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Linking triptycene to silole: a fruitful association†‡

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1,1'-Disubstituted-2,3,4,5-tetraphenylsiloles incorporating triptycene moieties **Tp-DMTPS** and **Tp-MPTPS** were prepared and characterized. Like other 2,3,4,5-tetraphenylsiloles, both compounds exhibit aggregation-induced emission (AIE) behavior. Unexpectedly, the solid state PL emission of **Tp-DMTPS** show dependence according to the degree of crystallinity of the powders. While precipitates display a blue-green emission, microcrystalline powders emit in the yellow-orange region. Moreover a rare reversible mechanohypsochromic phenomenon is observed: upon grinding, the emission of a microcrystalline powder changes from yellow-orange to blue-green, the original emission being restored by annealing the sample. The mechanism of this blue-shift upon crystal grinding was investigated by X-ray diffraction, ¹³C CP-MAS NMR and DFT calculations. Under mechanical stress, strong intermolecular CH/π interactions are found to promote the less energetically stable population of conformers present in the crystals, leading to this blue-shift. Finally the influence of the triptycene moieties on the thermal and structural stability of **Tp-DMTPS** and **Tp-MPTPS** was studied. Compared with **DMTPS** and **MPTPS** parents, a general enhancement of the properties is noticed, especially when used as active layer in OLED fabrication. Our results suggest that the attachment of triptycene moieties to π-conjugated molecules is an interesting way to improve their thermal, structural and photophysical properties for sensing or optoelectronic applications.

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Introduction

Limited to very few applications for a long time because of their complicated synthetic chemistry,¹ siloles or silacyclopentadienes experienced a spectacular rebirth thanks to the works of K. Tamao and S. Yamaguchi in the late 90s.^{2,3} Indeed, the general and versatile synthesis *via* an intramolecular reductive cyclization of diethynylsilanes they proposed allowed the preparation of various 2,5-difunctional siloles that would be

otherwise very difficult to obtain. Shortly afterwards, on account of their unique electronic properties, *i.e.*, their very low LUMO energy levels combined with high fluorescence quantum yields in the solid state, siloles were used successfully as both emissive and electron-transporting materials in organic light emitting diodes (OLED) manufacture.^{4–7} The origin of their electronic properties is the consequence of an efficient interaction between the σ* orbital of the silole silicon atom with the π* orbital of the butadiene fragment^{5,8} whereas the origin of their outstanding high solid-state fluorescence is attributed to the aggregation induced emission (AIE) phenomenon that was described for the first time with 1-methyl-1,2,3,4,5-pentaphenylsilole.⁹ Since then, AIE materials are the subject of intense scientific research and have found many applications that encompass various domains going from organic electronics to theranostic bioprobes.^{10–14} Moreover, with the growing number of AIE materials described in the literature, rather new and uncommon phenomena such as reversible mechanofluorochromism have started to be reported since their first observation with tetraphenylethene (TPE) and diphenyldibenzofulvene (DPDBF) derivatives.^{15–20}

In small molecules-based organic electronics, besides the device efficiency, the thermal and structural stabilities of the used organic materials are an important concern.^{21,22} Indeed, for instance, an operating OLED releases heat that may alter

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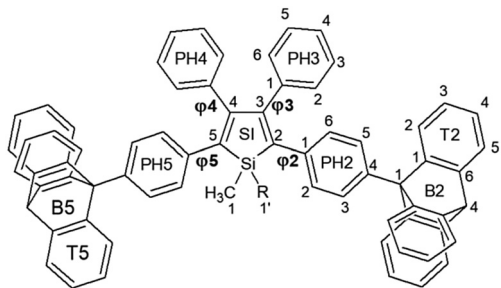


Fig. 1 Labelling scheme for **Tp-DMTPS** ($R_1' = \text{Me}$) and **Tp-MPTPS** ($R_1' = \text{Ph}$).

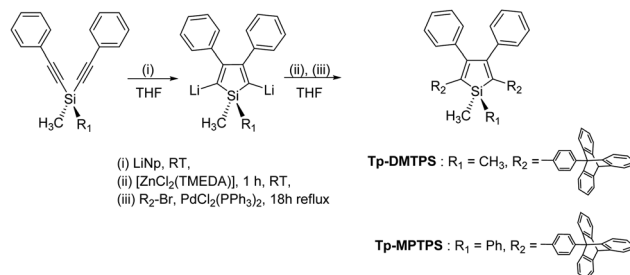
quickly its efficiency.²³ This is the reason why materials with high melting points and high glass transition temperatures (T_g) are desirable to achieve the fabrication of devices with good durability. One of the strategies used to increase the thermal stability of the organic layers is to crosslink the adequately functionalized molecules after their deposition.²⁴ Another strategy involves the control of the spatial organization, *i.e.*, distance and relative orientation of the constitutive molecules through the chemical synthesis and/or the use of an appropriate construction scaffold.²⁵ Triptycene with its fascinating paddle-wheel shape has been widely used for this purpose in supramolecular chemistry, polymer chemistry and materials science.^{26–28} However, in spite of the thermal stabilization afforded by its presence in the molecular structures, only few examples of the use triptycene-based luminescent materials in OLEDs have been reported so far.^{29–31}

With this in mind we report herein the synthesis and structural characterization of two novel silole derivatives incorporating triptycene moieties at the 2,5-positions (**Tp-DMTPS** and **Tp-MPTPS**, Fig. 1) with the first aim to use them as emissive layers in OLEDs. We will focus on the interplay between the triptycene side-groups and the silole core that induces an original behavior in terms of thermal and structural stability, luminescence and mechanofluorohypsochromism, phenomenon that was still rarely observed up to now.^{32–37} We show that the modulation of the structure in the solid state resulting from the incorporation of triptycene groups affords an enhancement of OLED performance by formation of morphologically stable non-crystalline emissive layers.

Results and discussion

Synthesis

The siloles **Tp-DMTPS** and **Tp-MPTPS** were conveniently prepared by the method previously described by Tamao *et al.* that involves the intramolecular reductive cyclization of 1,1-bis(phenylethynyl)silane, followed by a palladium-catalyzed cross-coupling reaction with the appropriate bromoaryl compound (Scheme 1).^{4,38} 9-(*p*-Bromophenyl)triptycene was prepared *via* a Diels–Alder reaction between *in situ* generated benzyne, and 4'-bromophenylanthracene.³⁹ **Tp-DMTPS** and **Tp-MPTPS** were isolated in 54 and 49% yields, respectively, as pale yellow powders.



Scheme 1 Synthetic route to **Tp-DMTPS** and **Tp-MPTPS** (see more details in ESI†).

Crystal structure

As shown in Fig. 2 (and Fig. S3–S6, ESI†), the molecular packing of **Tp-DMTPS** is mainly governed by the paving of the triptycene moieties in alternating up (one of the phenyl ring parallel to the *c*-axis) and down (antiparallel to the *c*-axis) columns leading to a layered structure. Inside the triptycene double layer, the 3,4-diphenylsilole moieties also adopt an up and down columnar packing corresponding to the orientation of the triptycene side-groups. Interestingly, the structure shows that the silole rings could be inclined either on the right or on the left with respect to a plane going through the middle of a column (Fig. 3). This situation leads to the co-existence of two conformers in the crystal, which will be named *R* and *L*. In the *R*-conformer, the methyl group C69 (see Fig. 3) is nestled between two phenyl

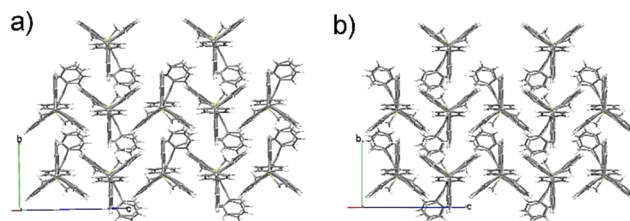


Fig. 2 Views of the crystal packing of **Tp-DMTPS** showing the triptycene paving in the *bc* plane for (a) *R*-conformers and (b) *L*-conformers.

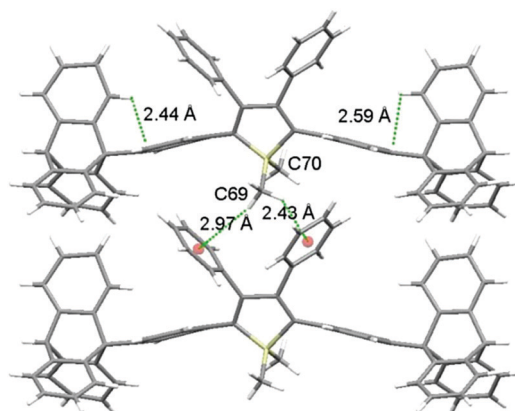


Fig. 3 View of the *R*-conformers of **Tp-DMTPS** in the *ab* plane showing the methyl C69 nestling between the aromatic rings. Intra and intermolecular CH/π interactions are marked with green dotted lines.

Table 2 Optical and electronic properties of **Tp-DMTPS** and **Tp-MPTPS**^a

	λ_{abs} (nm)		λ_{em} (nm)		$E_{\text{g}}^{\text{opt}}$ (eV)	HOMO ^c (eV)	LUMO ^c (eV)	E_{g}^{el} (eV)
	Soln	Thin film ^b	Soln (Φ_{F})	Solid (Φ_{F})				
Tp-DMTPS	357	365	486 (1.4)	561 (43)–533 (43) ^d	2.89	–5.54	–2.48	3.06
Tp-MPTPS	369	370	491 (1.2)	498 (24)	2.85	–5.54	–2.51	3.03

^a λ_{abs} = absorption maximum; λ_{em} = emission maximum; Φ_{F} = fluorescence quantum yield in CH_2Cl_2 solutions (Soln) and in the solid state (solid); $E_{\text{g}}^{\text{opt}}$ = energy gap calculated from the absorption edge; E_{g}^{el} = electrochemical gap obtained from HOMO and LUMO. ^b 100 nm thick film. ^c HOMO and LUMO levels determined from CVs in $\text{CH}_2\text{Cl}_2/\text{Bu}_4\text{NPF}_6$. ^d First values: microcrystalline powders, second values: ground powders. Excitation wavelength: 365 nm.

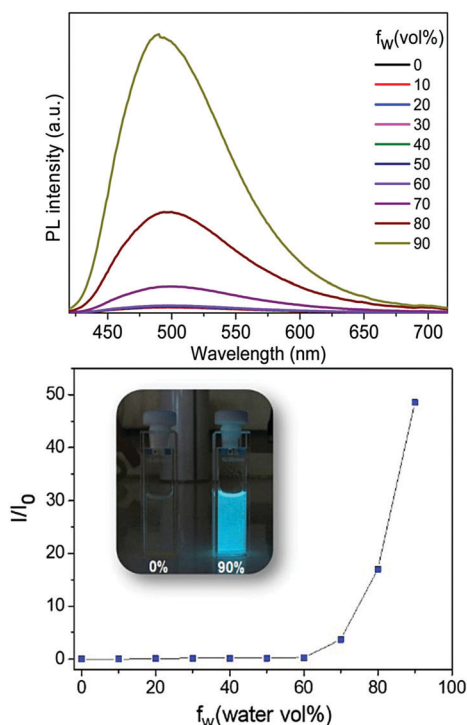


Fig. 8 Top: PL spectra of **Tp-DMTPS** in THF/water mixtures with different water fractions (f_w). Concentration: 10^{-5} M; excitation wavelength: 365 nm. Bottom: Plot of (I/I_0) values versus water fractions in THF/water mixtures. I_0 is the PL intensity in pure THF solution. Inset: Photographs **Tp-DMTPS** in THF/water mixtures ($f_w = 0$ and 90%) taken under UV lamp illumination.

with a 60-fold increase of the fluorescence intensity when f_w also reached 90% (Fig. S12, ESI†).

Moreover, we found that unlike **Tp-MPTPS**, the position of the emission of **Tp-DMTPS** in the solid state depends strongly on its degree of crystallization. Whereas rapid precipitation of **Tp-DMTPS** by addition of pentane affords a solid exhibiting blue emission under excitation at 365 nm, slow crystallization from acetone/dichloromethane mixtures leads to a yellow-orange emission for the obtained microcrystals (Fig. S11, ESI†). These changes in emission features should mainly originate from the transition from the crystal to the amorphous state as well as the changes in the molecular conformations.^{50–55}

Mechanofluorochromism

The dependence of the position of the **Tp-DMTPS** emission maximum on its procedure of isolation (precipitation/crystallization),

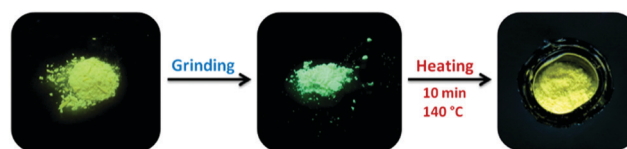


Fig. 9 Photographs of **Tp-DMTPS** under UV illumination before grinding (left), after grinding (middle) and after annealing at 140 °C for 10 min (right).

suggests that this compound could display mechanofluorochromism.^{18,56,57} This hypothesis was confirmed by simply grinding a sample of microcrystalline **Tp-DMTPS**. As shown in Fig. 9, the emission turned from orange to blue-green upon UV illumination. It is important to mention that this phenomenon called mechanohypsochromism is rarely observed, a red-shift being observed in almost all cases.^{32–37} Finally, the initial orange emission could be restored by heating the ground solid at 140 °C for 10 min. The choice of this annealing temperature was based on the DSC analyses of **Tp-DMTPS** after grinding, which shows an exothermic signal associated to a crystallization process (Fig. S13, ESI†).

The corresponding PL spectra (Fig. 10) shows that the grinding process is not only affecting the position of the emission maximum ($\lambda_{\text{em}}(\text{crystals}) = 561$ nm, $\lambda_{\text{em}}(\text{after grinding}) = 533$ nm), but is also modifying the peak shape, the solid state quantum yield of emission remaining the same. Interestingly, the emission of the aggregates generated by adding water to a THF solution shows a sharper emission peak ($\lambda_{\text{em}} = 498$ nm), which is very similar to the one obtained in solution (see Fig. 7). These emission changes should mainly be due to their different molecular conformations that are affected by the crystallinity in these solids.^{54,58}

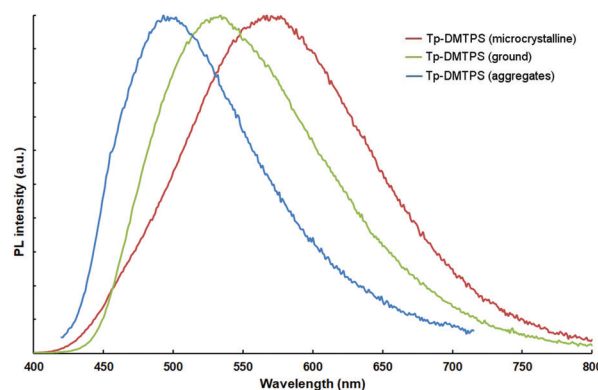


Fig. 10 PL spectra of **Tp-DMTPS** in various forms.

To evaluate the degree of crystallinity, we performed powder XRD analyses, the patterns indicate that grinding microcrystalline **Tp-DMTPS** leads to a dramatic decrease of its crystallinity, but not reaching complete amorphization (Fig. S14, ESI†). On the other hand, fast precipitation from a mixture of THF with “high” water content should lead to the formation of amorphous aggregates, as previously observed by Tang *et al.*^{50,55} Therefore, there is a clear dependency between the long-range molecular order and the emission: the higher the order, the stronger the emission is red-shifted. Interestingly, similar experiments conducted with microcrystalline **Tp-MPTPS** powders showed that the position of the emission maximum remains unaffected upon grinding.

Solid state NMR experiments

¹³C CP-MAS NMR spectra of either microcrystalline or ground powders of **Tp-DMTPS** are shown in Fig. 11. In comparison with the spectrum recorded in CDCl₃ solution, the peaks were observed at very similar chemical shifts. The signal arising from the resonance of the methyl groups SI(C1,C1') at $\delta = -3.6$ ppm is split into two, as well as the signals from the carbon atoms belonging to the silole ring SI(C3,C4) $\delta = 154.8$ ppm and SI(C2,C5) $\delta = 141.8$ ppm (see Fig. 1 for labelling). The same splitting is also observed for the carbon atoms PH2(C1) and PH5(C1) ($\delta = 139.0$ ppm), which are directly connected to the silole ring. It is noteworthy that this peak splitting is also noticed, in the ¹³C CP-MAS NMR spectrum of **DMTPS** but with a smaller extent (Fig. S15, ESI†). As shown in Fig. 11, grinding the microcrystalline powder does not affect the spectrum pattern to a large extent; only a peak broadening is observed.

These observations are in line with what has been learned from the crystal structure analysis, *i.e.* the splitting of the methyl group signals reflects their non-equivalent environment in the crystal lattice, one being nestled between two phenyl rings. As mentioned above, going from the *R*- to the *L*-conformer brings modifications of the torsion angles φ_2 , φ_3 , φ_4 and φ_5 . Because of them, the conjugation between the surrounding phenyl rings and the silole core should be affected and the resonance peaks corresponding to the carbon atoms involved in the conjugation pathway split into two. This is also what was observed for

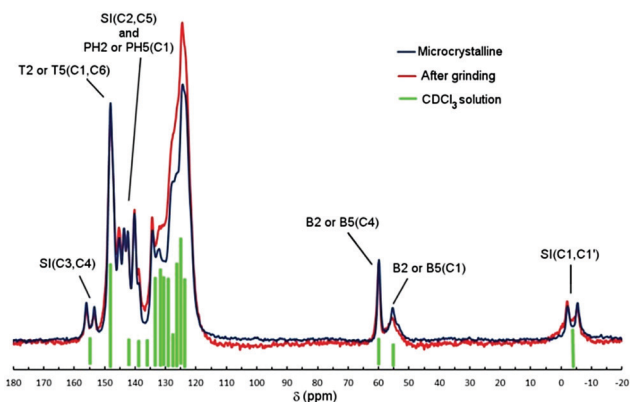


Fig. 11 ¹³C CP-MAS NMR spectra of **Tp-DMTPS** (microcrystalline and ground). Green bars represent the peaks observed in the ¹³C{¹H} NMR spectrum recorded in CDCl₃ solution. See Fig. 1 for labelling.

DMTPS, its crystal structure exhibiting two molecules in the asymmetric unit that mainly differ in the rotation of the phenyl groups with respect to the central silole ring.⁴⁷

From the ¹³C CP-MAS NMR experiments, we have shown that the spectrum of the ground powder is very similar to that of the crystalline one. The only difference consists in the broadening of some resonance peaks that should originate from the loss of crystallinity, as observed by XRD. Therefore, the two methyl groups remaining non-equivalent, this should indicate that a methyl group is always nestled between two phenyl rings both in the crystalline and the ground form. Interestingly, since the emission is blue-shifted, disordering the crystal packing upon grinding appears to favour the emission originating from the less conjugated *L*-conformer. This preference should be due to the stronger CH/ π interactions found with this conformer. Finally, when vacuum-deposited as thin films, the PL and EL spectra showed similarities with that measured in solution. This indicates that this deposition process does not promote a good molecular organization even at a very small scale. Contrastingly, **Tp-MPTPS** displayed a more conventional behavior since the conformation of the molecules do not show any noticeable change depending on their physical state as it is observed with its parent **MPTPS**.

Electrochemical properties

Cyclic voltammetry (CV) of **Tp-DMTPS** and **Tp-MPTPS** were recorded in CH₂Cl₂/Bu₄NPF₆ (0.2 M) both in oxidation and reduction. In oxidation (Fig. 12, up), both compounds show similar successive oxidation steps with maxima closed to 1.26,

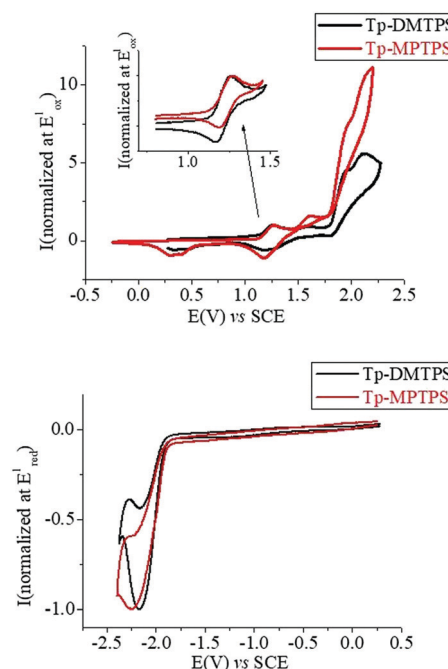


Fig. 12 Top: Cyclic voltammetry in CH₂Cl₂/Bu₄NPF₆ (0.2 M) of **Tp-DMTPS** (in black) and **Tp-MPTPS** (in red). Exploration in the anodic direction (top) and in the cathodic direction (bottom). Working electrode: platinum disk, sweep-rate: 100 mV s⁻¹.

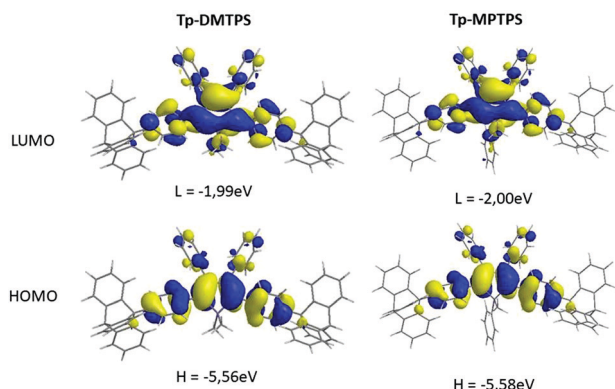


Fig. 15 Energy and shape of the HOMO and LUMO orbitals of optimized structures of **Tp-DMTPS** and **Tp-MPTPS**, as calculated at the B3LYP/6-31+G* level.

Surprisingly, the calculations took rather well into account the strong CH/ π interactions found in the crystal structures of both siloles with calculated bending angles of *ca.* 11° (**Tp-DMTPS**) and 15° (**Tp-MPTPS**) between the threefold axis of the triptycene group and the adjacent phenyl moiety. The HOMO orbitals of both derivatives are mainly located on the central silole core and phenyl rings at 2,5-positions while the substituents located at the 3 and 4-positions bear much weaker contributions. Calculated values are −5.56 and −5.58 eV for **Tp-DMTPS** and **Tp-MPTPS**, respectively, values that are close to the ones estimated from CV measurements (see Table 2). This indicates that the optimized structures are certainly close to the ones present in solution. For the LUMO orbitals, a significant σ^* -type orbital density is found on the two exocyclic Si–C bonds. This is typical for siloles and the resulting $\sigma(\text{Si-C}_{\text{exocyclic}})^*-\pi(\text{butadiene})^*$ hyperconjugation is responsible for the stabilization of the LUMO level; making those compounds good candidates for optoelectronic applications.⁷ The triptycene moieties are not involved in the frontier orbitals; **Tp-DMTPS** and **Tp-MPTPS** being therefore similar from an electronic point of view to their **DMTPS** and **MPTPS** parents.

Concerning *R*- and *L*-conformers of **Tp-DMTPS** (Fig. 16), as expected from the increased values of the torsion angles with respect to fully optimized structures (Table 1), both conformers

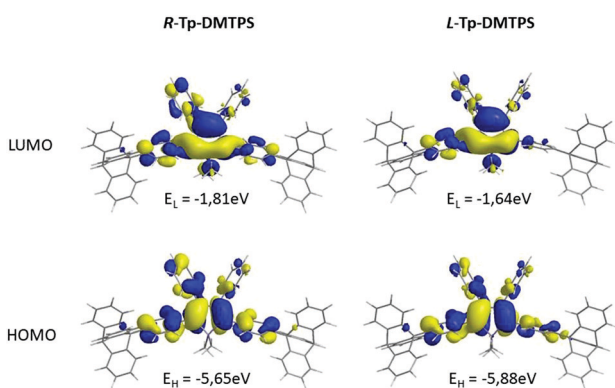


Fig. 16 Energy and shape of the HOMO and LUMO levels of constrained *R*- and *L*-conformers of **Tp-DMTPS** as calculated at the B3LYP/6-31+G* level.

display larger E_g values than for the optimized structure. Indeed, the *L*-conformer that is the less conjugated, displays the largest E_g value of 4.24 eV. Consequently, the emission of **Tp-DMTPS** is expected to be blue-shifted when passing from solution (calculated $E_g = 3.37$ eV) to the solid state, in contrast to experimental observations. This clearly suggests that the red-shift observed experimentally does not stem from the intrinsic properties of the molecules, but rather from the strong CH/ π intermolecular interactions that occur in the solid.^{65,66}

Charge transport calculations

Finally, we decided to perform quantum-chemical calculation to evaluate both the role the CH/ π intermolecular interactions and the conformational modifications in a supramolecular property such as charge transport. Therefore, the estimation of the hole and electron mobilities for both *R*- and *L*-conformers of **Tp-DMTPS** as well as **DMTPS** as a reference were carried out.^{67,68} Interestingly, our methodology reproduces nicely the measured electron-transporting character of **DMTPS**⁴⁷ with the highest calculated electron mobilities of 0.134 cm² (V s)^{−1}, compared to 0.038 cm² (V s)^{−1} for holes (see Fig. S24, ESI†). In contrast to **DMTPS** for which high transport properties are almost isotropic, **Tp-DMTPS** only exhibits a two-dimensional charge transport character within the *bc* plane, especially along the *b* axes. It is worthy to note that this is also in this direction that the main CH/ π intermolecular interactions are running (see above). The two-dimensional behavior is a result of the ‘insulating character’ of the triptycene moiety: since the HOMO and LUMO orbitals are localized on the TPS subunit and not on the triptycene, hole and electron hopping events are highly unlikely along the triptycene direction. Surprisingly, our simulations reveal that, compared to

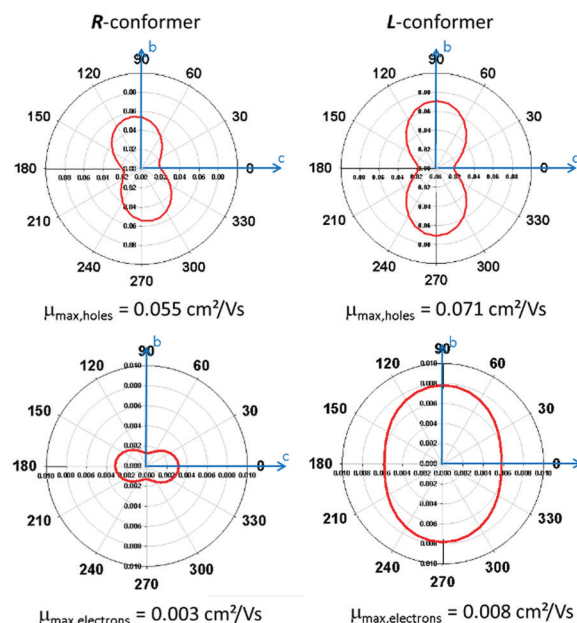


Fig. 17 Anisotropy of the hole (top) and electron (bottom) mobilities (in cm² (V s)^{−1}) in the *R*- (left) and *L*- (right) conformers of **Tp-DMTPS**. The horizontal [vertical] direction corresponds to the *c*-[*b*-] unit cell axis. Note that the mobility scale is different for holes and electrons.

DMTPS, hole mobilities are slightly enhanced while electron mobilities are significantly lowered, down to values never exceeding $0.008 \text{ cm}^2 (\text{V s})^{-1}$, see Fig. 17. Moreover, an increase of the mobilities is observed when passing from the *R*- to the *L*-conformer of **Tp-DMTPS**. This result is in good agreement with the conclusion drawn by the Hirshfeld surface analysis (see Fig. 5), indicating that the *L*-conformer display stronger CH/ π intermolecular interactions than the *R*-conformer. These calculations also show that these interactions are likely involved in the charge transport pathways.

Grafting a triptycene fragment on a TPS central core therefore strongly modifies its charge transport properties by (i) reducing its charge transfer character from 3-D to 2-D and by (ii) inducing a stronger hole-transporting character while keeping a moderate electron mobility. These results imply that **Tp-DMTPS** is able to transport both types of charge carriers reasonably well, consistent with the device performances described above.

Conclusions

Experimental and theoretical studies of two silole–triptycene derivatives **Tp-DMTPS** and **Tp-MPTPS** are presented. Both compounds display a very good AIE activity as well as increased thermal and structural stabilities in comparison with other silole congeners. Consequently, a substantial improvement is found in the formation of stable, amorphous thin films as well as in the performance of simple OLED. Further improvement of the devices performance should be reached through the correction of the charge-transport balance by molecular engineering.^{6,69} Among the two molecules, **Tp-DMTPS** displays a very interesting photophysical behavior. In contrast to what is frequently observed, an appreciable red-shift is observed when passing from either the solution or the tiny aggregates to the crystals. Moreover a pronounced reversible mechanohypsochromic phenomenon with a color emission changing from yellow-orange to blue-green is observed when microcrystalline powders are ground. Based on single crystal structural analysis, ¹³C CP-MAS NMR and theoretical calculations this behavior was rationalized. We have demonstrated the significance of both molecular conformation and intermolecular CH/ π interactions. ¹³C CP-MAS NMR experiments conducted either on microcrystalline or ground powders confirmed that despite of the loss of crystallinity upon grinding, strong intermolecular CH/ π interactions are preserved. This reflects the strong structure-directing properties brought by the triptycene groups. The origin of the red-shift observed when passing from isolated molecules to the crystal may be explained by the stabilization of the frontiers energy levels through CH/ π intermolecular interactions. On the other hand, the origin of the mechanohypsochromism could be explained by the fact that the more energetic conformer is favored when the crystal environmental strain is diminished. Our results therefore indicate that the attachment of triptycene moieties to π -conjugated molecules is an interesting way to improve their thermal, structural and photophysical properties for sensing or optoelectronic applications. However, further experiments and sophisticated calculations are needed to fully understand this very original behavior.

Conflicts of interest

There are no conflicts to declare.

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