Thiophene- and bithiophene-based π-conjugated Schiff base oligomers containing binaphthalene moieties in the backbone. Properties and computational simulations†

Alexis F. González, a Andrea P. Mariman, a René A. Hauyón, a Danitza Pavez-Lizana, a César Saldías, b Eduardo Schott, c Ximena Zarate, d Luis García, a Carmen M. González-Henríquez, e Ignacio A. Jessop, f Alain Tundidor-Camba, id Patricio A. Sobarzo a and Claudio A. Terraza a

New π-conjugated Schiff base oligomers \( \text{o-AZdAN1Th} \) and \( \text{o-AZdAN2Th} \) based on a binaphthalene core and containing thiophene or bithiophene units in their backbone were synthesized from the reaction between [1,1′-binaphthalene]-4,4′-diamine with thiophene-2,5-dicarbaldehyde and [2,2′-bithiophene]-5,5′-dicarbaldehyde by a high-temperature polycondensation method. These new materials were slightly soluble in non-protic polar solvents, such as chloroform and dichloromethane. From GPC analysis of the CHCl3-soluble fraction, \( \text{o-AZdAN1Th} \) was found to be a tetramer, whereas \( \text{o-AZdAN2Th} \) was a trimer with 1.4 kDa and 1.3 kDa average molecular weight \( (M_n) \), respectively. Both samples exhibited high thermal stability with \( T_{5\%} \) values of 452 °C and 456 °C and relatively high \( T_g \) values of 346 °C and 384 °C, for \( \text{o-AZdAN1Th} \) and \( \text{o-AZdAN2Th} \), respectively. The samples showed absorptions in the deep-blue (\( \text{o-AZdAN1Th} \)) and blue (\( \text{o-AZdAN2Th} \)) regions of the visible spectrum, and emission responses at 387 nm and 447 nm, respectively, with moderate Stokes shifts (77–95 nm). Their optical and electronic properties were similar to those described for thiophene-based materials, with optical bandgap values close to 2.4 eV. HOMO energy values of −5.98 and −5.95 eV and LUMO energy values of −3.87 eV and −3.84 eV were obtained for \( \text{o-AZdAN1Th} \) and \( \text{o-AZdAN2Th} \), respectively. Theoretical DFT and TD-DFT calculations were used to compare the effect of increasing thiophene units along the backbone for the real and also theoretical \( \text{o-AZdANxTh} \) samples \((x = 3 \text{ and } 4 \text{ thiophene units})\). According to our study, these two new thiophene-based can be proposed for optoelectronic applications.

Introduction

Highly π-conjugated materials, such as small molecules and polymers, have attracted the attention of researchers and technological companies since the discovery of conducting polymers by Shirakawa et al. due to their ubiquitous potential in industrial, technological and everyday life applications.1,2 The development of organic-based optoelectronics has been strongly driven by the extensive use of new conjugated materials in photovoltaic devices, organic transistors and energy storage, as well as in prototype devices for medical applications due to their suitable semiconducting, electrochemical and optical properties.3–4 Moreover, a broad class of π-conjugated polymers has been used as semiconductor materials for the generation of optoelectronic devices, such as polymeric solar cells (PSCs), polymeric light-emitting diodes, organic field-effect transistors, polymeric sensors, and energy storage.2–11 In addition, organic-based materials exhibit
excellent properties, such as low production cost, light weight and good flexibility, giving them comparative advantages over traditional materials.\textsuperscript{1,12,13}

Polythiophene derivatives have become the most widely used type of π-conjugated material in cutting-edge electronics research, as they exhibit suitable donor properties, which make them very versatile materials depending on the structural design of the respective monomers. This fact explains the explosive increase of published works on the synthesis and characterization of new polythiophenes and their derivatives.\textsuperscript{14,15} This type of building blocks provides electronic properties that lead to polymers with low bandgap value and a wide absorption range in the visible region. These properties can be easily tuned by modifying the structure of the thiophene units along the backbone.\textsuperscript{16,17} In photovoltaic devices, such as bulk heterojunction solar cells, these modulations lead to monomers with different structural configurations for new n- and p-type copolymers p-conjugated for the absorber layer in this multilayer structure device architecture.\textsuperscript{18} To date, improvements in solar energy conversion efficiency have been reported for polythiophene derivatives in relation to chemical design as well as device configuration, where the efficiency has scaled values above 15–20%.\textsuperscript{17,19–22}

Poly(azomethine)s (PAZs), also called polyimin(e)s or Schiff base polymers, are a type of π-conjugated polymeric materials. These polymers have imine bonds (R–CH=N–R') along their chains,\textsuperscript{23,24} which are isoelectronic with vinyl bonds (CH=CH–), allowing to obtain materials with optical and electronic properties similar to poly(vinylene) derivatives. These properties and their high thermo-mechanical stability play a key role in ensuring maximum efficiency for further integration of these organic-based materials into buildings, textiles and other structures.\textsuperscript{19,25,26} The great versatility of PAZs is also due to the type of polymerization that originates them and, therefore, to the structure of the monomers involved. Thus, the structural design of diamines, dialdehydes or oxidizable compounds containing imine groups allowing to modulate the electronic properties of the final material. In this way, hole transport processes can be promoted for photocurrent generation in the optoelectronic device, such as perovskite solar cells where long-term stability is improved with moderate efficiency (6–18% PCE).\textsuperscript{24–27} Aromatic diamines and dialdehydes with various structures can be used in polycondensation reactions to obtain new material architectures applicable to organic electronics.\textsuperscript{28} In addition, these materials can exhibit fluorescence, ferromagnetism, redox activity and activity as charge carriers.\textsuperscript{25,29,30}

In this context and according to the background, this research focused on the synthesis of two new binaphthalene-based oligo(azomethine)s as π-conjugated materials obtained from diamine and dialdehyde monomers by high-temperature polycondensation in solution. These new materials containing binaphthalene and thiophene/bithiophene units in the main chain were structurally characterized by spectroscopic techniques. Their physicochemical and thermal properties, absorption and emission behavior, as well as the energies of the frontier molecular orbitals were studied. Finally, the optical and electronic properties obtained and those calculated by DFT and TD-DFT theoretical methods were compared.

### Experimental

#### Materials

*p*-Toluenesulfonic acid monohydrate (TsOH), anhydrous N,N-dimethylacetamide (DMAC), tetrabutylammonium hexafluorophosphate (TBAHF), 1-naphthylamine, and anhydrous calcium sulfate were purchased from Sigma-Aldrich. 2,5-Thiophenicarboxaldehyde was obtained from AK Scientific, Inc. Sodium acetate, toluene (Tol), chlorobenzene (CB), chloroform, dichloromethane (DCM), tin(II) chloride dihydrate, 1,4-dioxane, dimethylsulfoxide (DMSO), and anhydrous magnesium sulfate were acquired from Merck. Anhydrous calcium chloride, sodium nitrite, and sodium sulfite were purchased from JT Baker. [2,2'-Bithiophen]-5,5'-dicarbaldehyde was obtained from TCI America. All reagents and solvents were used as received without further purifications.

#### Characterization techniques

FT-IR spectra were acquired on a JASCO FT-IR 4200 Spectrometer using KBr pellets. \textsuperscript{1}H and \textsuperscript{13}C NMR spectra were recorded on Bruker Avance III HD-490, CDCl\textsubscript{3} and tetramethylsilane were used as a solvent and internal standard, respectively. Elemental analyses were performed on a LECO CHNS-932 Elemental Analyzer equipment. Uncorrected melting points were obtained on a SMP3 Stuart Scientific. TGA analyses were performed on a Mettler Toledo TGA/SDTA 851 apparatus at a heating rate of 10 °C min\textsuperscript{−1} in a nitrogen atmosphere. DSC experiments were achieved on a Mettler Toledo DSC821 equipment at heating and cooling rates of 10 °C min\textsuperscript{−1} and 30 °C min\textsuperscript{−1}, respectively. The molecular weights of the samples were acquired through GPC experiments using THF as eluent on a Wyatt Technology Dawn Light-scattering Dawn EOS coupled with an Optilab DSP interferometric refractometer index detector at a flow rate of 1.0 mL min\textsuperscript{−1} at 25 °C. All measurements were performed at a concentration of 2.5 mg mL\textsuperscript{−1} in THF, filtered through a 0.45 μm nylon filter prior to analysis and calibrated with polystyrene standards in the range of 1020–1 944 000 g mol\textsuperscript{−1}. UV-vis and photoluminescent spectra were acquired from CB, DCM, DMSO, and Tol solutions at a concentration of 0.2 mg mL\textsuperscript{−1} using a PerkinElmer Lambda 35UV/VIS spectrometer and a Jasco FP-6200 Spectrofluorometer, respectively. The concentration of these solutions was adjusted to obtain an absorbance of 0.1 arb. units before proceeding to photoluminescent measurements. Edinburgh Instruments FS5 fluorimeter equipped with a xenon lamp at 25 °C in solution organic solvents such as Tol, DCM, and DMSO. The concentration of these solutions was adjusted to obtain an absorbance of 0.1 arb. units before proceeding to photoluminescent measurements. The PL quantum efficiency (PLQY, ϕ\textsubscript{PL}), relative to a known standard quinine bisulfate (ϕ\textsubscript{PL} = 0.546 in 0.5 M H\textsubscript{2}SO\textsubscript{4}) was estimated from
DCM solutions at room temperature. CV experiments were achieved on a CH Instrument 6200E electrochemical analyzer with a conventional three-electrode cell setup. A platinum disc was used as a working electrode, Ag/Ag⁺ as a reference electrode and a platinum wire as a counter electrode. All measurements were carried out using 0.1 M TBABF₄ in DCM solutions as support electrolyte with a scan rate of 100 mV s⁻¹ and calibrated against ferrocene/ferrocenium (Fe/Fe⁺) redox couple.

**Synthesis of diamine monomer**

[1,1’-Binaphthalene]-4,4’-diamine (dAN). The precursor ([E]-1,2-di(naphthalen-1-yl)diazene, AzN) was synthesized following a procedure already described. Briefly, the diazonium salt of naphthalen-1-amine was prepared using sodium sulfite in acid medium (pH 1) for 48 h. The product was dried under vacuum at 70 °C for 24 h to give an orange (o-AZdAN1Th) solid. The precipitate was then filtered under vacuum, washed with methanol solution (100 mL, 1 : 1 v/v) and stirred for 30 min. To this end, in a two-necked round bottom flask equipped with an anhydrous CaCl₂ trap, dialdehyde (1.00 mmol), TsOH (40 mg, 0.23 mmol) and anhydrous calcium sulfate (80 mg, 0.59 mmol) were dissolved in anhydrous DMAc (5 mL). The reaction mixture was stirred at 80 °C and then a solution of dAN (0.28 g, 1.00 mmol in 5 mL anhydrous DMAc) was slowly added. The system was stirred for 1.5 h and then allowed to reach 120 °C for 20 h. After cooling to room temperature, the mixture was poured into a water:methanol solution (100 mL, 1:1 v/v) and stirred for 30 min. The precipitate was then filtered under vacuum, washed with plenty of water and purified by Soxhlet extraction with methanol for 48 h. The product was dried under vacuum at 70 °C for 24 h to give an orange (o-AZdAN1Th) and reddish (o-AZdAN2Th) solid.


**Synthesis of Schiff base oligomers**

In agreement with previous reports, the oligomers were obtained by the polycondensation method at high temperature under nitrogen atmosphere. To this end, a two-necked round bottom flask equipped with an anhydrous CaCl₂ trap, diiodoethane (1.00 mmol), TsOH (40 mg, 0.23 mmol) and anhydrous calcium sulfate (80 mg, 0.59 mmol) were dissolved in anhydrous DMAc (5 mL). The reaction mixture was stirred at 80 °C and then a solution of dAN (0.28 g, 1.00 mmol in 5 mL anhydrous DMAc) was slowly added. The system was stirred for 1.5 h and then allowed to reach 120 °C for 20 h. After cooling to room temperature, the mixture was poured into a water:methanol solution (100 mL, 1:1 v/v) and stirred for 30 min. The precipitate was then filtered under vacuum, washed with plenty of water and purified by Soxhlet extraction with methanol for 48 h. The product was dried under vacuum at 70 °C for 24 h to give an orange (o-AZdAN1Th) and reddish (o-AZdAN2Th) solid.


**Computational details**

All computational calculations were performed using the Gaussian 09 computational package. The studied structures were optimized in their ground-state. Those calculations were carried out with Becke’s three-parameter nonlocal hybrid exchange functional and the Lee–Yang–Parr nonlocal correlation functional including the long-range interaction correction CAM-B3LYP. The 6-311G* basis set was used for C, S, N, and H atoms. The Hessian was also calculated for all derivatives studied to ensure that the structure obtained correspond to the local minimum. No frequencies with imaginary values were found. In all cases, a repetitive unit n = 3 (trimer) was considered, which accurately describes the obtained experimental results. Furthermore, time-dependent DFT (TD-DFT) calculations were performed using the same theory level to simulate the oligomeric UV-vis spectra. Thus, the performed calculations using the first-principles method were used to obtain accurate excitation energies and oscillator strengths related to the molar extinction coefficient. The continuous polarizable model (PCM) using DCM as solvent was used for optimization and TDDFTY calculations to include the effect of the solvent.

**Results and discussion**

**Synthesis and characterization of dAN and o-AZdANThs**

The azo-precursor (AzN) was synthesized in 52% yield according to a procedure described by Cohen et al. (Fig. 1). In this, naphthalen-1-amine is transformed in its respective diazonium salt and then subjected to a self-coupling reaction. Once this compound was obtained, it was subjected to SnCl₂ treatment followed by acid-catalyzed benzidine rearrangement. Diamine [1,1’-binaphthalene]-4,4’-diamine was obtained as a wheat-colored solid with 29% yield and its structure, like that of the precursor, was corroborated by spectroscopic techniques and elemental analysis.

The synthetic route for obtaining the oligomers is shown in Fig. 1. Through high-temperature polycondensation of dAN...
with commercial dialdehydes (2,5-thiophenedicarboxaldehyde and 2,2'-bithiophene-5,5'-dicarboxaldehyde) were achieved both one-thiophene (o-AZdAN1Th) and two-thiophene (o-AZdAN2Th) containing oligo(thiophene-azomethine)s.41

FT-IR, NMR and elemental analyses confirmed the proposed structure for the repeating unit of the oligomers. In the FT-IR spectra (Fig. 3), the C==N, C–H and C–N stretching bands of the imine function were observed at approximately 1605 cm\(^{-1}\), 1385 cm\(^{-1}\) and 3040 cm\(^{-1}\), respectively.26,29 Like to the azomethylene-based materials already described,18–40 both samples showed a C==O stretching band attributed to a terminal aldehyde (ca. 1670 cm\(^{-1}\)). Likewise, CO–H stretching bands were observed at 2851–2909 cm\(^{-1}\) (o-AZdAN1Th) and 2838–2849 cm\(^{-1}\) (o-AZdAN2Th), ratifying the presence of terminal aldehyde residues. Probably due to the shorter average length of its chains with respect to its homologous oligomer, only o-AZdAN2Th showed a terminal amine stretching signal (3304 cm\(^{-1}\)). The signals centered at 1140 cm\(^{-1}\) and 1195 cm\(^{-1}\) were associated to the p-disubstitution pattern of the benzene rings or thiophene units, just as the bands as 1605 cm\(^{-1}\) and 760 cm\(^{-1}\) were attributed to out-of-plane C–H bending of these rings.41

Due to the insolubility shown by o-AZdAN1Th in the deuterated solvents tested, only its counterpart, o-AZdAN2Th, was characterized by \(^1\)H NMR spectroscopy (Fig. S1†). The spectrum, collected in CDCl\(_3\) solution, evidence broad signals, where the presence of terminal aldehyde groups and imine function is ratified by singlets at 9.08 ppm and 8.93 ppm, respectively. In the interval 7.43–6.23 ppm the aromatic protons of the binaphthalene and thiophene units are found, being complex to make a detailed assignment of them.

**Solubility, molecular weights and thermal properties**

Both samples were not completely soluble under the conditions tested. On the contrary, the oligomers showed reduced solubility in the different common organic solvents tested despite the application of heat (Table S1†), which may be attributed to high aromatic content and the structural rigidity of the chains promoted by the imine bonds, which limits their solvation. However, in the case of thiophene polymers, it has been observed that as the number thiophene units in the backbone increases, their solubility also increases.15,42,43 In this regard, o-AZdAN2Th showed better solubility than o-AZdAN1Th, mainly due to a lower molecular weight (trimeric nature) and a higher local flexibility provided by the non-planar bithiophene units of the main chain.44,45 The determination of the soluble and insoluble fraction for each oligomer using DCM as solvent was carried out at room temperature and also at boiling (Table S1†). This solvent was used in the main characterizations in solution developed for the o-AZdANThs, thus accounting for the behavior of the soluble fraction of the material in this solvent. For both oligomers, the soluble fraction increases slightly at solvent boiling temperature reaching values of 45% and 46% for o-AZdAN1Th and o-AZdAN2Th, respectively.

The molecular weights, polydispersity index (PDI) and degrees of polymerization (DP) of o-AZdANThs were determined by GPC experiments from the THF-soluble fraction (Table 1 and Fig. S2†). The number average molecular weight (\(M_n\)) was similar for the two samples, whereas, contrary to expectations, the weight average molecular weight (\(M_w\)) of o-AZdAN1Th was almost 50% higher than that shown by o-AZdAN2Th (2.6 kDa vs. 1.8 kDa). In general, these new thiophene-based oligo(azomethine)s showed lower molecular weights than previously described thiophene-containing PAZs.46 This fact could be related to poor solvation of the growing oligomer during the polymerization process which is enhanced by the aromatic content as well as by the structural rigidity provided by the imine bond.

Despite the higher molecular weight shown by o-AZdAN1Th, the THF-soluble fraction of o-AZdAN2Th allows the inference that the higher molecular weight oligomers are insoluble. According to the results, the THF-soluble fractions were oligomers, with average chain sizes of four repeating units (tetramers) for o-AZdAN1Th and three repeating units (trimers) for o-AZdAN2Th. In both cases, the insoluble fraction was able to reveal high molecular weight chains with polymeric nature that were impossible to access by soluble-sample techniques.23 Likewise, the soluble fractions showed PDI of 1.9 (o-AZdAN1Th) and 1.4 (o-AZdAN2Th), indicating the obtaining of homogeneous size chains after the purification process.

To study the thermal behavior of the oligomeric samples, TGA and DSC analyses were performed (Fig. 4 and Fig. S3†), and the results were summarized in Table 1. o-AZdAN2Th
starts its decomposition ($T_{\text{onset}}$) 50 °C earlier than its counterpart, probably due to its more extended conformation (Fig. 8) which decreases the intra- and inter-chain attractive forces. On the other hand, the temperature at 5% weight loss ($T_{\text{5\%}}$) is similar between samples, however, $T_{\text{10\%}}$ is 27 °C higher for o-AZdAN1Th. In addition, the resulting solid residue of both samples at 850 °C ($R_w$) was remarkably similar. These results showed that o-AZdAN1Th had slightly higher thermal resistance than o-AZdAN2Th, which could be attributed to its higher molecular weight and closer conformation that promotes higher oligomeric stacking forces. DTGA curves showed that the maximum degradation rate is 27 °C higher for o-AZdAN1Th. Although AZdAN2Th has a longer π-conjugated repeating unit, the higher molecular weight promotes higher stacking strength between the chains in o-AZdAN1Th, which ratifies what was observed in the TGA curves.

According to DSC experiments (Fig. S3†), the oligomers showed high $T_g$ values; 346 °C for o-AZdAN1Th and 384 °C for o-AZdAN2Th, a fact associated with the rigidity of the oligomeric chains conferred through both imine bonds and aromatic units. Unlike previously described thiophene-based materials or oligo- and PAZs, the thermal behavior registered for the prepared thiophene-based oligo[azomethine]s could be a key property to define their potential applications in optoelectronic devices, avoiding morphological problems, such as thermal deformation of thin solid films, which is crucial for a viable processability.47

### Table 1  GPC and thermal results of the o-AZdANThs under a nitrogen atmosphere

<table>
<thead>
<tr>
<th></th>
<th>$M_n$ (kDa)</th>
<th>PDI$^a$</th>
<th>DP$^b$</th>
<th>$T_{\text{onset}}$ $^c$ (°C)</th>
<th>$T_{\text{5%}}$ $^d$ (°C)</th>
<th>$T_{\text{10%}}$ $^d$ (°C)</th>
<th>$R_w$ $^e$ (%)</th>
<th>$T_g$ $^f$ (°C)</th>
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<tr>
<td>o-AZdAN1Th</td>
<td>1.40</td>
<td>1.9</td>
<td>4</td>
<td>350</td>
<td>452</td>
<td>510</td>
<td>75</td>
<td>346</td>
</tr>
<tr>
<td>o-AZdAN2Th</td>
<td>1.30</td>
<td>1.4</td>
<td>3</td>
<td>300</td>
<td>456</td>
<td>483</td>
<td>72</td>
<td>384</td>
</tr>
</tbody>
</table>

$^a$ Polydispersity index ($M_w$/$M_n$). $^b$ Degree of polymerization ($M_n$/molecular weight of the repeating unit). $^c$ Onset temperature of thermal decomposition. $^d$ Temperature at 5% and 10% weight loss, respectively. $^e$ Residual weight at 850 °C. $^f$ Transition glass temperature (second scan).

### Optical and electronic properties

The optical properties of thiophene-based oligomers were studied by UV-vis and photoluminescence (PL) experiments in dilute solutions using DCM as solvent.

Fig. 5 shows the UV-vis spectra (solid line) and their numerical data are summarized in Table 2. Both samples evi-
denced broad absorption bands between 230 nm and 550 nm, corresponding to the π-π* and n-π* transitions of the aromatic systems and imine residues, respectively. As expected, the high aromatic content effect was observed for o-AZdAN2Th related to the increase of thiophene units in its repeating unit, although it has a lower molecular weight than o-AZdAN1Th. The red shift of the band of o-AZdAN2Th compared to that of o-AZdAN1Th is explained by a more effective π-overlap between the naphthalene rings provided by the binaphthalene moiety, which promotes a higher electronic delocalization along the oligomer chains. In this sense, the effect of increasing thiophene units with decreasing oligomer chains and, as a result, the high energy transition can be related to the higher degree of conjugation afforded by the bithiophene unit, highlighting that a gradual increase in thiophene units is paramount for the design of high PLQY materials.

Both samples were studied in different solvents with increasing polarity (Tol < CB < DCM < DMSO) to determine a possible solvatochromic effect, however, no absorption band shift was observed in the spectra of these solutions (Fig. S4†).

The photoluminescence behavior of the oligomers was analyzed at room temperature in dilute DCM solutions using the absorption band maximum ($λ_{abs}^{max}$) as the excitation wavelength (Fig. 5 and Table 2). o-AZdAN1Th and o-AZdAN2Th showed a strong emission band in the range of 340–560 nm and 380–620 nm, respectively, following the same pattern as the UV-vis absorption. o-AZdAN1Th showed an emission band centered in the dark blue region at 387 nm. In contrast, its counterpart presented a markedly red-shifted emission band at 447 nm in the blue region of the visible light spectra. The behavior of o-AZdAN2Th is due, as mentioned above, to its extended π-conjugated fluorophore system and a flatter conformation that increases the electronic conjugation length. In addition, the emission behavior of the samples was studied in organic solvents of different polarity (Fig. S4†). In the case of o-AZdAN1Th, no changes were found in the position of the emission maximum in the spectra, so the existence of locally excited emission was assumed. On the contrary, when DMSO was used as solvent, o-AZdAN2Th showed a slight red shift ($Δ = 24$ nm) indicating a change in the polarity of the excited state.

In addition, the emission of the samples was quantitatively evaluated by PLQY measurements in DCM solution, using quinine bisulfate ($Φ_{PL} = 0.546$ in 0.5 M H$_2$SO$_4$) as a standard (Table 2). Both samples showed similar low PLQY; 1.2% for o-AZdAN1Th and 2.3% for o-AZdAN2Th. The higher value evidenced for o-AZdAN2Th could be related to the higher degree of conjugation afforded by the bithiophene unit, highlighting that a gradual increase in thiophene units is paramount for the design of high PLQY materials.

The Stokes shift of the oligomers in DCM solutions was of 95 nm for o-AZdAN1Th and 77 nm for o-AZdAN2Th. The higher value evidenced for o-AZdAN2Th could be related to its higher molecular weight (tetramer). As a result, the sample absorbs more light due to the numerous chromophore groups present, such as imine bonds, thiophene and binaphthalene units, tending to extend the π-conjugation that stabilized the singlet excited state. The moderate Stokes shifts recorded may be useful in future optoelectronic applications, such as sensors or photovoltaic devices, becoming an essential parameter as it would avoid self-absorption and light scattering processes.

The optical bandgap ($E_g^{opt}$) was estimated for each oligomer from the absorption band edge ($λ_{abs}^{max}$), using the modified Tauc equation ($E_g^{opt} = 1240/λ_{abs}^{max}$). The lowest value was achieved by o-AZdAN2Th, which is favored by a flatter structure of binaphthalene- and thiophene bonds (Table 2). The small difference with respect to the o-AZdAN1Th bandgap could be related to the higher molecular weight of the latter (tetramer) that compensates for its lower π-conjugation efficiency along the chains with respect to the binaphthalene-based oligomer. Similar to previously reported PAZs, both oligomers were classified as wide bandgap materials due to their imine bonds, which could negatively affect the coplanarity of the oligomer chains and, as a result, the high energy transition can be reached. TRPL curves were obtained from toluene solutions, showing fast emission of both materials with lifetimes below 10 ns. This result is as expected from a fluorescent-type fluorophore in which emission occurs directly from the photoexcited singlet state $S_1$. Moreover, both oligomers showed two lifetimes that could be attributed to different solvent environments along the polymer chains. As for their emission lifetime, both materials showed similar values, although the second lifetime is longer in the sample with one-thiophene

<table>
<thead>
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<th>o-AZdAN1Th</th>
<th>o-AZdAN2Th</th>
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<tbody>
<tr>
<td>$λ_{abs}^{max}$ (nm)</td>
<td>509</td>
<td>513</td>
</tr>
<tr>
<td>$E_g$ (eV)</td>
<td>2.44</td>
<td>2.42</td>
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<tr>
<td>$λ_{abs}$ (nm)</td>
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<td>318; 370</td>
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<tr>
<td>$e_{max}$ (ev)</td>
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<td>3.14</td>
</tr>
<tr>
<td>Stokes shift (nm)</td>
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<td>$ΔE_{Stokes}$ (nm)</td>
<td>1.05</td>
<td>0.58</td>
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</table>

($a = 1240/λ_{abs}^{max}$).
unit, probably due to the different lengths in the conjugation pathway between the oligomers.

Cyclic voltammetry (CV) experiments were carried out to determine the frontier molecular orbitals (FMOs) energy levels and the electrochemical bandgap value by droplet casting of the oligomer solution onto a platinum electrode. The results are summarized in Table 2.

From the voltammograms (Fig. 7a) in the anodic area, it was possible to observe oxidation peaks centered at 2.02 V for o-AZdAN1Th and 1.95 V for o-AZdAN2Th. The cathodic zone for o-AZdAN1Th shows a reduction peak at −0.87 V. In the case of o-AZdAN2Th, the reduction peak was observed at −1.08 V. Although previously described polythiophenes and thiophene-based PAZs have shown reversible processes in CV experiments, both samples presented a non-reversible process. Thus, these oxidation peaks can be attributed to oxidation processes of the thiophenyl-linkages units promoted by the imine withdrawal effect on the oligomer chains, allowing the formation of polaron on them and the one-electron reduction of the imine groups (Fig. 7b).

The energy of the highest occupied molecular orbital ($E_{\text{HOMO}}$) was calculated using $E_{\text{HOMO}} = -e[E_{\text{onset}} + (4.80 - E_{\text{Fc/Fc+}})]$ whereas the lowest unoccupied molecular orbital energy value ($E_{\text{LUMO}}$) was obtained from $E_{\text{LUMO}} = -e[E_{\text{Red onset}} + (4.80 - E_{\text{Fc/Fc+}})]$. The values are shown in Table 2.

From the $E_{\text{HOMO}}$ values recorded, it is clear that the presence of two thiophene units (o-AZdAN2Th) slightly increases this parameter, which could be related to a more extended $\pi$-conjugated system and, as a result, a lower ionization potential that allows reaching values similar to the polythiophene derivatives used in optoelectronic applications. For oligomers, a slight increase was observed with more thiophene units in the repeating unit. Thus, the $E_{\text{LUMO}}$ was calculated to be −3.87 eV for o-AZdAN1Th and −3.84 eV for o-AZdAN2Th. Although imine bonds as electron-withdrawing groups in the $\pi$-conjugated materials increase the electron affinity, these results suggest that the lower $E_{\text{LUMO}}$ for these o-AZdANThs with respect to thiophene-based small molecules, polythiophene derivatives and thiophene-based PAZs could be related to the presence of the donor character of the binaphthalene units in the backbone.

From the HOMO and LUMO energies, the electrochemical bandgap value ($E_{\text{elect}}$) for thiophene-based o-AZdANThs was estimated to be 2.11 eV and no differences were found for both samples. The obtained bandgap values were very similar to those of poly(3-hexylthiophene) and some oligothiophene derivatives. Moreover, the obtained $E_{\text{elect}}$ value for o-AZdAN2Th was relatively lower than some reported PAZs, which could be directly related to lower values of ionization...
potential reached in electrochemical processes.\textsuperscript{38,56} The similar electrochemical bandgap values for the o-AZdANThs could be due to the length of the $\pi$-conjugated system, where it could be assumed that for higher molecular weight samples (o-AZdAN2Th), a lower value could be reached due to the presence of bithiophene-linkages similar to polythiophene derivatives.

Commonly, the performance of $\pi$-conjugated materials in optoelectronics depends mainly on their solution processability, optoelectronic, thermal and morphological properties when proposed as active or complementary layers in the design and study of optoelectronic devices, such as photovoltaic, light-emitting or sensor materials.\textsuperscript{47,49,61} Moreover, the introduction of binaphthalene units as building-blocks could be a good alternative for the design of the chemical structure in relation to the appropriate thermal properties of new Schiff base oligomers linked through imine groups to thiophene or alklythiophene units. In this way, it could to obtain processable materials in solution, and simultaneously with improved electronic properties to access new or better configurations in optoelectronic devices.\textsuperscript{55,62,63} In the case of o-AZdAN2Th, the suitable optoelectronic properties together with its high thermal stability, would allow to think about future works using this Schiff base oligomer as active layer or complementary material for PSCs using fullerene derivatives such as PC$_{71}$BM or non-fullerene materials as acceptor materials.\textsuperscript{17,47,55}

**DFT analysis of o-AZdANThs**

To better understand the geometrical, electronic and optical properties of the two synthesized oligomers, DFT and TD-DFT calculations were performed for model trimeric species. In addition, to analyze the behavior of future target structures, the oligomers, including three (o-AZdAN3Th) and four (o-AZdAN4Th) thiophene rings in the repeating units, were also realized.

As shown in Fig. 8, the geometrical optimization of the trimers showed a mostly linear structure, where the torsion between the different rings constituting the oligomers could be attributed to steric hindrance (Table S2\textsuperscript{†}). Similar behavior was observed for all the structures studied. The similarity in the structure could be related to the electronic delocalization along the structure and the similarity between the repeating units, which is related to steric hindrance in the structure and low flexibility.

As the electrochemical analysis shows, the HOMOs of all structures are located on the binaphthalene moiety, while the LUMOs are located on the thiophene rings (Fig. 9). Moreover, as the thiophene chain becomes larger, the HOMO–LUMO gaps ($E_D^{\text{DFT}}$) tend to become smaller (Table 3). In this sense, the HOMO and LUMO energies are similar to the observed electrochemical behavior and to the UV-Vis experimental results, suggesting that the proposed model reproduces the experimental results accordingly. Moreover, the HOMO energies show a clear tendency to increase in the following order o-AZdAN4Th > o-AZdAN3Th > o-AZdAN2Th > o-AZdAN1Th, which could be related to the effect of extensive $\pi$-conjugation conferred by an increase in thiophene-linkages that have been previously observed in small molecules, as well as in thiophene-based polymers and PAZs.\textsuperscript{33,41,48,64} This effect was observed in the experimental data with a slight decrease (0.03 eV) in HOMO and LUMO values in o-AZdAN1Th relative to o-AZdAN2Th.

TD-DFT simulations were performed for the four oligomers. In this way, it was possible to characterize the UV-vis absorption bands observed in the experimental analysis of the synthesized samples. As shown in Table 3, good agreement was obtained with the experimental results reported here; two non-synthesized oligomers were also included. In all cases, the calculated transition showed a $\pi$–$\pi^*$ character. These transitions showed good agreement with experimental results, where a shift of even 50 nm has been shown to be reasonable.\textsuperscript{65,66}
Moreover, all calculated transitions correspond to charge transfer between a thiophene portion of the calculated oligomer to other thiophene regions of the studied trimers.\textsuperscript{67,68} In addition, a bathochromic shift was observed as the thiophene units in the studied structures increased. As observed in Fig. S5,\textsuperscript{†} the orbitals involved are delocalized throughout the structure (Table 3), showing that the composition of these transitions produces an electronic rearrangement, which may be related to the luminescence of these structures.

### π-Conjugated azomethine-based materials comparison

The bandgaps and HOMO and LUMO energies of the new binaphthalene-based o-AZs were compared with previous reports on thiophene-based azomethylene-containing small molecules, o-AZs and PAZs to understand the structure–property relationship (Table 4 and Fig. 10). It is well known that some of the highlighted methodologies for the synthesis of thiophene-based π-conjugated materials lead to low bandgap values through a gradual increase in thiophene units.\textsuperscript{24,41,69} Although o-AZdANThs showed similar bandgap values with respect to polythiophene derivatives such as P3HT, the $E_{\text{HOMO}}$ values were lower due to a higher ionization potential, probably caused by a lower elec-

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**Table 3** Calculated ($\lambda_{\text{th}}$) wavelengths, oscillator strength ($f$), active FMOs, and their percentage contributions ($P$) for the studied oligomers in DCM solution

<table>
<thead>
<tr>
<th></th>
<th>$\lambda_{\text{th}}$</th>
<th>$f$</th>
<th>Composition</th>
<th>$P$ (%)</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>$E_{\text{g}}^{\text{DFT}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>o-AZdAN1Th</td>
<td>350</td>
<td>0.41</td>
<td>HOMO→LUMO+3</td>
<td>39</td>
<td>-5.15</td>
<td>-2.53</td>
<td>2.62</td>
</tr>
<tr>
<td>o-AZdAN2Th</td>
<td>390</td>
<td>0.44</td>
<td>HOMO→LUMO+4</td>
<td>24</td>
<td>-5.10</td>
<td>-2.59</td>
<td>2.51</td>
</tr>
<tr>
<td>o-AZdAN3Th</td>
<td>432</td>
<td>0.13</td>
<td>HOMO→LUMO</td>
<td>11</td>
<td>-5.08</td>
<td>-2.59</td>
<td>2.49</td>
</tr>
<tr>
<td>o-AZdAN4Th</td>
<td>466</td>
<td>0.28</td>
<td>HOMO→LUMO+3</td>
<td>20</td>
<td>-5.04</td>
<td>-2.57</td>
<td>2.47</td>
</tr>
</tbody>
</table>

---

**Table 4** Bandgap and FMOs energies for the synthesized o-AZdANThs and some thiophene-based π-conjugated materials

<table>
<thead>
<tr>
<th></th>
<th>$E_g$ (eV)</th>
<th>$E_{\text{HOMO}}$ (eV)</th>
<th>$E_{\text{LUMO}}$ (eV)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>o-AZdAN1Th</td>
<td>2.11</td>
<td>-5.98</td>
<td>-3.87</td>
<td>This work</td>
</tr>
<tr>
<td>o-AZdAN2Th</td>
<td>2.11</td>
<td>-5.95</td>
<td>-3.84</td>
<td>This work</td>
</tr>
<tr>
<td>P3HT</td>
<td>2.30</td>
<td>-5.45</td>
<td>-3.30</td>
<td>36</td>
</tr>
<tr>
<td>PTB7-Th</td>
<td>1.70</td>
<td>-5.20</td>
<td>-3.50</td>
<td>57</td>
</tr>
<tr>
<td>P6T-F100</td>
<td>1.90</td>
<td>-5.25</td>
<td>-3.30\textsuperscript{c}</td>
<td>70</td>
</tr>
<tr>
<td>PFI-co-Th</td>
<td>1.20</td>
<td>-4.88</td>
<td>-3.67</td>
<td>60</td>
</tr>
<tr>
<td>2225Th-DMB</td>
<td>2.60\textsuperscript{d}</td>
<td>-5.30\textsuperscript{c}</td>
<td>-2.70\textsuperscript{c}</td>
<td>38</td>
</tr>
</tbody>
</table>

\textsuperscript{a} $E_{\text{HOMO}} - E_{\text{LUMO}}$ \textsuperscript{b} 1241($\lambda_{\text{onset}}$)$^{-1}$ \textsuperscript{c} From DFT methods. \textsuperscript{d} From the onset of the oxidation peak ($E_{\text{Ox}}^{\text{onset}}$). \textsuperscript{e} From the onset of the reduction peak ($E_{\text{Red}}^{\text{onset}}$). \textsuperscript{f} $E_{\text{HOMO}} + E_{\text{opt}}$.

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**Fig. 10** Bandgaps and FMOs energies of the prepared o-AZdANThs compared with some thiophene-based π-conjugated materials.
tron retention effect of the imine bonds and the oligomeric nature of the samples.\textsuperscript{18,60} In contrast, the $E_{LUMO}$ of the o-AZdAN1Ths were similar to the values shown by the thiophene-based $\pi$-conjugated materials of reference.

From the analysis of thermal and optoelectronic properties and complemented with computational data, o-AZdAN1Ths define new thiophene-containing materials based on binaphthalene with an increasing number of thiophene units and appropriate electron-withdrawing building blocks to achieve high $E_{HOMO}$. Furthermore, the incorporation of electron-donor groups in the side chains could be allowed to achieve $E_{LUMO}$ similar to the polythiophene derivatives, with improved solubility as well as solution-processable capabilities.\textsuperscript{17,48,63,69} In agreement with the most widely studied low bandgap polythiophene derivatives, such as P3HTh, PTB7-Th, or extensive thiophene-based polymers, these new o-AZdAN1Ths are slightly low bandgap materials.\textsuperscript{41,62,63}

The results of this work show differences in the optoelectronic properties between the synthesized oligomers and some low bandgap polythiophene derivatives (Table 4 and Fig. 10). In addition, a proper tuning of the synthetic methodologies would ensure adequate ionization potentials and electronic affinities to obtain processable materials in solution, with suitable optical and electronic properties with a high potential as an active or hole transport materials (HTM) to study them in optoelectronic devices, such as PSCs or perovskite solar cells.\textsuperscript{24,71} Although these binaphthalene-based o-AZs showed an oligomeric nature, their extended $\pi$-conjugated system and low polydispersity could allow them to be proposed as an active layer in bulk heterojunction solar cells, prepared by high vacuum thermal deposition with PC\textsubscript{71}BM as an acceptor layer or used as a substitute for PEDOT:PSS as HTM in a perovskite solar cell.\textsuperscript{44,71,72}

Conclusions

New Schiff base oligomers (o-AZdAN1Th and o-AZdAN2Th) containing binaphthalene units and thiophene or bithiophene moieties in the backbone were synthesized from [1,1′-binaphthalene]-4,4′-diamine with thiophene-2,5-dicarbaldehyde and [2,2′-bithiophene]-5,5′-dicarbaldehyde, respectively, by the high-temperature solution polycondensation method using a polar aprotic solvent, an acid catalyst and a drying agent. These new materials were slightly soluble in non-polar apolar solvents, which was related to the high aromatic content and the structural rigidity conferred by the imine moieties. From GPC experiments, the size of the chains was established; o-AZdAN1Th was a tetramer, while o-AZdAN2Th a trimer. Thermal analyses indicated that both Schiff base oligomers exhibit high thermal stability ($T_{5\%}$) with values at 452 °C (o-AZdAN1Th) and 456 °C (o-AZdAN2Th), with relatively high $T_g$ values (7345 °C). The optical properties of these materials showed absorption in the deep blue (o-AZdAN1Th) and blue (o-AZdAN2Th) region of the visible spectrum, with a high emission response at moderate Stokes shifts (77–95 nm). From electronic measurements, the oligomers showed bandgap values similar to thiophene-based materials (2.44 eV), with lower $E_{HOMO}$ (ca. –5.97 eV) with an increase with increasing thiophene units in the backbone and LUMO energies similar to previous polythiophene derivatives. The experimental optical and electronic properties of the o-AZdAN1Ths were compared and supported with their respective trimers by computational simulations using DFT and TD-DFT methods. Theoretical structures of trimers with three and four thiophene units were also included in the study.

Author contributions


Conflicts of interest

There are no conflicts to declare.

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