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Novel luminescent phenothiazine-based Schiff bases with tuned morphology. Synthesis, structure, photophysical and thermotropic characterization

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ABSTRACT

New Schiff base dimers based on phenothiazine heterocycle have been obtained with high yield and purity by condensation of 3-formyl-10-methyl-phenothiazine with various amines. The structural characterization was performed by elemental analysis, FTIR, 1D and 2D NMR spectroscopy and single crystal and powder wide angle X-ray diffraction. The obtained compounds have high thermal stability and some of them self-assemble into cubic mesophase and form stable molecular glass. The thermotropic study performed by polarized optical microscopy and differential scanning calorimetry revealed the possibility to control the compound morphology by thermal annealing and blending miscible components. The photophysical characterization indicates green light emission, with good absolute fluorescence quantum yield, large Stokes shift and high purity and fully saturated color. The special thermal behavior and photophysical properties appear to be significantly dependent on the special supramolecular architecture generated by the hockey-stick shape of the imino-phenothiazine mesogenic core.

Collectively, the properties of these azomethines provide a starting point for new compounds with great advantages for optoelectronic applications.

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1. Introduction

The thermotropic symmetric dimers formed by two identical rigid cores linked via a single non-conjugated bridge, usually a flexible spacer, are interesting compounds from the academic and technological point of view and are investigated as models for polymers and for their special liquid crystalline behavior, different from those of the corresponding monomers. This is why the synthesis and investigation of the dimers is the expected step in designing new high performance materials, attracting constant interest of the scientific community. A quick overview of the literature reveals many types of rigid units - salicylaldimine [1], cyanophenylene [2], azobenzene [3], oxadiazole [4], thiophene [5], indol, pyrol, diphenyl [6], anthracene [7], pyrene [8], triphenylene [9], indolinobenzospiropyran [10], cholosteryl [11], metalloporphirine [12] and so on – used as rod-like, bent core or discotic mesogens in building dimers. Besides their rich mesomorphism, all these compounds exhibit interesting optical and/or electrical properties [13–15]. Among the reported dimers, azomethines, also named Schiff bases or imines, are widespread due to their excellent properties: high thermal stability, liquid crystalline potential, ability to form complexes, semiconducting, optical and therapeutic activity [16,17]. Besides, the azomethine connection is easily attainable in mild reaction conditions, with high purity and yield [2,7], essential features for electronic and optoelectronic applications [18,19].

On the other hand, many rigid cores are designed to contain heterocyclic units due to their ability to impart lateral and/or longitudinal dipole combined with changes in molecular shapes bearing a great potential for all optical signal processing, spatial light modulation, optical information storage, organic thin film transistors, fast switching ferroelectric materials, fluorescent probes for the detection and analysis of biomolecules and so forth [6]. A particularly interesting heterocycle studied for its therapeutical properties but also as a promising candidate for optoelectronic applications is phenothiazine [20,21]. Phenothiazine behaves as a very strong electron donating unit due to the nitrogen and sulfur as electron donating atoms. A thorough literature survey revealed that azomethines containing phenothiazine heterocycle received little attention [22,23]. Moreover, only few studies focused



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on polyazomethines containing this heterocycle [24,25]. Taking into account all the above mentioned reasons, we decided to obtain azomethine dimers containing phenothiazine heterocycle in the rigid core, as model molecules in building new compounds addressed to optoelectronic applications.

2. Material and methods

2.1. Reagents

4-Butoxyaniline 97%, 1,3-bis(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane 95%, 9,9-bis(*p*-aminophenyl)-fluorene 97%, *N*, *N*dimethylformamide (DMF) 99.5% and acetonitrile 99.9% were purchased from Sigma—Aldrich and used as received. 3-Formyl-10methyl-phenothiazine was synthesized according to literature [26], and the aromatic diamines containing a flexible spacer (1,2-bis[2-(4aminophenoxy)ethoxy]ethane, 1,8-bis-(4-aminophenoxy) octane, 1,10-bis-(4-aminophenoxy) decane) have been synthesized in our laboratory, too [7].

2.2. Equipments

Determination of carbon, hydrogen, nitrogen and sulfur content of the compounds has been performed on a 2400 Series II CHNS Perkin Elmer elemental analyzer.

Infrared (IR) spectra were recorded on a FTIR Bruker Vertex 70 Spectrophotometer in the transmission mode, by using KBr pellets.

The NMR spectra were obtained on a Bruker Avance DRX 400 MHz Spectrometer equipped with a 5 mm QNP direct detection probe and z-gradients. The spectra have been recorded in DMSO- d_6 , at room temperature, except for DPE for which the spectra were recorded at 60 °C. The chemical shifts are reported as δ values (ppm) relative to the residual peak of the solvent.

Crystallographic measurements on single crystals were carried out with an Oxford-Diffraction XCALIBUR E CCD diffractometer using graphite-monochromated MoKα radiation, under the conditions described in the literature [27].

Wide Angle X-Ray Diffraction (WAXD) was performed on a Bruker D8 Avance diffractometer, using the Ni-filtered Cu-K α radiation ($\lambda = 0.1541$ nm). The working conditions were 36 kV and 30 mA. All diffractograms were investigated in the 2/40° (2 theta degrees) range, at room temperature. The initial samples for X-ray measurements were crystalline or powder solids, as obtained by recrystallization. All diffractograms are reported as observed.

Thermogravimetric experiments were conducted on a Mettler TGA/SDTA 851e device. 3–3.5 mg of each sample were heated in Al_2O_3 crucibles with lids. The samples were heated from 30 to 600 °C at a rate of 10 °C/min, under nitrogen flow (5 mL/min).

Differential scanning calorimetry (DSC) measurements were performed with a Pyris Diamond DSC, Perkin Elmer USA system, under nitrogen atmosphere (nitrogen flow 20 ml/min, sample mass 3–4 mg). The transition temperatures have been read at the top of the endothermic and exothermic peaks.

The thermotropic behavior of the dimers and their mixtures was studied by observing the textures with an Olympus BH-2 polarized light microscope under cross polarizers with a THMS 600 hot stage and LINKAM TP92 temperature control system.

UV–Vis absorption and photoluminescence spectra were recorded on a Carl Zeiss Jena SPECORD M42 spectrophotometer and a Perkin Elmer LS 55 spectrophotometer, respectively, in solution and film, using 10 mm quartz cells and glass plates, respectively. The fluorescence quantum yield (Φ_F) of the samples was measured on a FluoroMax-4 spectrofluorometer equipped with a Quanta-phi integrating sphere accessory Horiba Jobin Yvon, by exciting the corresponding compound solutions at its maximum absorption, at

room temperature. The solution concentration was optimized to obtain an absorbance around 0.055. The slit widths and detector parameters were optimized to maximize but not saturate the excitation Rayleigh peak, in order to obtain a good optical luminescence signal-to-noise ratio.

Films of the dimers were spin-cast with a Midas SPIN-1200D Series spin process controller, at four different stages, starting from 200 rpm till 700 rpm for 25 s each one. The solutions of the dimers were prepared in DMF at 1 mg/ml concentration. The DP8, DPE and DP10 were warmed for 1 h at 120 °C because these dimers have poor solubility in DMF. Once spin-coating is complete, the probes were placed quickly onto a hot plate (100 °C) for several minutes to initially evaporate solvent and solidify the coating. The samples were finally placed into a vacuum oven, overnight, at 50 °C.

3. Experimental

Five azomethine dimers have been synthesized by classical condensation reaction of 3-formyl-10-methyl-phenothiazine with different diamines (Scheme 1), in a 2:1 M ratio, using dimethylformamide as a solvent. To avoid the formation of monoreacted compound, about 10% excess of aldehyde was used. The reaction mixture was refluxed for 20 h, under stirring and nitrogen purging, then allowed to reach room temperature and filtered off. The crude product was gently refluxed twice with methanol under stirring to remove unreacted reagents and DMF, filtered off and dried overnight in vacuum at 60 °C. A model compound was also synthesized (Scheme 1) according to the same procedure. The model compound was obtained as single crystals by recrystallization from acetonitrile.

The structure of the synthesized azomethines has been confirmed by two complementary methods, FTIR and ¹H NMR spectroscopies.

3-Formyl-10-methyl-phenothiazine, recrystallized from toluene, yellow single crystals.



¹H NMR (400.13 MHz, DMSO-*d*₆, ppm) δ = 9.81 (s, 1H, H15), 7.75 (d, 1H, H4), 7.61 (s, 1H, H2), 7.25 (t, 1H, H7), 7.18 (d, 1H, H9), 7.10 (d, 1H, H5), 7.04–7.01 (m, 2H, H6, 8), 3.39 (s, 3H, H17); ¹³C NMR (100.16 MHz, DMSO-*d*₆, ppm) δ = 190.63 (C15), 150.38 (C11), 143.66 (C14), 130.86 (C3), 130.42 (C4), 128.05 (C7), 127.25 (C2), 126.88 (C9), 123.54 (C8), 122.38 (C12), 121.40 (C13), 115.41 (C6), 114.51 (C5), 35.65 (C17).

MP4 recrystallized from acetonitrile, yellow single crystals, 86% yield.



¹H NMR (400.13 MHz, DMSO-*d*₆, ppm) δ = 8.50 (s, 1H, H15), 7.72 (d, 1H, H4), 7.67 (s, 1H, H2), 7.25–7.22 (m, 3H, H7, 18, 22), 7.18 (d, 1H, H9), 7.04 (d, 1H, H5), 7.01–6.98 (m, 2H, H6, 8), 6.95 (d, 2H, H19, 21), 3.97 (t, 2H, H25), 3.37 (s, 3H, H23), 1.70 (m, 2H, H26), 1.44 (m, 2H, H27), 0.94 (t, 3H, H28); ¹³C NMR (100.16 MHz, DMSO-*d*₆, ppm) δ = 157.15 (C20), 156.61 (C15), 147.46 (C11), 144.36 (C14), 143.98



Scheme 1. Synthesis of the dimers and the model compound.

(C17), 130.90 (C3), 128.68 (C4), 127.90 (C7), 126.82 (C9), 125.95 (C2), 122.98 (C8), 122.29 (C12), 122.26 (C18, 22), 121.44 (C13), 114.98 (C6), 114.86 (C19, 21), 114.51 (C5), 67.30 (C25), 35.41 (C23), 30.75 (C26) 18.71 (C27), 13.67 (C28).

FTIR (KBr, cm⁻¹): 3057 (=C–H stretch of the aromatic rings), 2955–2866 (C–H stretch of the aliphatic chains), 1619 (-C=N- stretch), 1599, 1504, 1463 (C=C stretch of aromatic ring), 1244 (C–O–C stretch), 838 (stretch of 1, 4 – phenylene ring).

Elemental analysis calc. for C₂₄H₂₄N₂OS (388.5): C 74.19; H 6.23; N 7.21; S 8.25. Found: C 73.81; H 6.53; N 7.44; S 8.19.

DP10, washed with methanol, yellow greenish powder, 90% yield.

FTIR (KBr, cm⁻¹): 3054 (=C–H stretch of the aromatic rings), 2932–2851 (C–H stretch of the aliphatic chains), 1618 (-C=N- stretch), 1600, 1505, 1467 (C=C ring stretch), 1240 (C–O–C stretch), 835 (stretch of 1,4 – phenylene ring).

Elemental analysis calc. for C₅₀H₅₀N₄O₂S2 (803.11): C 74.78; H 6.28; N 6.98; S 7.98. Found: C 74.62; H 6.31; N 7.13; S 7.91.

DPE, washed with methanol, yellow greenish powder, 88% yield.



Single crystal: $C_{24}H_{24} N_2 O S$; space group P 2₁; cell dimensions: $a = 8.2485(5) \ b = 8.0466(10) \ c = 15.3900(11)$; cell angles: $\alpha = 90.00(2) \ \beta = 90.243(5) \ \gamma = 90.00$; V = 1021.46; Z = 2, Z' = 0; R = 4.76%.

DP8, washed with methanol, fine green needles crystals, 92% yield.

FTIR (KBr, cm⁻¹): 3054 (=C–H stretch of the aromatic rings), 2933–2861 (C–H stretch of the aliphatic chains), 1618 (-C=N- stretch), 1600, 1504, 1466 (C=C stretch in aromatic rings), 1241 (C–O–C stretch), 834 (stretch of 1,4 – phenylene ring).

Elemental analysis calc. for C₄₈H₄₆N₄O₂S₂ (775.06): C 74.39; H 5.98; N 7.23; S 8.27. Found: C 73.92; H 6.37; N 7.51; S 8.14.

¹H NMR (400.13 MHz, DMSO- d_6 , 60 °C, ppm) δ = 8.47 (s, 1H, H15), 7.71 (d, 1H, H4), 7.65 (s, 1H, H2), 7.24–7.15 (m, 3H, H7, H18, H22), 7.16 (d, 1H, H9), 7.03–6.96 (m, 5H, H5, 6, 8, 19, 21), 4.12 (t, 2H, H25), 3.78 (t, 2H, H26), 3.65 (s, 2H, H28), 3.82 (s, 3H, H23).

FTIR (KBr, cm⁻¹): 3056 (=C–H stretch of the aromatic rings), 2961–2864 (C–H stretch of the aliphatic chains), 1619 (–C=N– stretch), 1600, 1503, 1467 (C=C stretch of aromatic ring), 1245 (C–O–C stretch), 833 (stretch of 1,4 – phenylene ring).

Elemental analysis calc. for C₄₆H₄₂N₄O₄S₂ (779.00): C 70.93; H 5.43; N 7.19; S 8.23. Found: C 70.58; H 5.51; N 7.27; S 8.11.

DPF, washed with methanol, deep yellow powder, 94% yield.



¹H NMR (400.13 MHz, DMSO-*d*₆, ppm) δ = 8.44 (s, 1H, H15), 7.95 (d, 1H, H28), 7.71 (d, 1H, H4), 7.64 (s, 1H, H2), 7.48 (d, 1H, H25), 7.42 (t, 1H, H27), 7.34 (t, 1H, H26), 7.23 (t, 1H, H7), 7.17–7.11 (m, 5H, H9, 18–22), 7.03–6.97 (m, 3H, H5, 6, 8), 3.36 (H30, overlap with H₂O from solvent); ¹³C NMR (100.16 MHz, DMSO-*d*₆, ppm) δ = 158.96 (C15), 150.63 (C24), 150.08 (C17), 147.85 (C11), 144.28 (C14), 142.98 (C20), 139.51 (C29), 130.56 (C3), 129.02 (C4), 128.44 (C18, 22 or 19, 21), 127.94 (C7, 26), 127.72 (C27), 126.85 (C9), 126.25 (C2), 126.00 (C25), 123.08 (C8), 122.35 (C12), 121.41 (C13), 120.99 (C19, 21 or 18, 22), 120.59 (C28), 115.05 (C6), 114.54 (C5), 64.31 (C23), 35.45 (C30).

FTIR (KBr, cm^{-1}): 3056 (=C–H stretch of the aromatic rings), 1620 (–C=N– stretch), 1594, 1500, 1465 (C=C stretch of aromatic ring), 840, 822 (stretch of 1,4 – phenylene ring).

Elemental analysis calc. for C₅₃H₃₈N₄S₂ (795.00): C 80.07; H 4.82; N 7.05; S 8.07. Found: C 79.92; H 5.01; N 7.16; S 7.98.

DPS, washed with acetonitrile, light brown powder, 73% yield.

FTIR spectra of the studied imines show an intense absorption band in the 1619–1641 cm⁻¹ range, ascribed to the stretching of the newly formed azomethine linkage, while the characteristic bands of the aldehyde (1700 cm⁻¹) and amine (3345 cm⁻¹) groups are missing, indicating the complete formation of an imine bond during the condensation reaction [28]. The aromatic-aliphatic imine linkage of the DPS stretch at 1641 cm⁻¹, while the wavelength number value of the aromatic–aromatic imine linkage (MP4, DP8, DP10, DPE, DPF) is lower (1618, 1620 cm⁻¹) due to the lower energy of the CH = N bond related to the better conjugation of the π -electrons with the phenyl ring π -electrons [29]. The other characteristic absorption bands of the synthesized compounds are present as well.

The ¹H NMR spectra of the obtained compounds further confirmed the targeted structures; the imine proton signal is present at about 8.5 ppm, while the total absence of the amine (4.5–4.9 ppm) and aldehyde (9.8 ppm) proton signals indicate that the condensation reaction takes place according to Scheme 1 [28]. The ratios of the integrals corresponding to the azomethine *vs.* the aromatic or aliphatic protons agree well with the calculated ones for the proposed structures. The assignment**s** of all the signals in the 1D NMR spectra of compounds MP4, DPF and 3-formyl-phenothiazine were performed using 2D NMR experiments – H,H-COSY, H,C-HMQC and H,C-HMBC.

4.2. Structural and supramolecular characterization

The MP4 model compound has been obtained as single crystals, allowing its structural and supramolecular characterization.



¹H NMR (400.13 MHz, DMSO- d_6 , ppm) δ = 8.16 (s, 1H, H15), 7.53– 7.47 (m, 2H, H4, 2), 7.24–7.14 (m, 2H, H7, 9), 7.04–6.98 (m, 3H, H5, 6, 8), 3.48 (t, 2H, H17), 3.33 (H23, overlap with H₂O from solvent), 1.64– 1.57 (m, 2H, H18), 0.52–0.45 (m, 2H, H19), 0.049 (s, 6H, H20, 21).

FTIR (KBr, cm⁻¹): 3059 (=C–H stretch of the aromatic rings), 2952–2822 (C–H stretch of the aliphatic chains), 1641 (–C=N– stretch), 1600, 1576, 1466 (C=C stretch of aromatic ring), 1047 (absorbtion band for Si–O), 839 (stretch of 1,4 – phenylene ring), 813 (bending band for Si–O).

Elemental analysis calc. for C₃₈H₄₆N₄S₂Si2O (695.12): C 65.6; H 6.67; N 8.06; S 9.23. Found: C 65.42; H 6.71; N 8.15; S 9.21.

4. Results and discussions

4.1. Synthesis and characterization

Five phenothiazine containing azomethine dimers have been synthesized by condensation of 3-formyl-10-methyl-phenothiazine and five different diamines. Four of the five diamines contain spacers with different degree of flexibility and the last one contains fluorene as a bulky group (Scheme 1). A model compound containing phenothiazine and a butoxy end group has been synthesized too, in order to verify the synthetic pathway and to better understand the dimer properties. The structure of the studied compounds has been confirmed by elemental analysis, FTIR, 1D and 2D NMR experiments.

In MP4, the phenothiazine unit adopts a butterfly shape, bended along the S N axis; the angle formed by the neighboring S carbons is 98.5° and the angle formed by the neighboring N carbons is 118.7°, while in 3-formyl-10-methyl-phenothiazine the angle formed by the neighboring S carbons is 97.7° and the angle formed by the neighboring N carbons is 118.4° (Fig. 1). The wing containing the imine unit adopts a conformation with the C10-C8-N3-C4 torsion angle of -13.4° and a smaller N3–C4–C7–C6 torsion angle of 9.4° , indicating a good conjugation of the imine linkage with the phenothiazine unit. Moreover, the wider angles in MP4 compared the 3-formyl-10-methyl-phenothiazine reagent, indicate to a smaller bending of phenothiazine in MP4 relative to that of the 3formyl-10-methyl-phenothiazine reagent, attributed to a better π electron delocalization. As compared to the literature data which indicate a strong non-planarity of the aromatic azomethine compounds consisting in twisted aromatic rings related to the CH = N plane of 55° and 10°, respectively [30], the MP4 model compound of the synthesized dimers exhibits a more coplanar molecular conformation of the aromatic azomethine framework. The planarity of the aromatic azomethine framework combined with the bended phenothiazine unit gives a hockey-stick rigid core (Fig. 1), which significantly influences the supramolecular architecture and hence the optical and thermotropic properties.

In the crystal, the molecules are packed forming ribbons with the intermolecular distance around 8 Å, extending parallel to the



Fig. 1. The structure of the 3-formyl-10-methyl-phenothiazine (A) and MP4 molecule with the atom numbering scheme (B).



Fig. 2. The packing of MP4 molecules to generate the 3D structure (A); intermolecular distance (B).

a axes. The molecular ribbons are arranged in anti-parallel directions with the inter-ribbons distance around 3.8 Å, forming molecular layers (Fig. 2). The inter-layers distance is about 15.4 Å. This arrangement of the molecules inside the layers suggests the forming of a lateral and a longitudinal dipole of the phenyl-imine-phenothiazine mesogenic core. Bond lengths and angles are given in supplementary information.

To have an insight upon the 3D architecture of the studied dimers, their wide angle X-ray diffraction (WAXD) has been performed and the obtained diffractograms have been compared to the WAXD pattern of the MP4 model compound.

The WAXD diffractogram of the **MP4** crystalline sample shows intense reflections in the medium and wide angle regions (Fig. 3). The corresponding distances have been calculated using the Bragg law, and their values are enclosed in Table 1. The distances found by the two different X-ray diffraction methods gave close values; the most intense WAXD reflections correspond to the intermolecular, inter-ribbons and inter-layer distances measured by Single Crystal crystallography.

As compared to the model compound, the WAXD pattern of the dimers is characterized by lower intensity peaks, situated in positions close to those of MP4 model compound. The compounds containing an aliphatic spacer show many reflections at smaller angles, indicating different inter-layer distances. This is explained by two concurrent factors: the position of the aliphatic spacer between the two rigid end units which hinder its free rotational movement to adopt the lowest energy *trans* conformations, and, on the other hand, the low solubility and high self-assembling potential that led to a fast crystallization and forced the aliphatic spacer to adopt various proportion of gauche conformers. These peaks in the low angle region are missing into the WAXD pattern of the fluorene containing dimer, due to the absence of the flexible unit which favors the layering. The d-spacing values calculated for the reflections in the wide angle region are close to the intermolecular and inter-ribbon distances of the model compound.



Fig. 3. X-ray diffraction patterns of the phenothiazine compounds (a) MP4, (b) DP8, (c) DP10, (d) DPE, (e) DPF.

Table 1

The c	l-spacing/	A of the	phenothiazine	compounds.

Code	d-spacing/Å (corresponding 2θ angle)
MP4	15.01 (5.89); 7.8 (11.53); 5.15 (17.4); 3.91 (23.16); 3.17 (29.04)
DP8	34.1 (2.59); 19.9 (4.43); 16.7 (5.29); 11.6 (7.61); 10 (8.83); 8.7 (10.19);
	8.32 (10.67); 4.59 (19.6); 3.75 (24.26)
DP10	42.25 (2.09); 21.19 (4.17); 12.21 (7.25); 8.61 (10.31); 7.4 (12.02); 5 (17.8);
	3.76 (24.14)
DPE	31.21 (2.83); 15.65 (5.65); 10.46 (8.47); 7.87 (11.29); 5.11 (17.52); 3.95
	(22.92)

DPF 9.62 (9.21); 8.61 (10.31); 7.78 (11.41); 5.96 (14.96); 4.79 (18.76); 4.35 (20.72); 3.88 (23.4)

Bold signifies the d-spacing corresponding to the intermolecular, inter-ribons and inter-layer distances.

Due to the structure and X-ray pattern similarities between the MP4 model compound and the dimers containing flexible spacers (DP8, DP10, DPE), a similar 3D structure is proposed.

4.3. Photophysical properties

The dimers containing polymethylene and triethoxy spacers (DP8, DP10, DPE) show a similar absorption trace to the MP4 model compound, consisting in a broad absorption pattern with three maxima around 288, 324 and 384 nm, which indicate three different chromophores (Fig. 4).

Taking into consideration the structural characteristics of the MP4 model compound (see structural characterization) and literature data, the 288 nm (4.3 eV) peak has been ascribed to the $\pi - \pi^*$ electronic transition into the phenylene ring [31]; the 324 nm (3.8 eV) peak corresponds to the chromophoric unit formed by conjugation of the imine linkage with the phenothiazine ringsystem: the broad maximum around 384 nm (3.2 eV) has been ascribed to the chromophoric unit formed by an extended conjugation of the imine linkage with both phenylene and phenothiazine units. This attribution is sustained by the absorption spectrum of the siloxane spacer containing dimer, which presents only one maximum around 308 nm (4.02 eV) due to the chromophoric unit formed by conjugation of the imine bond with the phenothiazine ring; the other two peaks are missing due to the absence of the phenylene ring. The fluorene containing dimer presents an absorption pattern similar to the flexible spacer containing compounds, due to the similar conjugation possibilities; the broader peak around 290 nm is due to the fluorene ring. All



Fig. 4. UV–Vis spectra of the phenothiazine containing imines.

compounds exhibit a similar absorption edge around 450 nm (2.75 eV). Compared to other reported Schiff bases [16], the absorption of studied dimers around 384 nm indicates a very good conjugation, confirmed by Single Crystals diffraction as well.

The new dimers display daylight fluorescence characterized by remarkable large Stokes shifts determined by absorption/emission spectroscopy.

The luminescence properties of the studied dimers, in both solution and film, have been explored by excitation at their absorption maximum wavelengths. All compounds emit green light (around 526 nm), except for DPS, which emits greenish light (484 nm) (Fig. 5A), reflecting the influence of the conjugation length upon emission wavelength. The emission spectra are characterized by a sharp emission band, the position and intensity of which does not significantly depend on the wavelength of exciting light (Fig. 5B). This indicates that the main fluorophore is the one needing the smallest energy amount for electronic transition and thus having the most extended conjugation, which is the unit formed by conjugation of the phenothiazine moiety with the phenylene ring through the imine linkage. The blue shifting of the λ_{max} of DPS emitted light sustains once more this attribution; the emission wavelength being controlled by conjugation, in the absence of the phenylene ring the conjugation length is less extended and the DPS emits greenish light. By the contrary, the λ_{max} of the emitted light of the DPF fluorene containing dimer is red shifted by 10 nm due to the supplementary stabilization of the DPF



Fig. 5. Emission spectra of (A) studied compounds, excited at their maximum of minimum energy absorption, (B) DP8, excited at all maxima of absorption.

1	a	b.	le

Photophysical characteristics of the studied azomethines.

Code	$\lambda_{max \ abs/nm}$ a	λ _{max} em./nm ^a	Eg ^b /eV	Stokes shift ^c /nm	$\varPhi_{\rm sol} {}^{\rm d}$	$\Phi_{\rm film}$ f	1931 CIE x; y ^g
MP4	288, 322, 384	525 (502)	3.22	141	0.125	0.08	0.398; 0.598
DP8	288, 326, 382	526 (504)	3.24	144	0.126	0.08	0.404; 0.588
DP10	288, 326, 382	526 (504)	3.24	144	0.125	0.08	0.424; 0.627
DPE	288, 322, 384	526 (502)	3.22	142	0.127	0.09	0.405; 0.610
DPF	384 (392)	535 (526)	3.22	151	0.375	0.17	0.468; 0.547
DPS	308	484 (483)	4.02	176	_e	_e	_e

^a In DMF, values in parenthesis are for thin film samples.

^b Spectroscopically determined energy gap taken from the absorption maxima $(Eg = 1240)\lambda_{max})$.

^c Stokes shift between the absorption and emission of the chromophores.

^d Absolute fluorescence quantum yield in solution, at room temperature.

Not available.

^f Absolute fluorescence quantum yield in film, at room temperature.

^g Chromaticity coordinates [39].

quinoid structure as a consequence of the electron-donor effect of fluorene [32].

The fluorescence spectra of the solid films obtained by casting 10^{-5} w/v solution on glass, registered in similar conditions as in the case of solutions, show the same optical parameters in terms of emission wavelength and intensity, suggesting little fluorescence quenching. Taking into account the structure of the model compound, this can be explained by the long intermolecular distances which hinder the non-radiative decay by intermolecular energy transfer, under molecular aggregation conditions [33]. The photophysical parameters are given in Table 2.

The fluorescence quantum yield ($\Phi_{\rm fl}$) of the studied azomethines, in solution and solid-state, was measured using an integrating sphere [34]. The azomethine linkage is known to quench the fluorescence of even the most intrinsically fluorescent fluorophores [35,36]. However, as seen in Table 2, the studied phenothiazine-based azomethine compounds show good absolute $\Phi_{\rm fl}$ values, comparable to polyfluorene vinylene, used in emitting devices [37]. The dimers show good $\Phi_{\rm fl}$, even in thin films, suggesting that there is little self-quenching. Remarkably, the highest $\Phi_{\rm fl}$ in solution and solid-state, was obtained for the dimer containing phenothiazine and fluorene chromophores, the two fluorophores do not seem to quench each other.

The Stokes shift values are comprised between 141 and 176 nm, resulting in a negligible overlap between the absorption and emission spectra of the studied azomethines, preventing the reabsorption of the emitted light (Fig. 6) [38]. This large Stokes shift allows unique advantages for detection of emitted light fluorescence in biological applications and is very important in order to avoid undesired loses in the optoelectronic devices.

In the color perception study, one of the first mathematically defined color spaces is the CIE-1931 XYZ color space [39]. The chromatic perception of human eyes to a specific optical spectrum is usually characterized by a chromaticity diagram. According to the available CIE standard, the chromaticity coordinates of the studied compounds have been calculated (Table 2) and they indicated that MP4 and DP8 are situated in the yellow green region, while DPF is in the greenish yellow region. They are on the periphery zone, i.e. they emit high purity and fully saturated color (Fig. 7).

4.4. Thermal properties

The thermal properties of the studied dimers have been monitored by thermogravimetric analysis (ATG), differential scanning calorimetry (DSC) and polarized optical microscopy (POM).

All compounds present good stability at high temperature; the onset of decomposition was registered around 400 °C, except for



Fig. 6. Stokes shift of DP8.

the compound containing the siloxane spacer (DPS) whose decomposition started around 260 °C. The decomposition process ended around 500 °C and the residual chair percent ranged between 35 and 52. These thermal parameters indicate a good thermal stability, which makes these compounds suitable for applications requiring prolonged and repetitive exposure to high temperature or high-intensity lasers. Some representative thermogravimetrical curves are given in Fig. 8.

To establish the thermodynamic behavior of the studied compounds and their morphological stability, respectively, two complementary measurement techniques, differential scanning calorimetry (DSC) and polarized optical microscopy (POM), have been applied with a heating/cooling rate of 5<u>o</u>C/min. Thus, in the DSC thermogram, the MP4 model compound shows a sharp left tailed endothermic peak in the first heating scan, corresponding to melting. A broad exothermic peak is present in the first cooling scan, corresponding to the slow and incomplete crystallization. An exothermic and an endothermic peak appear in the second heating scan, corresponding to the cold crystallization and melting, respectively (Fig. 9A).



Fig. 7. The chromaticity diagram.



Fig. 8. Thermal stability of studied dimers evidenced by thermogravimetric graphs.



Fig. 9. A) DSC curves of (a) first heating, (b) first cooling, and (c) second heating of MP4, and first heating of (d) DP8 and (e) DP10. (B) DSC thermogram of DPE (a) first heating, (b) first cooling, (c) second heating.

Interestingly enough, in POM, during the heating scans with 1oC/min, the crystalline sample melted in a mosaic texture (Fig. 10a), then the sample became optically isotropic, which state nucleates in birefringent straight-edged squares, rhombic, hexagons and rectangles (Fig. 10b). The textures appeared in a narrow temperature interval (2 °C), corresponding to the endothermic tail. Based on its typical behavior, the second texture has been ascribed to a three-dimensional thermotropic cubic mesophase [40]. In cooling scans, the crystallization occurs in the form of spherulites.

The dimers containing polymethylene spacer (DP8 and DP10) have a thermotropic behavior guite similar to that exhibited by the MP4 model compound. In the DSC thermogram, they show two close endothermic peaks in the first heating scan (Fig. 9A), an exothermic peak in the first cooling scan and a left tailed endothermic peak in the second heating scan. In POM, between the two endothermic peaks, in the first heating scan, the crystalline sample melts to a fine texture (Fig. 10c) which transforms in an optically isotropic liquid that further nucleates in a clear mosaic texture,



MP4: 2H, 140 °C, crystalline – smectic transition





DP8: 1H, 220 °C, fine texture





DP8: 2H, 222 °C, cubic mesophase texture



DP8: C, 223 °C, mosaic texture



DP8: C, 218 °C, marbled texture Fig. 10. POM microphotographs of the MP4 and DP8 compounds (H: heating; C: cooling).

ascribed to a cubic mesophase, as well (Fig. 10d). By cooling from the isotropic state, the crystallization occurs in the form of a fine granular texture. Under special conditions - slowly cooling the sample before the complete isotropization - a mosaic texture appears when cooling the sample by 1°C/min (Fig. 10e) or a marble texture occurs when cooling the sample by 5 °C/min (Fig. 10f). Both textures lack fluidity. This behavior suggests the ordering difficulties of the molecules in the absence of nucleation centers, because of the non-coplanar structure of the phenothiazine ring-system which leads to weak intermolecular forces and thus high intermolecular distances (see Structural and supramolecular characterization). The self-assembling in the tridimensional cubic mesophase is driven by the special supramolecular architecture generated by the hockey-stick shape of the phenothiazine-iminephenylene core, which consists in long intermolecular distances but short inter-ribbon and inter-layer distances. Due to this architecture, when increasing temperature the intra-ribbons ordering is lost before losing the supramolecular ordering. As a consequence, in the short temperature range of coexistence of both intra-ribbon disordering and supramolecular ordering, the cubic mesophase appears.

The dimer containing a triethoxy spacer behaves as a molecular glass [19]. In the DSC thermogram, the DPE sample exhibits two endothermic peaks in the first heating scan, an inflexion of the cooling trace, an exothermic and an endothermic peak in the second heating scan (Fig. 9B). By POM, corresponding to the short temperature range between the two DSC endothermic peaks, a fine viscous texture appears which exhibits fine crystals in isotropic liquid, under mechanical stress. This behavior is attributed to a dimensional polydispersity of the crystallites and to the coexistence of various order degrees which lead to different melting temperatures. By cooling from the isotropic state, the DPE sample freezes, giving an amorphous glass and in the second heating scan a high temperature cold crystallization before melting occurs (Fig. 11a). This behavior is reproducible in many heating/cooling scans in DSC and POM as well. Under slow cooling rates, a viscous fine granular texture is induced in a short temperature range, indicating a monotropic mesophase (Fig. 11b). Depending on the thermal treatment, an amorphous or mesomorphic glass is obtained as continuous films, without defects. The amorphous glass remains morphologically stable at room temperature, even after two month, due to the high cold crystallization point.

The fluorene containing dimer exhibits two broad endohermic peaks in DSC thermograms, corresponding (in POM) to the appearance of a fine viscous texture under mechanical stress (Fig. 11c) and its slow isotropization, respectively. This type of fine viscous texture, named plastic mesophase, is often exhibited by stiff-chain thermotropic polymers without flexible spacers, hardly ordering in molten state [2,28,41–43]. In the next cooling/heating cycles, the sample exhibits only high glass transition; the sample





DPE: 2H, 96 °C, spherulites growing to form crystalline state



DPF: 1H, 260 °C, fine texture





DP10 + DPF mixture: 2H, 130 °C, crystalline state obtained by coalescence of small spherulites

Fig. 11. POM microphotographs of the DPE and DPF compounds and DP10 + DPF mixture (H: heating; C: cooling).

gives a stable amorphous glass at room temperature. By cooling the sample from the plastic mesophase, a birefringent glass, without defects has been obtained.

The siloxane containing dimer shows only one glass transition in heating and cooling scans. The thermodynamic behavior is summarized in Table 3.

In conclusion, the thermodynamic behavior studied by DSC and POM indicates a versatile behavior of the phenothiazine containing dimers, depending on the single non-conjugated bridge nature and thermal treatment, suggesting the possibility of tailoring the morphology of the samples.

4.5. Physical mixtures

The obtaining of polycrystalline films is one of limiting factors of mass production of organic electronics. Uncontrollable grain growth, their randomness in orientation and grain boundary effect are the main factors hindering the formation of uniform films. Therefore, obtaining highly uniform organic films with acceptable optic and/or electrical performances from cost-effective thermal processing is one of the key challenges for commercializing large scale organic optoelectronic devices [18,19].

The versatile thermotropic behavior of the studied phenothiazine containing imines and on the other hand the importance of stable, controlled morphology for optic and optoelectronic applications inspired us to investigate the possibility of tuning morphology, by obtaining mixtures of compounds containing the same rigid core. Taking into account the thermotropic behavior of the studied dimers, two kinds of binary mixtures have been produced: crystalline–crystalline (MP4 + DP8; MP4 + DP10; DP8 + DP10) and crystalline–amorphous (MP4 + DPF; DP8 + DPF; DP10 + DPF; DP8 + DPS). The blending of the samples has been realized in 1:1 M ratio. Their thermal behavior was monitored by DSC and POM measurements (Table 4).

The mixture of crystalline compounds leads to a crystalline blend. When the mixed compounds exhibit large differences between their melting points (MP4 + DP8; MP4 + DP10), the

Table 3

Thermotropic	behavior c	of studied	l azomethines.
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Code	DSC transitions/ <u>o</u> C	Observations
	(J/g)	
MP4	1H: Cr 140 (114.8) I	The endothermic peak is left tailed; corresponding
	1C: I 93 (-64.4) Cr1	to the temperature range of the endothermic tail
	2H: Cr1 101 (-37.3)	a cubic mesophase is evidenced by POM, in special
	Cr2 140 I	conditions
DP8	1H: Cr 215 (19.7) Cub	A cubic mesophase is formed during the heating
	224 (83.4) I	cycle
	1C: I 188 (-89) Cr	
	2H: Cr 221 Cub 224	
	(89.9) I	
DP10	1H: Cr 205 (28.6) Cub	A cubic mesophase is formed during the heating
	216 (93) I	cycle
	1C: I 173 (–85.3) Cr	
	2H: Cr 216 (95.8) I	
DPE	1H: Cr1 179 Cr2 181	Typical behavior of molecular glass, reproducible
	(87.4) I	on many heating/cooling scans
	1C: I 58 G	
	2H: G 55 I 95 (-41.7)	
	Cr 177 (57.6) I	
DPF	1H: Cr1 217 (13) PM	An amorphous glass has been obtained by cooling
	265 (42.3) I	from isotropic state
	1C: I 142 G	A mesomorphic glass has been obtained by
	2H: G 141 I	cooling from plastic mesophase state
DPS	1C: I 14 G	An amorphous glass has been obtained at low
	2H: G 14 I	temperature

The transition temperatures have been read at the top of DSC peaks. Cr: crystalline; I: isotropic; Cub: cubic mesophase; PM: plastic mesophase; G: glassy state.

Table 4

Thermotropic	behavior	of physical	mixtures.
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Code	DSC transitions/oC	Observations
couc	(I/g)	observations
MP4 + DP8	IH: Cr1 139 (42.3) II;	Many heating/cooling scans lead to an
	CI2 I90 (33.7) I2	nomogeneous crystannie phase
	10:11+12 185(-42.4)	
	(12; 115(-13.1))	
	4C; 1 158 (-50) Ci	Many bosting/appling same load to an
MP4 + DP10	IH: CI1 138 (30) II; Cr2 102 (50) I2	homogonoous gratalling phase
	CI2 I92 (59) I2	nomogeneous crystannie phase
	10.11 + 12 159(-01.2)	
	AC: 1124(-60.6) Cr	
	$1H \cdot Cr 200 (115.2) I$	The mixture behaves as a single
DI 8 + DI 10	10.167(-76.8) Cr	crystalline compound
	$2H \cdot Cr 200 (76.2) I$	erystannie compound
$MP4 \perp DPF$	1H: (r1 137 (29 2) I1	An amorphous glass has been obtained
MI 4 + DI I	Cr2 195 (5 4) I2	after the mixing of the two components
	1C·184 G	after the mixing of the two components
	2H: G 84 I	
DP8 + DPF	1H: Cr1 198 (60 4) I1:	Behavior typical for molecular glass
	Cr2 239 (9.2) I2	
	1C: I 85 G	
	2H: G 85 I 132 (-38.8)	
	Cr 193 (19.2) I	
DP10 + DPF	1H: Cr1 197 (53) I1;	Behavior typical for molecular glass
	Cr2 240 (11.4) I2	
	1C: I 89 G	
	2H: G 86 I 134 (-26.2)	
	Cr, 193 (29.5) I	
DP8 + DPS	1H: Cr1 205 (13.3) I	The two components maintain their own
	1C: I 141 (-27.7) Cr	behavior, even after four heating/cooling
	4H: Cr 204 (11) I	cycles

mixture shows phase separation with two well delimited melting points and two crystallizations corresponding to the two components, in the first heating/cooling scan. But their delimitation decreases when they reach the fourth heating/cooling scan; the occurrence of only one melting/crystallization process indicates a homogeneous crystalline mixture. When the mixed compounds have close melting/crystallization points (DP8 + DP10), they behave as a single crystalline compound even from the first heating/cooling scan.

Interestingly enough, crystalline—amorphous blends lead to amorphous glasses. When using amorphous DPF, a typical behavior of molecular glass exhibiting a high glass transition in the cooling



Fig. 12. DSC thermogram of DP10 + DPF mixture.

scan and a cold crystallization and melting in the heating scan has been detected after mixing the components in the molten state. This behavior is reproducible in many heating/cooling scans. As an example, Fig. 11d illustrates the cold crystallization of the DP10 + DPF mixture under POM, while Fig. 12 shows its DSC thermogram. On the other hand, when using amorphous DPS, the two components kept their own behavior even after four heating/ cooling scans. The different behavior of the two kinds of crystalline–amorphous mixtures is explained by the different mixing and ordering capacity of the two amorphous compounds.

Thus, to conclude, while the mixing of two crystalline compounds leads to a homogeneous crystalline blend, the mixing of a crystalline and an amorphous compound containing the same mesogenic core, in a 1:1 M ratio, leads to stable molecular glasses. The blending of two components containing the same fluorophoric core proves to be an effective processing alternative to highly uniform organic films.

5. Conclusions

New phenothiazine containing azomethine dimers have been synthesized as model compounds for designing optoelectronic materials. The dimers were obtained with high yield and purity. The phenothiazine-imine-phenylene mesogenic core adopts a hockey-stick shape which significantly influences the thermal and optical properties. On the one hand, the phenothiazine nonplanarity leads to long intermolecular distances which preclude the non-radiative decay of the emitted light, and, on the other hand, the strong conjugation of the electron withdrawing imine linkage with electron-donor S and N in the phenothiazine unit gives a stable fluorophore emitting green light with reasonable quantum yield, large Stokes shift and high purity and fully saturated color.

The special supramolecular structure generated by the hockeystick shape of the phenothiazine-imine rigid units facilitates the occurrence of the thermotropic cubic mesophase, a less observed mesophase for thermotropic liquid crystalline systems, and of a stable molecular glass, too. This design provides high thermal stable compounds.

The study indicates that phenothiazine containing Schiff bases are a good compromise in terms of facile synthesis and good photophysical and thermal properties. Besides, pathways of obtaining films with tuned uniform morphology are provided.

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