, 2H), 2.69 (t, J=7.3 Hz, 2H), 1.75-1.65 (m, 4H), 1.39-1.19 (m, 28H), 0.88 (t, J=6.8 Hz, 3H), 0.87 (t, J=6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 161.5, 161.2, 148.2, 147.4, 146.1, 145.6, 140.6, 135.8, 133.5, 132.6, 132.8, 130.0, 129.6, 127.5, 127.1, 125.2, 123.7, 122.6, 32.1(2C), 30.9(2C), 30.5(2C), 29.8(2C), 29.7(2C), 29.5(2C), 29.4(2C), 29.0(2C), 22.8(2C), 14.3(2C); HRMS-MALDI (m/z): $(M)^{\bullet+}$ calcd for $C_{48}H_{58}BrN_5S_2$, 847.3317, found 847.3298 (100%); UV-vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ =305 nm (34800 L.mol^{-1}.cm^{-1}), 354 nm (34000 L.mol^{-1}.cm^{-1}) and 441 nm (25100 L.mol^{-1}.cm^{-1}); Characterisations of **6**: mp: 90 °C; IR (ν_{max}/cm^{-1}): 2923, 2853, 1591, 1548, 1492, 1461, 1329, 1282, 1180, 1070, 837; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.12 (s, 2H), 7.38 (d, J=8.7 Hz, 4H), 7.31 (dd, J=8.2 and 7.8 Hz, 8H), 7.18 (d, J=7.8 Hz, 8H), 7.12 (d, J=8.7 Hz, 4H), 7.08 (t, J=7.3Hz, 4H), 2.75 (t, J=7.8 Hz, 4H), 1.65 (tt, J=7.3 and 6.9 Hz, 4H), 1.40-1.27 (m, 28H), 0.89 (t, J=6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 161.1, 148.1, 147.4, 145.9, 140.5, 133.3, 132.8, 129.9, 129.5, 127.2, 125.1, 123.6, 122.6, 32.0, 30.1, 29.7 (2C), 29.6 (2C), 29.5, 29.0, 22.8, 14.3; HRMS-MALDI (m/z): $(M)^{\bullet+}$ calcd for $C_{66}H_{72}N_6S_2$, 1012.5254, found 1012.5240; UV-vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$=306 nm (49100 L.mol^{-1}.cm^{-1}) and 441 nm (49300 L.mol^{-1}.cm^{-1})

4-((6-morpholino-*s*-tetrazin-3-yl)ethynyl)-*N*,*N*-diphenylaniline 7 To a solution of 4-ethynyl-*N*,*N*-diphenylaniline **26** (205 mg, 0.61 mmol, 1.0 eq) in distilled THF (2 mL) at – 78 °C under argon was added butyllithium (2.5 M in hexane, 0.330 mL, 0.825 mmol, 1.08 eq). Mixture was stirred for 3h30 from -80°C to room temperature. Then it was added to a solution of 4-(6-chloro-*s*-tetrazin-3-yl)morpholine **21** (153 mg, 0.761 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 solubilized in 2 mL of THF. 18 mL of petroleum ether were added and product precipitated. A red solid was obtained by filtration (39 mg, 12%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.49 (d, J=8.7 Hz, 2H), 7.30 (dd, J=8.3 and 7.3 Hz, 4H), 7.14 (d, J=7.8 Hz, 4H), 7.10 (t, J=7.3 Hz, 2H), 7.00 (d, J=8.7 Hz, 2H), 4.05 (t, J=4.9 Hz, 4H), 3.86 (t, J=4.9 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.9, 151.6, 149.4, 146.9, 133.4, 129.7, 125.6, 124.3, 121.4, 113.2, 95.2, 82.6, 66.6, 43.8; IR (σ in cm^{-1}): 2215, 1586, 1547, 1537, 1509, 1493, 1333, 1316, 1287, 1266, 1165, 1113, 1043, 946, 837; m.p.: 196°C; HRMS-ESI, m/z : $[M+H]^+$ calcd. for $C_{26}H_{22}N_6O$ $[M+H]^+$ 435.1928, found 435.1925; UV-vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$=295 (23900), 373 (32900); E° (C, CH_2Cl_2) *vs* ferrocene: -1.46, 0.42 V

3,3'-(*s*-tetrazine-3,6-diyl)bis(*N*,*N*-bis(4-methoxyphenyl)aniline) 8 To a solution of 3,3'-(*s*-tetrazine-3,6-diyl)bis(*N*-(4-methoxyphenyl)aniline) **27** (85 mg, 0.18 mmol, 1.0 eq) and cesium carbonate Cs_2CO_3 (190 mg, 0.58 mmol, 3.3 eq) in distilled toluene (10 mL) under argon were added 1-bromo-4-methoxybenzene (0.20 mL, 1.6 mmol, 9.0 eq) and bis(tri-*tert*-butylphosphine)palladium(0) $Pd(PtBu_3)_2$ (15 mg, 0.029 mmol, 0.15 eq). Mixture was refluxed under argon for 6 days. 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%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.17 (dd, J=2.3 and 1.8 Hz, 2H), 8.06 (ddd, J=7.3, 1.8 and 0.9 Hz, 2H), 7.35 (dd, J=7.8 and 7.8 Hz, 2H), 7.15 (ddd, J=8.2, 2.3 and 0.9 Hz, 2H), 7.09 (d, J=8.7 Hz, 8H), 6.83 (d, J=9.2 Hz, 8H), 3.80 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.9, 156.2, 150.0, 140.5, 132.7, 130.0, 126.9, 124.2, 119.8, 119.0, 115.0, 55.6; IR (ν_{max}/cm^{-1}): 1582, 1504, 1451, 1383, 1240, 1034, 917, 828; mp: 256 °C; HRMS-ESI (m/z): $(M+H)^+$ calcd for $C_{42}H_{36}N_6O_4$, 689.2876, found: 689.2885; UV-vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$=306 (71000) ; 422 (3100); E° (C, CH_2Cl_2) *vs* ferrocene: -1.32, 0.30 V.

3-methoxy-6-(4'-triphenylamine)-*s*-tetrazine 9 To a solution of 3-methoxy-6-methylthio-*s*-tetrazine **22** (100 mg, 0.63 mmol, 1.0 eq) and 4-(*N*,*N*-diphenylamino)phenylboronic acid (279 mg, 0.97 mmol, 1.5 eq) in 1,2-dimethoxyethane (5 mL) were added copper thiophene-2-carboxylate (239 mg, 1,26 mmol, 2,0 eq) and tetrakis(triphenylphosphine) palladium(0) $Pd(PPh_3)_4$ (40 mg, 0.03 mmol, 5 mol%). Mixture was heated at 180 °C 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 purified by a silicagel column chromatography (PE/DCM (7/3 to 5/5)) to give a red solid (39 mg, 15%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.32 (d, J=8.7 Hz, 2H) ; 7.33 (dd, J=7.8 and 7.3 Hz, 4H) ; 7.20-7.11 (m, 8H), 4.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.6, 163.0, 151.4, 146.8, 129.7, 128.5, 125.8, 124.4, 124.0, 121.4, 56.5; IR (ν_{max}/cm^{-1}): 2918, 1587, 1493, 1383, 1273, 1173, 1041, 942, 849; mp: 96 °C; HRMS-ESI (m/z): $(M)^+$ calcd for $C_{21}H_{17}N_5O$, 355.1433, found: 355.1427; UV-vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$=360 (29900) ; E° (C, CH_2Cl_2) *vs* ferrocene: -1.31, 0.65 V

3-(4'-triphenylamine)-6-morpholino-*s*-tetrazine 10 To a solution of 3-methylthio-6-morpholino-*s*-tetrazine **23** (62 mg, 0.29 mmol, 1.0 eq) and 4-(*N*,*N*-diphenylamino)phenylboronic acid (166 mg, 0.57 mmol, 2.0 eq) 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) $Pd(PPh_3)_4$ (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%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.23 (d, J=9.2 Hz, 2H), 7.29 (dd, J=8.2 and 7.3 Hz, 4H), 7.17-7.13 (m, 6H), 7.08 (t, J=7.3 Hz, 2H), 4.02 (t, J=4.8 Hz, 4H), 3.86 (t, J=4.8 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.5, 159.5, 150.4, 147.2, 129.6, 127.4, 125.5 (2C), 124.0, 122.1, 66.6, 43.9; IR (ν_{max}/cm^{-1}): 2917, 2850, 1589, 1511, 1491, 1450, 1393, 1316, 1177, 1118, 942, 847; mp: 170 °C; HRMS-ESI (m/z): $(M)^+$ calcd for $C_{24}H_{22}N_6O$, 410.1855, found: 410.1846; UV-vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$=289 (13400) ; 360 (23900); E° (C, CH_2Cl_2) *vs* ferrocene: -1.34, 0.57 V

General procedure for Pinner reaction and oxidation

To a solution of nitrile (1.0 eq) in ethanol (0.3 M) were added monohydrate hydrazine (4.0 eq) and sulfur (0.6 eq). The mixture was refluxed until complete reaction as judged by TLC. All volatile substances were removed by concentration under reduced pressure to give a yellow solid used without further purification. The yellow solid (1 eq) was dissolved in dichloromethane (0.3 M). A solution of sodium nitrite (6 eq) in water (0.3 M) was added. Acetic acid (5 eq) was added dropwise at 0 °C. The mixture was stirred at room temperature until complete reaction as judged by TLC. Organic compounds were extracted with dichloromethane. The combined organic phases were dried over anhydrous sodium sulfate, filtrated and concentrated under reduced pressure. The crude product was purified by silica gel flash chromatography to give a pink or red powder.

3,6-bis(3'-bromophenyl)-*s*-tetrazine 13 General procedure for Pinner reaction and oxidation with 3-bromobenzonitrile (1.8 g, 9.9 mmol). Chromatography conditions: CH_2Cl_2/Petroleum Ether(PE): 5/5; Yield: 74% (1.43 g); mp: 244 °C; IR (ν_{max}/cm^{-1}): 1433, 1381, 1299, 1091, 1056, 922, 888, 795, 767, 738, 686, 679; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.83 (dd, J=1.8 and 1.8 Hz, 2H), 8.60 (ddd, J=7.8, 1.8 and 0.9 Hz, 2H), 7.79 (ddd, J=7.8, 1.8 and 0.9 Hz, 2H), 7.51 (dd, J=7.8 and 7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 163.4, 136.0, 133.7, 131.1, 131.0, 126.7, 123.7; HRMS-MALDI (m/z): $(M+H)^+$ calcd for $C_{14}H_8Br_2N_4$, 392.9173 (100%), 390.9194 (51%), 394.9153 (49%), found: 392.9184 (100%), 390.9187 (52%), 394.9172 (48%); UV-vis (CH_2Cl_2): λ_{max}=294 and 547 nm

3,6–bis(4'-bromophenyl)-*s*-tetrazine 14 General procedure for Pinner reaction and oxidation with 4-bromobenzonitrile (1.8 g, 10.0 mmol). Chromatography conditions: CH_2Cl_2; Yield: 35% (686 mg); mp: > 260 °C (lit.,[108,109] 290-292 and 337 °C); IR

(ν_{max}/cm^{-1}): 1587, 1406, 1392, 1105, 1068, 1006, 915, 836, 825; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.87 (d, J=8.7 Hz, 4H); 7.64 (d, J=8.7 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 167.4; 132.7; 129.4; 129.0; 125.9; UV-vis (CH_2Cl_2): λ_{max}=314 and 547 nm

Synthesis of *N,N*-diphenyl-4-tributyltinaniline 15 1.6 M solution of *n*BuLi 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 45min at this temperature. Bu_3SnCl (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%). ^{1}H NMR (400 MHz, $CDCl_3$) 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), 1.60-1.50 (m, 6H), 1.38-1.29 (m, 6H), 1.05-1.00 (m, 6H), 0.89 (t, J=7.3 Hz, 9H)

3,6-bis(5-bromo-4-decylthiophen-2-yl)-*s*-tetrazine 16 General procedure for Pinner reaction and oxidation with 5-bromo-4-decylthiophene-2-carbonitrile (0.75 g, 2.3 mmol). Chromatography conditions: CH_2Cl_2/PE:8/2; Yield: 65% (0.51 g); mp: 83 °C; IR (ν_{max}/cm^{-1}): 2950, 2911, 2849, 1551, 1471, 1454, 1437, 1394, 1372, 1264, 1182, 1069, 910, 852, 837; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.93 (s, 2H), 2.63 (t, J=7.6 Hz, 4H), 1.65 (tt, J=7.5 and 7.5 Hz, 4H), 1.34-1.27 (m, 28H), 0.88 (t, J=6.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 160.8, 144.8, 135.1, 131.6, 118.1, 32.0, 29.8, 29.74, 29.70, 29.6, 29.52, 29.47, 29.3, 22.8, 14.3; HRMS-EI (m/z): $(M)^{\bullet+}$ calcd for $C_{30}H_{44}{}^{79}BrN_4S_2$, 682.1374, found: 682.1379

3-decylthiophene 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 diethylether (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-bromothiophene (2.0 mL, 21 mmol, 1.0 eq) and dichloro(1,3-bis(diphenylphosphino)propane)nickel (135 mg, 0.25 mmol, 0.01 eq) in diethylether (20 mL). The reaction mixture was refluxed for 16 hours under argon and then cooled down to room temperature. Water (50 mL) was added and organic compounds were extracted with diethylether (5*100 mL). The combined organic phases were washed with saturated sodium chloride solution (300 mL), dried over anhydrous sodium sulfate, filtrated and concentrated under reduced pressure. The crude product was purified by a silicagel column chromatography (hexane) to give a colorless liquid. Yield: 96% (4.61g). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.21 (m, 1H), 6.92-6.90 (m, 2H), 2.60 (t, J=7.8 Hz, 2H), 1.59 (tt, J=7.8 and 6.9 Hz, 2H), 1.30-1.15 (m, 14H), 0.86 (t, J=6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 143.4, 128.4, 125.2, 119.9, 32.1, 30.7, 30.4, 29.9, 29.78, 29.77, 29.6, 29.5, 22.9, 14.3

2-bromo-3-decylthiophene 18 To a solution of 3-decylthiophene (2.0 g, 8.9 mmol, 1.0 eq) in a mixture of solvents acetic acid/chloroform (1/1, 30 mL) was portionwise added *N*-bromosuccinimide (1.6 g, 8.9 mmol, 1.0 eq) at 0 °C and without light. The reaction mixture was stirred at room temperature for 17 hours before being poured into iced water (100 mL). Organic compounds were extracted with chloroform (5*100 mL). The combined organic phases were washed with water (2*200 mL) and saturated sodium chloride solution (200 mL), dried over anhydrous sodium sulfate, filtrated and concentrated under reduced pressure. The crude product was purified by a silicagel column chromatography (hexane) to give a colorless liquid. Yield: 69% (1.9 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.16 (d, J=5.6 Hz, 1H), 6.77 (d, J=5.6 Hz, 1H), 2.54 (t, J=7.6 Hz, 2H), 1.55 (tt, J=7.6 and 7.6 Hz, 2H), 1.30-1.25 (m, 14H), 0.86 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.1, 128.4, 125.3, 108.4, 32.1, 29.9, 29.8, 29.7, 29.6, 29.54, 29.48, 29.4, 22.8, 14.3.

5-bromo-4-decylthiophene-2-carboxaldehyde 19 At -78 °C under argon, to THF (12 mL) was added first Et_2NLi (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 (3*100 mL). The combined organic phases were washed with saturated sodium chloride solution (250 mL), dried over anhydrous magnesium sulfate, filtrated and concentrated under reduced pressure. The crude product was purified by a silicagel column chromatography (CH_2Cl_2/PE) to give a colorless liquid. Yield: 70% (1.4 g). IR (ν_{max}/cm^{-1}): 2971, 2921, 1669, 1427, 1407, 1394, 1377, 1233, 1150, 1066, 1057, 1028, 892, 879, 868; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.75 (s, 1H), 7.48 (s, 1H), 2.59 (t, J=7.4 Hz, 2H), 1.61 (tt, J=7.4 and 7.4 Hz, 2H), 1.5-1.2 (m, 14H), 0.88 (t, J=6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 181.7, 143.9, 142.9, 136.7, 121.9, 31.9, 29.6, 29.6, 29.5, 29.4, 29.34, 29.32, 29.1, 22.7, 14.1

5-bromo-4-decylthiophene-2-carbonitrile 20 33% Ammoniacal solution (42 mL) was added 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 (3*30 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 (CH_2Cl_2/PE: 3/7) to give a colorless oil. Yield: 87% (0.72 g). IR (ν_{max}/cm^{-1}): 2950, 2912, 2850, 2217, 1552, 1454, 1437, 1394, 1182, 1069, 910, 852, 837; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.30 (s, 1H), 2.55 (t, J=7.6 Hz, 2H), 1.56 (tt, J=7.3 and 7.3 Hz, 2H), 1.32-1.22 (m, 14H), 0.81 (t, J=6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 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

4-(6-chloro-*s*-tetrazin-3-yl)morpholine 21 To a solution of morpholine (0.58 mL, 6.62 mmol, 1.0 eq) in anhydrous CH_2Cl_2 (125 mL) were added 3,6-dichlorotetrazine (1.00 g, 6.62 mmol, 1.0 eq), and 2,4,6-collidine (0.88 mL, 6.62 mmol, 1.0 eq). The mixture was stirred at room temperature for 1 hour then concentrated under reduced pressure. The crude product was purified by a silica gel column chromatography (DCM) to give a red solid (1.30 g, 97%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.99 (t, J=4.8 Hz, 4H), 3.85 (t, J=4.8, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.5, 159.7, 66.4, 44.0; IR (σ in cm^{-1}): 2980, 2915, 2988, 2861, 1535, 1445, 1361, 1269, 1251, 1189, 1119, 962, 945, 852; m.p.: 120°C (lit.[110] 115-117).

3-methylthio-6-morpholino-*s*-tetrazine 23 To a solution of 3,6-di(methylthio)-*s*-tetrazine **28** (343 mg, 1.93 mmol, 1.0 eq) in acetonitrile (7 mL) was added morpholine (0.21 mL, 2.4 mmol, 1.3 eq). Mixture was refluxed for 96 hours. All volatile compounds were removed by concentration under

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%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3,92 (t, J=4.6 Hz, 4H), 3.83 (t, J=4.6 Hz, 4H), 2.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.7, 160.5, 66.5, 43.8, 13.7; IR (ν_{max}/cm^{-1}): 2930, 2861, 1364, 1189, 1038, 942; mp: 138 °C (lit.[96] 131-132).

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 was added triphenylamine (5.00 g, 20 mmol, 1.0 eq). The 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 CH_2Cl_2 (3*20 mL). The combined organic layers were dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. The crude product was purified by a silica gel flash chromatography [DCM] to give **24** (4.22 g, 77%) as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.80 (s, 1H), 7.67 (d, J=8.7 Hz, 2H), 7.34 (dd, J=7.8 and 7.8 Hz, 4H), 7.16 (m, 6H), 7.01 (d, J=8.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 190.6, 153.5, 146.3, 131.4, 129.9, 129.2, 126.4, 125.2, 119.5; IR (σ in cm^{-1}): 1687, 1583, 1504, 1488, 1330, 1304, 1289, 1220, 1155, 824; m.p.: 132°C (lit.[111] 132).

4-ethynyl-*N*,*N*-diphenylaniline 26 To a solution of Ohira Bestmann reagent (377 mg, 1.96 mmol, 1.52 eq) in methanol (10 mL) were added a solution of de 4-(*N*,*N*-diphenylamino)benzaldehyde **24** (353 mg, 1.29 mmol, 1.0 eq) in dichloromethane (10 mL) and potassium carbonate K_2CO_3 (677 mg, 4.90 mmol, 3.80 eq). The mixture was refluxed under argon at room temperature for 24 hours. The crude product was filtrated on clarcel and neutralized with a solution of sodium hydrogenocarbonate $NaHCO_3$ (10%, 20 mL). Aqueous phase was extracted with dichloromethane (3*20 mL). The organic phase was washed with brine (60 mL), dried on anhydrous sodium sulfate Na_2SO_4, filtrated and concentrated under reduced pressure. The crude product was purified by a silicagel column chromatography (PE to PE/DCM (9/1)) to give a white solid (253 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.35 (d, J=8.7 Hz, 2H), 7.28 (dd, J=7.8 and 7.3 Hz, 4H), 7.13 (dd, J=7.8 and 0.9 Hz, 4H), 7.07 (tt, J=7.3 and 0.9 Hz, 2H), 7.00 (d, J=8.7 Hz, 2H), 3.02 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.4, 147.2, 133.1, 129.5, 125.1, 123.7, 122.4, 114.9, 84.0, 76.4; IR (σ in cm^{-1}): 3289, 3265, 2988, 2901, 2102, 1585, 1503, 1484, 1406, 1394, 1382, 1283, 1261, 1066, 1057, 1028, 893, 880, 847, 829; m.p.: 110°C (lit.[112] 108-109).

3,3'-(*s*-tetrazine-3,6-diyl)bis(*N*-(4-methoxyphenyl)aniline) 27 To a solution of anisidine (178 mg, 1.45 mmol, 1.9 eq) and cesium carbonate Cs_2CO_3 (761 mg, 2.34 mmol, 3.1 eq) in distilled toluene (8 mL) under argon were added 3,6-bis(3'-bromophenyl)-*s*-tetrazine **13** (300 mg, 0.765 mmol, 1.0 eq) and bis(tri-*tert*-butylphosphine)palladium(0) $Pd(PtBu_3)_2$ (42 mg, 0.081 mmol, 0.1 eq). Mixture was refluxed under argon for 19 hours. Anisidine (88 mg, 0.72 mmol, 0.9 eq), $Pd(PtBu_3)_2$ (18 mg, 0.035 mmol, 0.04 eq) and Cs_2CO_3 (350 mg, 1.07 mmol, 1.43 eq) were then added. Mixture was refluxed under argon for 17 hours. All volatile compounds are removed by concentration under reduced pressure. The crude product was purified by a silicagel column chromatography (DCM) to give a red solid (146 mg, 40%). ^{1}H NMR (400 MHz, DMSO) δ: 8.28 (s, 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); ^{13}C 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 (ν_{max}/cm^{-1}): 3384, 1598, 1504, 1452, 1381, 1292, 1236, 1226, 1033, 934, 841; mp: 185 °C; HRMS-ESI (m/z) : $(M+H)^+$ calcd for $C_{28}H_{25}N_6O_2$, 477.2039, found 477.203

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