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The intriguing case of cyclic triimidazole: an emerging scaffold for the preparation of multiemissive, bio-medical and hybrid inorganic-organic materials

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Among organic small molecules characterized by multifaceted behaviour, triimidazo[1,2-a:1',2'-c:1",2"e][1,3,5]triazine, TT, having a triazinic central ring with three annelated imidazoles, represents a fascinating but still underinvestigated scaffold endowed with intriguing luminescence and coordination properties. Here we comprehensively gather studies, mainly conducted by our research group, on several fully organic or hybrid inorganic-organic TTs revealing their AIE, RTP, mechanochromic and excitation dependent photoluminescence behaviours. Preliminary applications of TTs in sensing and biomedicine are also reported, opening avenues for further studies in these fields and widening the potentiality of Π and its derivatives. On the whole, the results shown here clearly demonstrate that cyclic triimidazole can be rightfully included in the toolbox of powerful scaffolds inspiring the preparation of multifunctional molecular materials.

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1. Introduction

The engineering of organic small molecules characterized by multifaceted properties is certainly a longstanding research goal. In this regard, nitrogen-containing heterocyclic compounds represent an appealing class for different reasons: (i) they are important building blocks to generate bio-probes with significant therapeutic potential; 1-3 (ii) they can be used to obtain organic and hybrid inorganic-organic polymeric materials; 4-6 and (iii) they present structural features exploitable for the preparation of supramolecular assemblies through intermolecular interactions. In particular, several luminescent systems have been obtained by π - π stacking interactions and hydrogen or halogen bonds.7-11

Among different nitrogen-heterocycles, imidazoles and triazines represent versatile scaffolds, which have been used to develop several bioactive compounds with anticancer, antibacterial, antifungal, antitubercular, analgesic, and anti-HIV activities. 12-17 Moreover, imidazole and its derivatives have been frequently employed in the synthesis of metal compounds, e.g. numerous luminescent M(I, II) d10 complexes and coordination polymers (CPs), due to the electron-rich

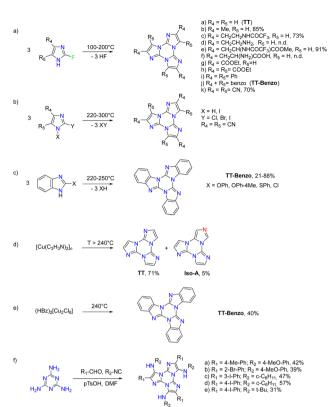
nature of the five-membered imidazole ring. 18-21 Besides, the triazine moiety with its three N atoms has been exploited to build molecules able to establish multiple supramolecular interactions resulting in rigidified structures with enhanced emissive features. 22-25 Importantly, triazine cores have also gained significant attention in the past few decades as building blocks for the preparation of covalent triazine frameworks (CTFs) as promising porous organic materials. 26-28

In this regard, triimidazo[1,2-a:1',2'-c:1'',2''-e][1,3,5]triazine or cyclic triimidazole (hereafter TT) represents an intriguing molecule formed by a triazinic central ring with three annelated imidazoles (see Scheme 1a). It possesses C_{3h} molecular symmetry and three nitrogen atoms available for coordination. While TT is known since 1973, 29 its properties and reactivity remained mainly unexplored until the recent publication of a convenient synthetic procedure.30 This is the reason why studies on TT are still limited despite its promising potentialities as highlighted in the past few years mainly through investigations performed by our research group. Specifically, TT and a large family of its derivatives (TTs) have been prepared and characterized for their emissive and coordination features. The multicomponent fluorescence and phosphorescence behaviours of most TTs have been discovered but only preliminarily exploited for sensing and bioimaging.

In this perspective, after a brief overview of fused π -extended nitrogen rich cores exploited for the preparation of multifunctional materials, we focus on the TT family detailing the

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Scheme 1 Synthesis of TT derivatives.

synthetic procedures and the outstanding emissive features of the core itself and its many fully organic or hybrid inorganicorganic derivatives. Specifically, a deep photophysical investigation of TT functionalized with halogens, ethynyl, carboxyl and chromophoric (including pyrene, pyridines, carbazole and thiophene) groups has been conducted in previous works and summarized and rationalized here together with results obtained for selected hybrid metal compounds with TTs as ligands. Finally, an additional paragraph related to the use of TTs as sensors and biomolecules is included.

It is our belief that the present perspective could be a spring of inspiration for other researchers so that the potentiality of the TT scaffold could be more deeply exploited.

2. Overview of selected π -extended fused aza-heterocycles

In the past few decades, polycyclic aromatic hydrocarbons based on fused nitrogen-rich heterocycles have attracted increasing attention from the scientific community for their possible applications in various fields of supramolecular chemistry and materials science. The introduction of the nitrogen heteroatom in combination with the annealing of the aromatic rings has proven to be an efficacious strategy to prepare stable compounds. Fused aza-heterocycles are, in fact, characterized by a lower susceptibility to degradation through oxidation or dimerization in comparison with their nitrogen-free counterparts.31 Consequently, the rigid, planar and electron

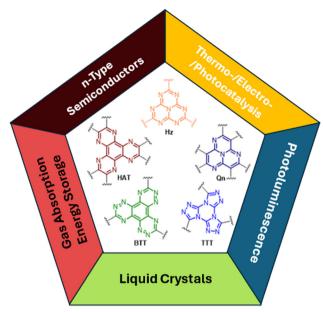


Fig. 1 Examples of π -extended fused aza-heterocycles and their main fields of applications

deficient aromatic scaffolds of heptazine (Hz), quinazoline (Qn), hexaazatriphenylene (HAT) and benzotristriazine (BTT) have been exploited as cores for the preparation of promising functional materials, including covalent organic and metalorganic frameworks, to be used in different areas spanning from liquid crystals, n-type semiconductors, sensors, nonlinear optical chromophores, gas absorption, energy storage, and catalysts to photo- and electro-luminescence (Fig. 1). 32-38

In particular, among planar and rigid nitrogen-rich aromatic scaffolds, tris[1,2,4]triazolo[1,3,5]triazine (TTT) has recently emerged as a useful tecton for the preparation of liquid crystals and TADF (thermally activated delayed fluorescence) emitters. TTT, characterized by a central triazinic core with three annulated triazoles, with its nine sp2 hybridized nitrogen atoms and C_3 symmetry, closely resembles cyclic triimidazole and therefore, in the present work, deserves closer inspection of the results so far obtained with its derivatives.

The first TTT described in the literature was pyroguanazole, synthesized in 1912 by thermal treatment of 3,5-diamino-1,2,4triazole or guanazole.39 However, since that early report, it remained mainly unexplored until 1961 when a seminal work by Huisgen and coworkers reported the synthesis of triphenylsubstituted TTT by reaction of cyanuric chloride with 1phenyltetrazole.40 This synthetic protocol was thoroughly explored later on, starting from the 2000s, when the ability of TTTs to self-assemble into columnar superstructures with mono-dimensional conducting properties was foreseen as a great opportunity to be exploited in molecular electronics and in the realization of discotic liquid crystals. 41-46 Interestingly, the strong coupling between lateral donor substituents and the central acceptor aromatic core together with the octupolar geometry endowed TTTs with linear and non-linear optical features (i.e. fluorescence and two-photon absorption). 47,48

Moreover, the thermal stability and highly ordered structures of discotic materials led to development of compounds characterized by high charge mobility together with light emission capability exploitable in electroluminescent devices.

Through appropriate functionalization of the central electron-acceptor core with donor groups (e.g., phenoxazines, acridines, biacridines or carbazoles) the twisted D-A geometry of TTTs results in blue and green TADF emitters endowed, in some cases, with aggregation-induced enhanced emission (AIEE). 49-54 Furthermore, appropriately designed TTT-based dendrimers have been proposed as hot exciton materials to be used for the preparation of efficient and stable OLEDs. 55,56

More recently, it has been found that the introduction of thiophene bridges in between bulky donor groups (di-3,6-tertbutyl-carbazole or 9,9-dimethyl-9,10-dihydroacridine) and the TTT acceptor core provides solutions with an impressive emissive behavior comprising delayed fluorescence (associated with triplet-triplet annihilation, TTA) and RTP. The latter has been justified by the positive effect of the bulky donor groups on inhibiting non-radiative decays from the triplet state, as confirmed by the similar lifetimes recorded in solution and in the solid state in the Zeonex matrix.⁵⁷

Other interesting photoluminescence features have been observed for TTTs with a phenothiazine heterocycle as a donor functionality. Modulation of the donor strength and steric constraints through the incorporation of methyl groups at different positions of the emitter provided multifunctional materials exhibiting AIEE, dual-TADF, aggregation-induced delayed fluorescence (AIDF), and RTP characteristics. In addition, by appropriately choosing the polarity of the host matrix and by controlling the singlet-triplet energy gap, the possibility to switch between RTP and TADF processes has been demonstrated.58

3. The TT family

Synthetic procedures for TT and TTs

The first report on TT dates back to 1973 when the selfcondensation at 373 K of 2-fluoro-imidazole into its cyclic trimer was reported.²⁹ Trimerization reactions were also successfully performed by using as starting materials 2-fluoro- and 2-chloro-imidazoles variously substituted in 4,5-positions or 1iodo-2-X-4,5-dicyanoimidazoles (X = Cl, Br, I) (Scheme 1a and b). 59-62 In a similar way, thermolysis of 2-aryloxybenzimidazoles was reported for the preparation of tris(benzimidazo)-[1,2-a:1',2'-c:1'',2''-e][1,3,5]triazine (**TT-Benzo**) (Scheme 1c).⁶³ An alternative and more effective synthetic route for the preparation on a multigram scale of TT and TT-Benzo was further proposed by exploiting solvent-free thermolysis of copper(II) imidazolates. In particular, treatment in vacuum of the blue polymorph of copper(II) diimidazolate $[Cu(C_3H_3N_2)_2]_n$ at temperatures above 513 K afforded TT together with, as the byproduct in a 1 to 5 ratio, isomer Iso-A showing an imidazole ring with 1,5- instead of 1,2-annelation (see Scheme 1d). 30,64 Similarly, treatment at 513 K of bis-benzimidazolium

hexachlorodicuprate(II) (HBz)₂[Cu₂Cl₆] produced TT-Benzo in fairly good yields (see Scheme 1e).65

More recently, a multicomponent approach based on selective multiple Groebke-Blackburn-Bienaymé (GBB) reactions performed on the melamine substrate yielded novel hexasubstituted cyclic triimidazoles. 66,67 By appropriately choosing the isocyanide and aldehyde reactants, five different TT-based derivatives were easily isolated in fairly good yields (Scheme 1f). In the case of the halo-aryl substituted products, post-transformation into more complex tripodal scaffolds was further achieved by intramolecular Ullmann-type amination or multiple Suzuki-Miyaura cross-coupling reactions, the latter providing star-shaped compounds with nanometric dimensions.66,67

3.1.1 Haloderivatives. The introduction of one or multiple halogen atoms, X (X = Cl, Br, I), on the TT scaffold was investigated in order to address several issues including the preparation of derivatives suitable for further functionalization and the investigation of the effect of halogen atoms on TT photophysics (see later). It is, in fact, well known that phosphorescence may be positively affected by heavy halogen atoms due to strong SOC that facilitates singlet-triplet ISC. Chlorinated, brominated and iodinated triimidazole derivatives, hereinafter nX (n = 1, 2 and 3; X = Cl, Br and I) (see Scheme 2), were prepared by chlorination, bromination and iodination of TT under mild conditions by using N-chloro-, N-bromo- and N-iodo-succinimide (NXS), respectively, according to Scheme 2.68-71

Interestingly, the reactive positions in halogenation, as well as in all functionalization reactions of TT further described, are the chemically equivalent 3, 7 and 11 ones. Since halogenation through NXS is not specific and provides mixtures of products, a careful control of reaction conditions (NXS equivalents, solvent and addition of catalytic acid) and purification procedures were necessary to obtain 1-3X in good yields.

1-3Cl were synthetized by mild chlorination of the TT scaffold with N-chlorosuccinimide (NCS).⁶⁸ Electrophilic chlorination is not a selective reaction and provides a mixture of mono-, di- and trisubstituted compounds in relative quantities related to the amount of NCS employed. To assess the best synthetic conditions, catalysts, solvents and NCS equivalents were screened. The isolation of 1-3Cl in good yields (47%, 61% and 16%, respectively) was obtained by treating TT with NCS in acetonitrile or dioxane at room temperature with the addition of a protic acid such as trifluoroacetic or p-toluenesulfonic acid. The three compounds were isolated using chromatographic techniques and characterized by NMR and MS.

1-3Br were prepared by mild bromination using one, two or three equivalents of N-bromosuccinimide (NBS),

Scheme 2 Synthesis and chemical structures of 1-3X (X = Cl, Br, I)

respectively. 69,70 The synthesis of 3Br required an acetonitrile (ACN)/dichloromethane (DCM) mixture and the addition of trifluoroacetic acid as a catalyst. Products were purified by chromatography affording 1Br and 3Br in good yields (85 and 90%) while 2Br was obtained in 40% yield together with 1Br and 3Br as by-products. NMR structural assignment of 1Br and 2Br, despite an extensive investigation comprising 1D (¹H and ¹³C) and 2D (COSY, ¹H-¹³C HSQC, ¹H-¹³C HMBC, and ¹H-¹⁵N-HMBC) experiments, was difficult due to the lack of crucial and diagnostic long-range correlations between quaternary carbon and proton signals. Implementation of the experimental results by DFT calculations highlighted ⁴J_{H-C} correlations about twice the ³J_{C-H} ones, allowing the proper chemical shift assignment for both compounds.⁷²

Finally, mild electrophilic reaction of TT with N-iodosuccinimide (NIS) and catalytic amounts of trifluoroacetic acid in ACN provided 1I and 2I, both compounds being isolated and purified by chromatography and crystallization techniques.⁷¹

3.1.2 Overview of C-C and C-N bond formation. The isolation of halo-TTs, in particular the brominated ones, enabled the functionalization of the scaffold with different groups selected for their chemical, physical and photophysical properties. Pyrene and carbazole were chosen for their well-known chromophoric properties (i.e. a high quantum yield for the former and RTP features for the latter). The idea was to investigate the synergistic effect of TT and a photoluminescent moiety. Thiophene and pyridine were chosen for their versatile chemistry to get polymers for optoelectronic applications (the first) or ligands for metal complexation (the latter).

1-3Br were extensively used in Suzuki-Miyaura, Stille, Sonogashira and Ullmann cross-couplings mediated by Pd(0) or

Cu(1) (see Scheme 3) with yields comparable to or slightly lower than those obtained from other brominated aryls (e.g. phenylbromide) using the same catalysts. 73-75 1-3Br react at high temperature, usually above 90 °C, otherwise leading to dehalogenation. The yields decrease, as expected, in polysubstitution reactions (values are in line with those reported for phenylbromide taken as a reference). 76,77

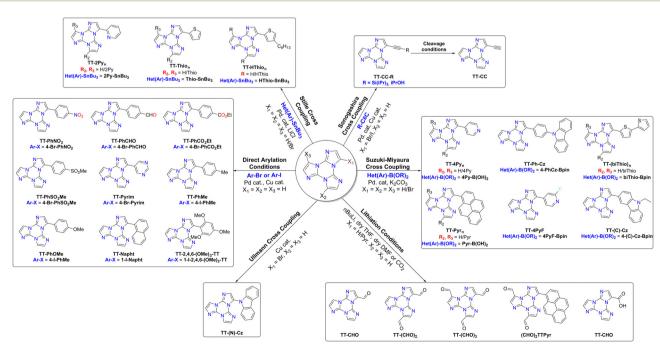
Suzuki-Miyaura cross-coupling: 1-3Br were reacted with commercially available boronic acids/esters such as pyrid-4-yl-,78 pyren-1-yl-boronic acid^{79,80} or 9*H*-carbazolyl-phenyl-,⁸¹ 2-fluoropyrid-4-yl-, 82 2,2'-bithiofen-5-yl-, 83 and 9-ethyl-9*H*-carbazole-3boronic acid pinacol ester⁸⁴ in the presence of a Pd(0) precursor and a base, resulting in the isolation of different TTs (Scheme 4).

Stille cross-coupling reaction: in the same way, brominated TTs can react in Stille cross-coupling reaction. In this regard, 1-3Br were reacted with pyrid-2-yl-, 78,85 thiophen-2-yl-,83 and 4-hexylthiophen-2-yl⁸⁶ tributylstannyls in dry refluxing toluene for 16 h under an inert atmosphere (Scheme 5).

Ullmann-type cross-coupling reaction: moreover, 1Br was reacted according to Ullmann-type cross-coupling reaction mediated by CuI with carbazole, affording TT-(N)-Cz in good yield (Scheme 6).84

Sonogashira cross-coupling reaction: halogenated TTs were also tested in Sonogashira type cross-coupling reactions. Recently, functionalization of TT with an ethynyl group was performed by following two different synthetic procedures using either 1Br or 1I as the starting material, both methods converging to TT-CCH (Scheme 7).87

Formylation reaction: formyl-TTs (TT-(CHO)₁₋₃) were prepared by direct formylation of the scaffold via a lithium salt intermediate followed by quenching with DMF.78 The same synthetic route was exploited in the formylation of TTPyr,



Scheme 3 Overview of C-C coupling products.

TT-4FPv 60%

Scheme 4 Synthesis of TT derivatives by Suzuki-Miyaura cross-coupling

TT-Ph-Cz 66%

TT-(C)-Cz 67%

Scheme 5 Synthesis of TT derivatives by Stille cross-coupling

Scheme 6 Synthesis of TT derivatives by Ullmann-type cross-coupling.

resulting in the formation of the (CHO)₂TT-Pyr derivative, in which the two carbonyl groups are directly connected to the central triazinic core (Scheme 8).88 Moreover, the TT-COOH ligand has been obtained through quenching of the lithium salt using CO₂.89

Synthesis of TT derivatives by Sonogashira cross-coupling

Scheme 8 Synthesis of TT derivatives by formylation.

Synthesis of TT derivatives by direct arylation.

Direct arylation: recently, a new synthetic approach based on direct and regioselective palladium-catalyzed C-H functionalization of the 3-position of the TT scaffold has been reported. 90 Optimization of the reaction conditions allowed achieving high conversion and selectivity with either electron-rich and electron-poor or sterically demanding (hetero)aryl halides (Scheme 9).

3.2 Electrochemical properties

In order to obtain a deeper insight into the structure/property relationship of TTs (Scheme 10), a systematic cyclic

Scheme 10 Chemical structures of [TTMe][CF $_3$ SO $_3$], TT-4Py $_{1-3}$, TT-Thio $_{1-3}$ and TT-biThio $_{1-3}$.

voltammetry investigation was performed.83,91 TT is characterized by little electrochemical activity, with first oxidation and first reduction requiring extreme potentials, close to the DMF potential window limits, and with the three imidazole units behaving as three nearly independent redox sites. On the other hand, Iso-A is slightly more reactive, due to the electron-rich nature of the 1,5-annelated ring, which undergoes first oxidation at a milder potential, while reduction, centred on the remaining two almost equivalent 1,2-annelated moieties, is similar to that of TT. Methylation of one nitrogen atom of the imidazolic ring in [TTMe][CF3SO3] resulted in a significant positive shift of the first reduction potential, due to the electron poor nature of the alkylated N site. In 1-3Br, the electrochemical cleavage of the C-X bond is only slightly influenced by the number of halogens. These findings further strengthened the hypothesis that each imidazole unit in the cyclic trimer acts as an almost independent redox site, with very poor heteroannular aromaticity.91

Comparison of the electrochemical activity of **TT** substituted with a pyridine moiety attached to the *ortho* (**TT-2Py**) or *para* (**TT-4Py**) position revealed that the effect of the linking position of the pyridyl group is more effective on the HOMO or oxidation process (mostly centred on **TT**) than the LUMO or reduction (mostly pyridine-centred). In the case of **TT-2Py**, a slight negative shift of the first oxidation potential was observed, probably due to a conjugation, rather than the inductive effect, between the **TT** core and the 2Py moiety.

On the other hand, a remarkable positive shift of both reduction and oxidation processes was observed for TT-4Py. As a result, both derivatives display a HOMO-LUMO gap dramatically decreased with respect to TT, although

significantly smaller for TT-2Py than for TT-4Py. The introduction of multiple 4Py moieties in TT-4Py₂ and TT-4Py₃ favoured the reduction process, as pointed out by the less negative values with increasing number of pyridine substituents (TT-4Py_n -2.64/-2.60/-2.54 V for n = 1/2/3, respectively).

In the case of a more electron rich substituent, as the thiophene moiety in the TT-Thio₁₋₃ series, the TT core is endowed with more favourable first oxidation and first reduction potentials and a narrower HOMO-LUMO gap. The derivatives are not only significantly electron richer than the pyridine-substituted ones, but display also a more effective conjugation efficiency, as confirmed by DFT calculations disclosing the significant involvement of the thiophene terminals in both HOMOs and LUMOs. However, no electrochemical coupling reactions have been observed for TT-Thio₁₋₃, probably due to the fact that the thiophene pendants are too small in comparison with the TT core.

In order to efficiently promote coupling and formation of an electroactive film on the electrode surface, the bithiophene TTbiThio₁₋₃ series was investigated, revealing smaller energy gaps than their thiophene counterparts, with the HOMO and the LUMO mainly located on the bithiophene moiety. Electrodeposition experiments in monofunctionalized TT-biThio solutions, despite the formation of an electroactive product on the electrode surface, did not provide evidence of active film growth, probably due to the formation of a dimeric layer on the electrode surface. On the other hand, di- and trisubstituted monomers TT-biThio₂₋₃ produced fast and regular growth of electroactive films on the electrode surface upon potential cycling around their first oxidation peak (Fig. 2). These promising results on the fast and reproducible oxidative electrodeposition of oligo/polymer films based on alternate TT and tetrathiophene units constitute an attractive springboard for the development of highly electroactive TT-based materials.83

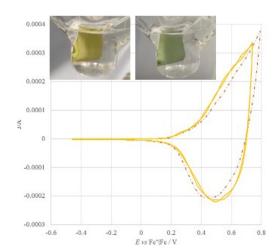


Fig. 2 First and fourth stability cycles in monomer-free solution and electrochromism of [TT-biThio₂]_n films electrochemically formed on the ITO electrode. Reproduced from ref. 83 under the terms of the Creative Commons CC BY license. Copyright 2023, Published by Elsevier Ltd.

3.3 Photophysical and structural properties

Single component materials characterized by rich emissive behaviour including synergic aggregation induced emissive (AIE) and room temperature long lived (room temperature phosphorescence, RTP) features are receiving growing attention from the scientific community due to the benefits they offer in different fields (e.g. bioimaging, 92-95 anti-counterfeiting, 96-100 and displays 101). Long lived RTP can be achieved through organic compounds but phosphorescence is traditionally considered as the exclusive realm of heavy metal complexes. In fact, inter-system crossing (ISC) and, consequently, phosphorescence lifetime, depend on spin-orbit coupling (SOC), which is large in the presence of heavy atoms. However, through appropriate molecular design and supramolecular engineering, pure organic long-lived phosphors have become numerous and have been already tested for different applications. 102-104

Many TTs revealed a rich photophysical behaviour comprising multiple fluorescence and phosphorescence of molecular and supramolecular origins, anti-Kasha emissions and excitation dependent photoluminescence (see the following). Multiple emissions derived from molecular electronic levels can originate from the anti-Kasha mechanism, that is, radiative deactivation from high energy S_n (or T_n) states, or from the presence of different conformers either in the ground or in the excited states. While anti-Kasha behaviour is frequently associated with a large S1-S2 energy gap and a high S0-S2 oscillator strength (f), it can also occur in systems having a smaller S_1 – S_2 gap, but S_n - S_1 internal conversion (IC) prohibited on symmetry grounds. 105 Examples of both anti-Kasha mechanisms have been observed for TTs (see simplified mechanisms in Fig. 3).

The reported excitation dependent behavior of many TTs can be explained as the selective suppression of stronger signals (usually fast components at high energy) allowing the monitoring of the weaker ones (typically red shifted phosphorescence) by low energy excitation to singlets of aggregated species or of different conformers or, less frequently, by direct triplet population. Moreover, halogenated derivatives of TT represent remarkable examples of excitation dependent deactivation paths. These systems, in fact, display phosphorescence from T1 only when excited at sufficiently high energy to

populate an S_n from which ISC to T_n is favorable. Subsequent IC to T_1 results in the observed phosphorescence (see later).

3.3.1 The protoype: cyclic triimidazole. The TT prototype shows crystallization induced (CIE) and mechanochromic emissive behaviour, together with room temperature ultralong phosphorescence (RTUP) under ambient conditions. 106 More specifically, dilute DCM solutions of TT display at 298 K a very weak absorption at 285 nm, with a first sizable peak at about 220 nm, and a hardly discernible emission (at about 400 nm). Based on DFT/TDDFT calculations, the high (ideally C_{3h}) symmetry of the compound is responsible for 'silent' (i.e. characterized by oscillator strength, f, equal to zero) low-energy singlet states. The compound crystallizes in the $P\bar{1}$ space group with significant distortion from the expected C_{3h} symmetry, a result of the establishment of strong intermolecular π - π stacking interactions.30 TT molecules, in fact, pack in an alternating AB face-to-face antiparallel fashion forming columnar aggregates where relatively electron-rich and electron-poor regions approach each other (Fig. 4). This structural pattern represents a distinctive feature of the TT scaffold being observed, with obvious variations in relative distances and orientations, in almost all TTs, as shown below.

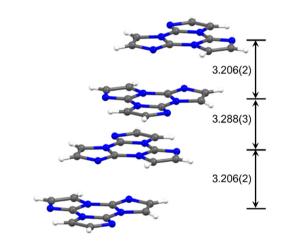


Fig. 4 Crystal packing of TT exhibiting AB stacking arrangement with distances between molecular planes given in Å

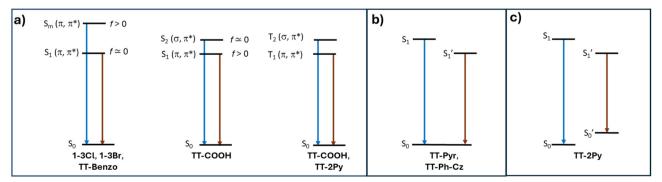


Fig. 3 Simplified energy level for organic TTs displaying anti-Kasha behavior (a) and multiple emissions from different excited (b) or ground (c) state

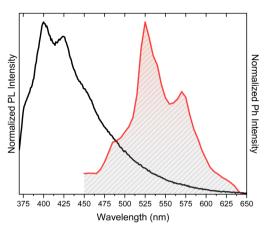


Fig. 5 Photoluminescence (PL, black line, λ_{exc} = 350 nm) and phosphorescence (red line, time delay 472 ms, $\lambda_{\rm exc}$ = 374 nm) of TT crystals at 298 K.

Crystals of TT display at 298 K an intense vibrationally resolved fluorescence at 400 and 424 nm with a RTUP (lifetime, τ , $\cong 1$ s) low energy tail (overall quantum yield, Φ , equal to 30%), which was well disclosed in the delayed spectrum where vibrationally resolved peaks at 525 and 570 nm become visible (Fig. 5). After grinding in a mortar, a loss of the vibronic components of both prompt and RTUP emissions was observed together with a quantum efficiency reduction from 30% to 22%.

Geometry optimizations based on either DFT calculations on dimeric and tetrameric aggregates¹⁰⁶ or hybrid QM/MM calculations¹⁰⁷ highlighted the role of π - π interactions in distorting TT from the C_{3h} symmetry, as experimentally observed. It was also evidenced107 that low- and middlefrequency normal modes, that is, the triazine/imidazole twisting and stretching motions, respectively, are effective only for the isolated (in vacuo or DCM solution) molecule, while they are suppressed for a molecule restricted in a cluster. These restrictions result in a strong increase of the quantum yield and are therefore responsible for the observed AIE behaviour of TT. The phosphorescence efficiency in the solid state was explained by the strong decrease in the S₁-T₁ energy gap when going from the isolated molecule to aggregates 106,107 and by a remarkable intersystem crossing ($k_{\rm ISC}$) and negligible reverse intersystem crossing (k_{rISC}) rates, 107 in agreement with the lack of delayed fluorescence.

The π - π interactions observed in many **TTs** are therefore expected to be relevant in affecting their photophysics. As a further proof, many of them, including TT itself, display mechanochromic features (see the following and Table 3).

These results, in agreement with previous reports on the active role played by H-aggregation in activating RTUP, 108,109 were further confirmed by investigation of the photophysics of Iso-A, the isomer of TT having one imidazole ring with 1,5instead of 1,2-annelation. This compound, crystallizing in the $P2_1/c$ space group, is characterized by CIE behaviour, being slightly emissive in solution at 298 K (in DCM, $\Phi = 2.8\%$) but quite so in crystals due to a strong fluorescence at about 415 nm ($\Phi = 13\%$). The absence of a long-lived component

was confirmed also at 77 K. Its single crystal XRD analysis revealed aggregation of π - π stacked ribbons formed by dimeric units interconnected through cyclic C-H···N hydrogen bonds (HBs) and joined by co-crystallized water molecules. Weaker π - π interactions are suggested by the greater slippage of the parallel-packed columns and longer distance between centroids of the triazinic rings when compared to TT, in agreement with the lack of the ultralong emission component.

Owing to its inherent asymmetry associated with the presence of nitrogen atoms, TT is a prochiral molecule and its deposition on a surface generates two enantiomers. 110 The two are stabilized by π -metal interaction and their interconversion is not possible since it would require flipping the molecule out of plane by 180°. Along the surface plane, TT self-assembles through symmetric HB pairing of its left- (S) or right-turning (R) enantiomers, giving rise to spontaneously resolved twodimensional hexameric networks consisting exclusively of S- (or R-) enantiomers (Fig. 6 top), as experimentally observed for TT deposited on a Ag(111) substrate. 110 The heterochiral assembly, though possible, was predicted by DFT calculations to be less stable than the homochiral one. STM images revealed

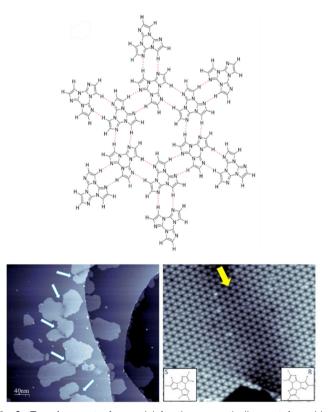
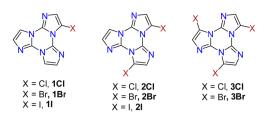


Fig. 6 Top: fragment of a model for the energetically most favorable homochiral 2D assembly of TT (the S-enantiomers are shown). Bottom: STM images of the nanoporous 2D networks formed by deposition of Π molecules on Ag(111) showing the kidney-shaped islands formed by TT (left, 400×400 nm, 1 V, 20 pA image) and one specific interface zone between two different domains of the hexagonal network (right, 40 imes40 nm, 1 V, 40 pA image). Adapted with permission from ref. 110 under the terms of the Creative Commons CC BY license. Copyright 2023, American Chemical Society



Scheme 11 Chemical structure of nX

the presence of kidney-shaped enantiomeric islands, consisting of hexagonal porous networks of TT on the metal surface separated by a dark region, which was associated with a defective zone where RR islands 'capture' S enantiomers (and vice versa) during the deposition process (Fig. 6 bottom).

3.3.2 Halo-derivatives. The functionalization of TT with halogens (Scheme 11) greatly enriched the photophysical behaviour thanks to both molecular mechanisms and aggregation induced phenomena related to intermolecular interactions resulting in new emissive states.

In fact, 1-3X display a quite complex, excitation dependent photoluminescence with emissions including dual fluorescence, molecular phosphorescence and supramolecular RTP and RTUP covering a wide portion of the visible region.⁶⁸⁻⁷¹

3.3.2a Chlorine derivatives. Dilute DCM solutions of 1-3Cl display at 298 K absorption bands at the wavelength below 300 nm and hardly discernible emissions (Φ < 1%) whose low quantum yield represented an impediment for the full interpretation of the molecular properties in solution.

1-3Cl crystallize in the $P\bar{1}$, C2/c and $P2_1/c$ space groups, where molecules form hydrogen bonded corrugated layers, which stack in a slipped manner, evidencing the presence of π - π stacking interactions between TT units and, only for 3Cl, very short ($r_{\text{Cl}\cdots N}$ = 3.014 and 3.151 Å) halogen bonds (XB) corresponding to 8.7 and 4.5% shortening with respect to the sum of the vdW (van der Waals) radii.

Crystals of 1-3Cl are characterized by multiple, excitation dependent emissive features (Φ of about 24, 12 and 10% respectively) comprising dual fluorescence (a high energy component, HEF, in the 330-350 interval, and a low energy one,

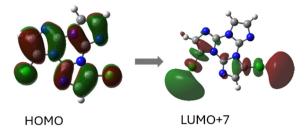


Fig. 8 Main molecular orbitals involved in the (π, σ^*) T^{σ} state of **2Cl** (isosurface value: 0.02).

LEF, in the 350-400 nm portion of the spectrum) and triple phosphorescence (HEP 405-440 nm, MEP 480-550 nm and LEP 550-560 nm) with the lowest energy contribution (LEP) visible only at 77 K (see Fig. 7 and Table 3).

Through spectroscopic, structural and computational analyses, HEF, LEF, HEP and LEP were assigned to excited states of molecular origin while MEP was interpreted as derived from aggregated species. More specifically, HEF corresponds to radiative deactivation from a high energy singlet level (S_n) of (π,π^*) character and large oscillator strength, while an S₁ state of (π,π^*) character and much lower energy and oscillator strength is responsible for LEF. Altogether these features result in the observed anti-Kasha behaviour. Regarding the three phosphorescence types, HEP was correlated to T_1 of (π,π^*) character, while LEP to high energy triplets of (π, σ^*) character $(T^{\sigma}, Fig. 8)$. Aggregation induced MEP, whose intensity increases by increasing the crystalline grade of the samples and the strength of π - π interactions in the crystal structure (intensity increasing in the order: $1Cl < 3Cl \cong 2Cl$), was assigned to TT stacking interactions.

3.3.2b Bromine derivatives. Dilute DCM solutions of 1-3Br display at 298 K a very sharp absorption band (at 230, 235 and 245 nm, respectively) with a low-energy tail in the 250-280 nm range. The emission spectra comprise a weak fluorescence (with maxima at 328, 380 and 370 nm, respectively), with Φ equal to 3% for 1Br and almost vanishing for 2Br and 3Br. At 77 K, however, a very intense and broad phosphorescence in the

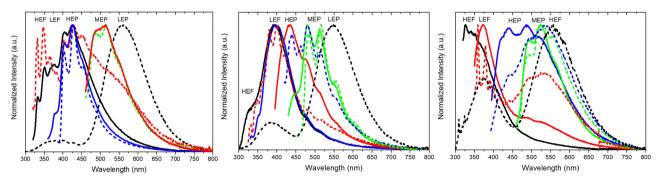


Fig. 7 Normalized PL emission spectra of **1–3Cl** crystals at 298 K (full lines) and 77 K (dashed lines). Left **1Cl**, 298 K: λ_{exc} = 300 nm (black), λ_{exc} = 340 nm (blue) and λ_{exc} = 440 nm (red). 77 K: λ_{exc} = 280 nm (black), λ_{exc} = 300 nm (red), λ_{exc} = 370 nm (blue) and λ_{exc} = 440 nm (green). Middle **2Cl**, 298 K: λ_{exc} = 470 nm (slue) and λ_{exc} = 440 nm (green). 280 nm (black), $\lambda_{\rm exc}$ = 308 nm (blue), $\lambda_{\rm exc}$ = 375 nm (red) and $\lambda_{\rm exc}$ = 413 nm (green). 77 K: $\lambda_{\rm exc}$ = 280 nm (black), $\lambda_{\rm exc}$ = 308 nm (red), $\lambda_{\rm exc}$ = 400 nm (blue) and $\lambda_{\rm exc}$ = 434 nm (green). Right **3Cl**, 298 K: $\lambda_{\rm exc}$ = 300 nm (black), $\lambda_{\rm exc}$ = 330 nm (red), $\lambda_{\rm exc}$ = 374 nm (blue) and $\lambda_{\rm exc}$ = 440 nm (green). 77 K: $\lambda_{\rm exc}$ = 280 nm (black), $\lambda_{\rm exc}$ = 330 nm (red), $\lambda_{\rm exc}$ = 373 nm (blue) and $\lambda_{\rm exc}$ = 440 nm (green).

Perspective

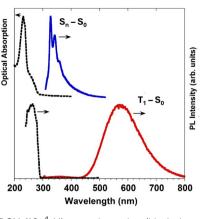


Fig. 9 1Br in DCM (10⁻⁴ M): top: absorption (black dotted line) and PL emission (λ_{exc} = 280 nm; blue solid line) at 298 K. Bottom: excitation profile (λ_{em} = 580 nm; black dotted line) and PL emission (λ_{exc} = 280 nm; red solid line) at 77 K. Adapted with permission from ref. 70. Copyright 2017, John Wiley and Sons.

570-590 nm range dominates the spectra by exciting below 280 nm (see Fig. 9 for 1Br).

On the basis of DFT and TDDFT calculations, the RT emission was assigned, according to an anti-Kasha mechanism, to a high energy S_n state of (π,π^*) character, while the phosphorescence observed at 77 K was explained by the presence of high energy ${}^{3}(\sigma,\sigma^{*})$ and, only for 3Br, ${}^{3}(\sigma,\pi^{*})$ levels, which facilitate an efficient ISC (by both El Sayed and heavy atom effects) from the closest S'_n level, followed by IC to T_1 . By exciting at longer wavelengths, in fact, the appropriate high energy S'_n level cannot be populated and only fluorescence from S_n was observed.

1-3Br crystallize in the $P2_1/c$, $P\bar{1}$ and $P2_1/c$ space groups respectively, forming π -stacked arrangements of dimeric (3Br) or columnar (1Br and 2Br) TT units (see Fig. 10) with π - π stacking interactions' strength in the order 2Br > 3Br > 1Br.

The structures of 2Br and 3Br highlight the presence of Br. Br XBs with formation of tetrameric Br_4 (2Br, see Fig. 10 centre) and trimeric Br₃ (3Br) units. The centrosymmetric Br₄ synthon (2Br) is characterized by high rigidity, as evidenced by both its approximate coplanarity and Br...Br distances 4 and 1% shorter than two times the bromine vdW radius. In the Br₃ unit (3Br), instead, only two molecules have close Br...Br contact (3% shortening), while the third one is rather far from the other two and significantly out from their ls (least squares) plane, indicating a less stable XB supramolecular aggregation.

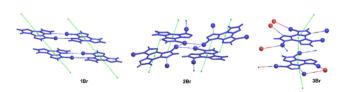


Fig. 10 Views of the π - π stacking in **1-3Br**; Br atoms are shown as spheres and XB interactions are highlighted by blue dashed lines. Red spheres in 3Br refer to atoms belonging to different layers. Reproduced with permission from ref. 69. Copyright 2018, John Wiley and Sons.

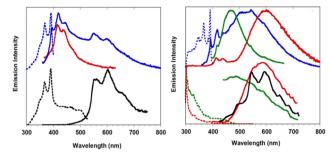


Fig. 11 Powders of **3Br** left: at 298 K. Top: Prompt emission (λ_{exc} = 280 nm, red solid line; λ_{exc} = 340 nm, blue solid line) and excitation profiles (λ_{em} = 420 nm, dashed blue line). Bottom: Delayed emission ($\lambda_{\rm exc}$ = 340 nm, 1 ms delay, window 50 ms; black solid line) and excitation profiles (λ_{em} = 550 nm, dotted black line). Right: at 77 K. Top: prompt emission (λ_{exc} = 280 nm, red solid line; λ_{exc} = 340 nm, blue solid line; λ_{exc} = 385 nm, green solid line) and excitation profiles (λ_{em} = 420 nm, dotted blue line). Bottom: delayed emission λ_{exc} = 360 nm, 100 μs delay, window 500 μ s, red solid line; $\lambda_{\rm exc}$ = 385 nm, 100 μ s delay, window 500 μ s, green solid line; λ_{exc} = 385 nm, 5 ms delay, window 10 ms, black solid line) and excitation profiles (λ_{em} = 523 nm, dotted green line; λ_{em} = 600 nm, dotted red line). Adapted with permission from ref. 69. Copyright 2018, John Wiley and Sons.

Crystals of 1-3Br display excitation dependent multicomponent spectra ($\Phi < 0.1$ for **1Br** and **3Br** and about 14% for **2Br**) including the S_n - S_0 emission, HEF, only observed in solution at RT, with maxima in the 330-440 nm interval. In addition, in **1Br** and **3Br**, the S_1 - S_0 fluorescence LEF (with maxima in the 430-530 nm interval) is activated owing to distorting packing forces that reduce the symmetry of the molecular π -electron system (see Fig. 11 for 3Br), resulting in dual fluorescence. The broad long-lived component detected at 470 nm for 2Br at 298 K and at 490 nm for 3Br at 77 K was ascribed to the extrinsic heavy atom effect caused by the bromine atom in the Br...Br XB motifs (the Br₄ cyclic units in 2Br and the Br₃ cyclic units in 3Br). The structured RTUP (at about 550-650 nm), observed in the emission spectra of powders of 2Br and 3Br (see Fig. 11 for 3Br), was associated with the presence of stacking interactions among TT units. This RTUP cannot be totally excluded even for 1Br since the crystallinity degree and the crystal size of the examined samples may play a role in the relative intensity of phosphorescence emissions. Finally, the three compounds display at 77 K and upon excitation at short wavelengths (280 nm) the strong phosphorescence (at 573, 558 and 590 nm for 1Br, 2Br and 3Br, respectively) observed also in the frozen solutions and therefore assigned to molecular features.

3.3.2c Iodine derivatives. DCM solutions of 1I display an absorption band at about 240 nm with a tail in the 250-270 nm range and no emission at 298 K. At 77 K, a weak emission at about 420 nm, ascribed to deactivation from S1, appears in the spectrum by exciting at low energy (λ_{exc} = 340 nm, see Fig. 12) while, at high energy excitation (below 300 nm), an intense, broad phosphorescence (630 nm) dominates the spectrum. Such molecular phosphorescence is largely red-shifted (by about 50 nm) and its lifetime is one order of magnitude shorter than those of 1-3Br due to the enhanced heavy atom effect of

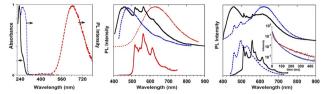


Fig. 12 Left: 11 in DCM: absorption spectrum at 298 K (black solid); PL emission and excitation spectra at 77 K ($\lambda_{\rm exc}$ = 280 nm, red dashed; $\lambda_{\rm em}$ = 648 nm, blue dotted); centre: emission spectra of 11 crystals at 298 K: top: PL at $\lambda_{\rm exc}$ = 300 nm (red dotted), $\lambda_{\rm exc}$ = 370 nm (black solid), $\lambda_{\rm exc}$ = 415 nm (blue dashed); bottom: phosphorescence spectrum ($\lambda_{\rm exc}$ = 370 nm, delay 50 ms, window 200 ms, red solid); right: emission spectra of 11 crystals at 77 K. Top: PL at $\lambda_{\rm exc}$ = 320 nm (blue dotted), $\lambda_{\rm exc}$ = 370 nm (black solid); bottom: phosphorescence spectra at $\lambda_{\rm exc}$ = 320 nm (delay 10 ms, window 50 ms, blue dotted) and $\lambda_{\rm exc}$ = 370 nm (delay 50 ms, window 200 ms, black solid). Phosphorescence decays at λ_{em} = 460 nm (λ_{exc} = 320 nm, blue points) and λ_{em} = 558 nm (λ_{exc} = 370 nm, red points) with their threeexponential fits (black lines) are shown in the inset. Adapted with permission from ref. 71. Copyright 2019, John Wiley and Sons.

iodine with respect to bromine, which makes SOC even more efficient. Accordingly, the easier singlet-to-triplet and triplet-tosinglet ISCs explain, respectively, the lack of RT fluorescence and the faster phosphorescence of 1I. Based on TDDFT calculations, the latter emission was explained, similarly to 1-3Br, by the presence of a ${}^{3}(\pi,\sigma^{*})$ state close to a high energy singlet state of $^{1}(\pi,\pi^{*})$ character, allowing easy singlet-to-triplet ISC and then phosphorescence from a lower energy triplet state. The reduced heavy atom effect of chlorine in 1-3Cl justifies the lack of such phosphorescence in their dilute solutions.

1I and 2I crystallize in the C2/c and $P\bar{1}$ space groups, respectively, where XB and π - π stacking interactions act in a cooperative way. In 1I, non-equivalent I···N XB bonds $(r_{I···N} =$ 2.878 and 3.020 Å, corresponding to 18 and 14% shortening with respect to the sum of the vdW radii) are established on both sides of the molecule, giving rise to helicoidal chains (see Fig. 13). Four halogen bonded chains are intervolved along the helix axis, so that the pitch of the helix, 16.388 Å long, comprises four molecules with the interplanar distance (3.309 Å) facilitating strong π - π interactions. The crystal structure of 2I is isomorphous with that of 2Br, where molecules form tetrameric I···I XB cyclic units, I_4 , slightly more rigid than the Br_4 ones. The I···I distances, 3.717 and 3.780 Å, are in fact 6 and 5% shorter than two times the iodine vdW radius, to be compared with 4 and 1% shortening observed in the Br₄ unit.

Crystals of 1I and 2I show at room temperature quite similar excitation dependent emissive features (Φ < 0.1 and 7%, respectively). In particular, upon low energy excitation, 1I and 2I display a broad fluorescence (at 476 and 443 nm, respectively) (see Fig. 12 for 1I) similar to that observed in solution at 77 K and analogously attributed to radiative deactivation from S₁. At higher excitation energy, RTUP becomes visible (at 517, 563, 612 nm and 625 nm, respectively). By exciting at very shorter wavelengths (<300 nm) the molecular phosphorescence (630 and 680 nm, respectively) present also in solution at 77 K is activated. Investigation of crystals of 1I at 77 K (Fig. 12) revealed an additional phosphorescence contribution

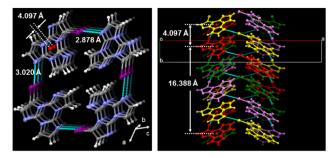


Fig. 13 Partial views along b- (left) and c-axes (right) of 11 crystal structure showing columnar $\pi - \pi$ stacks (centroids of the triazinic rings shown as red circles) interconnected through I···N XB (light blue dashed lines) to form intervolved quadruple helices along the b-axis. Reproduced with permission from ref. 71. Copyright 2019, John Wiley and Sons.

at 460, 495 and 530 nm. Even in this case, RTUP was assigned to π - π aggregates while the new 77 K phosphorescence of ms order observed at 460 nm, firstly ascribed to the presence of I···N XB, was, after investigation of $[MI(TT)]_n$ coordination polymers (see later), interpreted as due to I···C intermolecular electronic coupling with partial orbital overlapping¹¹¹ between the heavy iodine atom and the TT unit. Finally, the molecular phosphorescence of 1I and 2I, visible also at 298 K, is much more intense than that observed at 77 K for nBr, in agreement with the presence of the heavier iodine atom on the molecule.

Comparison of the photophysical behaviour of halogenated compounds is reported in Fig. 14. The effect of the heavy halogen atoms can be accurately evaluated only through lifetimes of LEP, decreasing from 1Cl to 1I. In fact, LEP is associated with molecular electronic levels and it is observed for all 1X under the same conditions (solid state, 77 K) allowing a reliable comparison.

To evaluate the extrinsic iodine heavy atom effect on the photoluminescence of TT isolated from the intrinsic one, a structural and spectroscopic investigation was performed on TT-DITFB, the 1:1 cocrystal self-assembled through I···N XB between TT and 1,4-diiodotetrafluorobenzene (see Fig. 15), DITFB.

Its crystal structure $(P2_1/n \text{ space group})$ consists of heteromeric zig-zag infinite 1D chains self-assembled through I...N XB, where TT acts as double XB acceptor and DITFB as a double XB donor (Fig. 15) with I···N distances, $r_{\text{I···N}} = 3.031$ and 3.006 Å, shorter by 14 and 15%, respectively, than the sum of vdW radii. Adjacent chains are connected through strong π - π stacking interactions among TT units.

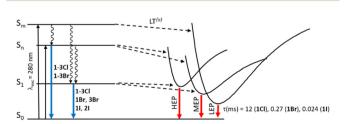


Fig. 14 Comparison through a simplified Jablonski diagram of solid 1-3X. Lifetimes of LEP for 1X are reported.^a Even at RT for 1-2I.

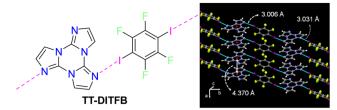


Fig. 15 Left: chemical structures of **TT-DITFB**. Right: partial view of its crystal structure showing columnar $\pi - \pi$ stacks of **TT** (centroids of the triazinic rings shown as red circles) interconnected through $I \cdots N$ XB (light blue dashed lines) with **DITFB** to form infinite 1D zig-zag chains. Adapted with permission from ref. 71. Copyright 2019, John Wiley and Sons.

Crystals of **TT**·**DITFB** show at 298 K (overall Φ equal to 5%) only broad fluorescence (at about 410 nm) and structured phosphorescence (at 496, 528 and 566 nm), while at 77 K broad, red phosphorescence (at 720 nm) dominates the spectrum comprising additional bands (Fig. 16). π - π stacking interactions among TT units were recognized as responsible for the structured phosphorescence, while the low energy contribution was associated through DFT/TDDFT calculations to the iodine extrinsic heavy atom effect, resulting in the presence of ${}^{3}(\sigma,\sigma^{*})$ and ${}^{3}(\pi,\sigma^{*})$ levels allowing SOC from close singlet states of different characters. This 'extrinsic-molecular phosphorescence', observed only at 77 K, is less efficient than the intrinsic one observed also at 298 K for 1I and 2I. Among the other bands observed at 77 K, additional phosphorescence was recognized through delayed spectra (at 463, 497, and 537 nm) and associated with the I···C intermolecular electronic coupling (T^I-S_0) , similarly to what concluded for 11.

Based on these results, it was established that the molecular phosphorescence is better activated through an intrinsic heavy atom effect, being observed at 298 K only in 1I and 2I. Moreover, the I···C induced phosphorescence was confirmed as an extrinsic heavy atom effect, being observed in both 1I and TT-DITFR

On the whole, studies on 1-3X revealed 1-3Cl as the best performing among the full series, preserving the solid state

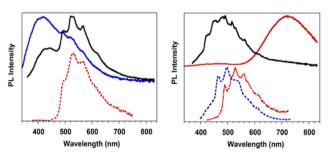


Fig. 16 Left: Emission spectra of **TT-DITFB** at 298 K: top: PL at $\lambda_{\rm exc}$ = 300 nm (blue) and $\lambda_{\rm exc}$ = 350 nm (black); bottom: phosphorescence ($\lambda_{\rm exc}$ = 350 nm, delay 0.5 ms, window 1 ms, red dashed); right: emission spectra of **TT-DITFB** crystals at 77 K: top: PL at $\lambda_{\rm exc}$ = 340 nm (black), $\lambda_{\rm exc}$ = 300 nm (red); bottom: phosphorescence at $\lambda_{\rm exc}$ = 320 nm (delay 10 ms, window 50 ms, blue dashed) and $\lambda_{\rm exc}$ = 370 nm (delay 10 ms, window 50 ms, red dotted). Adapted with permission from ref. 71. Copyright 2019, John Wiley and Sons.

тт-ссн

Scheme 12 Chemical structure of TT-CCH.

multifaceted emissive behaviour but with enhanced AIE features (highest quantum yield) with respect to the bromine and iodine analogues. Moreover, the role of the extended network of intermolecular interactions in activating multiple radiative deactivation channels comprising fast and long-lived components was fully disclosed. In particular, strong $\pi-\pi$ interactions dominating the crystal structures of all halo derivatives were deemed responsible for the RTUP, while extrinsic heavy atom effect was recognized as efficaceous in activating green phosphorescence only in the case of Br and I derivatives, owing to the low heavy-atom effect played by chlorine.

3.3.3 TT-CCH. In DCM solutions, 3-ethynyltriimidazo[1,2-a:1',2'-c:1",2"-e][1,3,5]triazine, **TT-CCH** (Scheme 12), displays absorption at 240, 270 and 287 nm and a single, broad fluorescence at about 360 nm (Fig. 17) (Φ equal to 2%). 87

For polymethylmethacrylate (PMMA)-blended films with low fluorophore loading (dye/matrix w/w% equal to 0.1) a single, unstructured fluorescence, HEF (at 330 nm), and a broad phosphorescence (at 442 nm), HEP, were observed at an appropriate excitation wavelength (Fig. 18). Blended films with higher loadings (w/w% equal to 5) display dual fluorescence (HEF at about 342 nm and LEF at about 383 nm) and dual phosphorescence (HEP at 442 nm and LEP at about 522 nm).

The compound crystallizes in the monoclinic $P2_1/c$ space group forming infinite ribbons with **TT-CCH** molecules connected through quite short CH···N HBs forming cyclic patterns $(r_{\text{H···N}} = 2.33 \text{ and } 2.48 \text{ Å}$, the former involving the acidic C(sp)-H bond). The ribbons are overlapped giving rise to columnar π - π aggregates.

Crystals of **TT-CCH** show excitation dependent behaviour ($\Phi = 16\%$) comprising dual fluorescence (HEF at 314, 326,

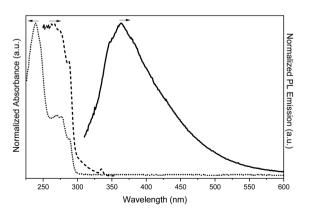


Fig. 17 Absorption (dotted line), excitation (dashed line, λ_{em} : 374 nm) and PL emission (continuous line, λ_{exc} : 290 nm) spectra of **TT-CCH** in DCM.

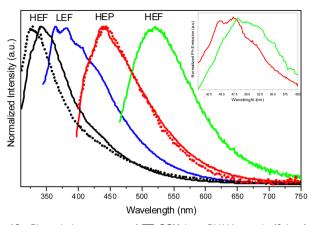


Fig. 18 PL emission spectra of TT-CCH in a PMMA matrix (0.1 w/w%, dotted line; 5 w/w%, full line) at 298 K. λ_{exc} : 290 nm (black lines), 330 nm (blue line), 380 nm (red lines) and 445 nm (green line). Inset: The delayed spectra are shown for the 5 w/w% concentration at short (40 µs delay, 200 µs window; red line) and long (4 ms delay, 20 ms window; green line) delay times.

338 nm and LEF at 354, 367, 377 nm) and dual phosphorescence (HEP at 434 nm and LEP at 538 nm). The relative intensity of the two fluorescent signals is temperature and grinding dependent, with LEF being attenuated through grinding and by increasing the temperature (Fig. 19). Of the four emissions, HEF and HEP were interpreted as molecular phenomena, while LEF and LEP as due to the supramolecular ones. In agreement with this hypothesis, in PMMA films, LEF and LEP appear only by increasing the dye-loading and HEF/LEF relative intensity shows mechanochromic dependence.

The origin of LEF was clarified through DFT/TDDFT calculations on both the isolated molecule and different small aggregates, comprising CH···N and/or π ··· π stacked dimers and tetramers. The computed molecular S_1 level possessing (π, π^*) character is localized on the $C \equiv C$ bond and the portion of the TT moiety directly bonded to it and lies very close to a triplet state from which HEP is originated. For the CH···N aggregates, S₁ gradually red shifts and acquires an impressive increase of its oscillator strength, from 0.25 (monomer) to 0.74 (dimer) and

TT-COOH

Scheme 13 Chemical structure of TT-COOH

then 1.64 (tetramer). For π - π stacked dimeric and tetrameric species a much lower increase in oscillator strength was computed, indicating that appearance of LEF is due to the strong HB characterizing the TT-CCH crystal structure and not to π - π stacking interactions, which are instead responsible for LEP as often observed among TTs.

3.3.4 TT-COOH. Triimidazo[1,2- α :1',2'-c:1",2"-e][1,3,5]triazine-3-carboxylic acid, TT-COOH (Scheme 13), displays dual fluorescence (HEF at 327, 343 nm and LEF at 404 nm, overall Φ = 3.8%) in dilute DMSO solution.⁸⁹ The compound crystallizes in the centrosymmetric triclinic $P\bar{1}$ space group with the formation of intramolecular OH···N hydrogen bonding and π - π stacking interactions involving the **TT** units. Crystals of **TT-COOH** display excitation dependent behaviour ($\Phi = 26\%$, Fig. 20) comprising dual fluorescence (HEF at about 342 nm and LEF at 386, 408 and 432 nm) and triple phosphorescence (HEP at 445 nm, MEP at 487 nm, LEP at 549, 590 and 642 nm).

Based on spectroscopic, structural and theoretical investigations, the emissions were recognized as molecular (HEF, LEF, HEP and MEP) or π - π aggregate (LEP) features (Fig. 20). The molecular contributions were associated with the presence of low energy excited states of (π,π^*) and (σ,π^*) symmetries, justifying separate deactivation radiative paths. Moreover, calculations on H-bonded dimers did not result in a remarkable increase of the S₁ oscillator strength as instead obtained for TT-CCH, as a consequence of the weaker interaction in TT-COOH. Therefore, the latter was classified as an anti-Kasha emitter differently from the former.

3.3.5 Functionalization chromophoric with Organic RTP emitters have recently proved to be attractive

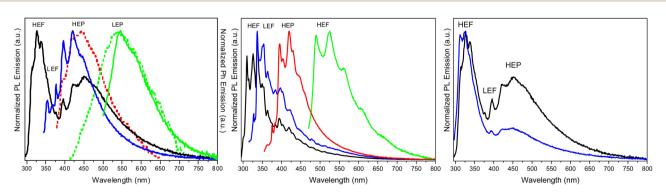


Fig. 19 Normalized PL emission spectra of TT-CCH crystals. Left at 298 K: Prompt (full line) and delayed (dashed line) spectra; $\lambda_{\text{exc.}}$: 275 nm (black); 330 nm (blue) and 486 nm (green); $\lambda_{exc.}$: 310 nm (dashed red, delay 15 μ s, window 400 μ s; dashed green, delay 1 ms, window 15 ms). Middle at 77 K: prompt spectra; $\lambda_{\text{exc.}}$: 275 nm (black); 300 nm (blue); $\lambda_{\text{exc.}}$: 340 nm (red); $\lambda_{\text{exc.}}$: 450 nm (green). Right at 298 K: before (black) and after (blue) manual grinding in a mortar; $\lambda_{exc.}$: 275 nm.

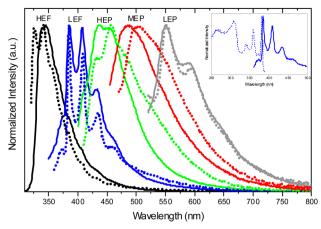
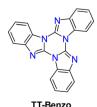


Fig. 20 Normalized PL emission spectra of TT-COOH crystals at RT (continuous lines) and 77 K (dotted lines). $\lambda_{\rm exc}$ = 300 nm (black); 340 nm (blue); 390 nm (green); 440 nm (red) and 500 nm (grey). Inset: Normalized emission (continuous, λ_{exc} = 340 nm) and excitation profiles (dotted, λ_{em} = 409 nm) at 77 K.

luminescent materials for different applications, including, in particular, the field of biological sensing and imaging. 102-104 To be used in this area, however, RTP luminophores need to meet stringent requirements such as long wavelengths, bright RTP emission, suitable size and good water dispersibility. Organic substituents are expected to modify the emissive properties at both molecular and, through different packing modes, solidstate levels, though in a not completely predictable way. In order to extend the scope of the TT scaffold in view of possible biological applications, two main directions were envisaged. On one hand, the role of suitable chromophoric substituents (e.g. heteroaromatic substituents with red emission) in shifting the emission of TT towards the red while preserving the long lifetime of its triplet state was considered. On the other hand, the effect of extending the condensed polycyclic structure of TT on the photophysics of the organic emitter was examined, even though the latter aspect is still in its infancy and certainly deserves further investigation.

3.3.5a TT-Benzo. Benzo[4,5]imidazo[1,2-*a*]benzo[4,5]imidazo-[1,2-c]benzo[4,5]imidazo[1,2-e][1,3,5]triazine, TT-Benzo (Scheme 14), shows in trifluoroacetic acid (TFA) at 293 K an intense absorption band at 277 nm of (π,π^*) character, which in DMSO is red-shifted to 285 nm with appearance of an additional band at 300 nm. A strong solvent effect was also observed for the (π,π^*) emission at 380 nm in TFA, blue shifted



Scheme 14 Chemical structure of TT-Benzo

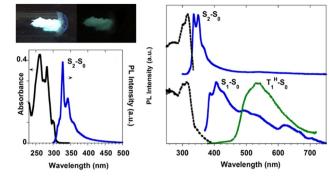


Fig. 21 (left) Top: powders of TT-Benzo at 77 K with UV irradiation on (left) and off (right). Bottom: DCM solutions at 298 K: absorption (black) and PL emission (blue, λ_{exc} = 260 nm). Right: Powders at 298 K: top: excitation (dashed black, λ_{exc} = 348 nm) and PL emission (blue, λ_{exc} = 260 nm). Bottom: excitation (dashed black, λ_{em} = 408 nm), PL emission (blue, λ_{exc} = 370 nm), and phosphorescence (green dotted, 10 ms delay, window 50 ms, $\lambda_{\rm exc}$ = 358 nm). Reproduced with permission from ref. 70. Copyright 2017, John Wiley and Sons.

and vibrationally resolved with maxima at 329 and 344 nm in DMSO⁶⁵ and 327, 341, 359 nm in DCM.⁷⁰

TT-Benzo crystallizes in the $P\bar{1}$ space group¹¹² in an arrangement very similar to that of TT but with a higher intermolecular distance along its π - π columnar aggregates. At 298 K, microcrystalline powders of TT-Benzo show excitation dependent properties comprising both dual fluorescence (at 335, 350, 366 nm and 407 nm, the first being quite similar to the one observed in solution) and RTUP (at 530 nm); the latter is assignable to π - π stacking interactions (Fig. 21). The dual fluorescence was interpreted through DFT/TDDFT calculations, which revealed the presence of an S_0 - S_1 transition of (π,π^*) character and zero oscillator strength for symmetry reasons, and two almost degenerate transitions at slightly higher energy with large oscillator strength (So-S2 and So-S3). These electronic conditions are effective in producing anti-Kasha behaviour 105,113,114 and, on this basis, the high energy fluorescence observed in solution and in the solid state was associated with S2-S0 radiative deactivation. In the solid state, the S0-S1 transition acquires intensity due to the partial loss of molecular symmetry through intermolecular interactions, resulting in the S₁-S₀ fluorescence.

3.3.5b TT-pyrenes. Dilute DMSO solutions of TTPy r_{1-3} (Scheme 15) show two absorptions at 257, 268, and 279 nm and 332 and 347 nm of main pyrene character. 79,80 The strong red shift and broadening with respect to the parent compound were associated with the increased conformational freedom as

Scheme 15 Chemical structure of TTPyr₁₋₃.



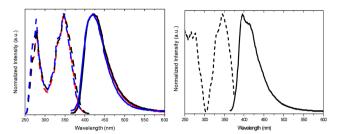


Fig. 22 Normalized PL emission (solid lines) and excitation (dashed lines) spectra at 298 K. Left: DMSO solutions of TTPyr1 (blue line), TTPyr2 (red) and **TTPyr₃** (black), $\lambda_{\text{exc}} = 350$ nm, $\lambda_{\text{em}} = 420$ nm. Right: **TTPyr₁** in PMMA (5% w/w), $\lambda_{\text{exc}} = 345 \text{ nm}$; $\lambda_{\text{em}} = 397 \text{ nm}$.

determined by DFT studies, resulting in an increased number of the involved excited states. An intense very broad single fluorescence emission (at about 420 nm) was observed for all of them (see Fig. 22) with impressively high quantum yield (92, 78 and 74% for TTPyr1, TTPyr2 and TTPyr3, respectively), when compared with pyrene itself (33.4%) under the same conditions, suggesting the positive role of the TT moiety in suppressing the ACQ (aggregation caused quenching) phenomenon affecting pyrene fluorescence. 115-117 Spin-coated blended films of TTPyr₁ in PMMA (0.5 and 5 wt%) show an intense, vibronically resolved fluorescence at 396 nm (Φ about 75%), which is blue-shifted with respect to the one observed in DMSO solution. Based on DFT studies, two conformational minima, corresponding to different orientations of pyrene with respect to the TT moiety, were located on the So potential energy surface (PES). These conformations were individuated in crystal structures of TTPyr1 (see below). In dilute solution, both conformations are populated owing to the flatness of the surface, resulting in a broad fluorescence emission, while in PMMA films the chromophore is frozen in the absolute minimum, and a narrower higher energy emission was observed.

Only for TTPyr₁ single crystals suitable for XRD analysis were obtained by various methods. In particular, three crystalline forms, namely TTPyr(RT) $(P2_1/c \text{ space group, Fig. 23})$, TTPyr(Et) (C2/c space group, Fig. 24) and TTPyr(HT) (Pna2₁ space group, Fig. 25), were isolated. The asymmetric unit of TTPyr(Et) contains one TTPyr and half ethanol molecule interacting via hydrogen bonds (Fig. 24).

In TTPyr(RT) and TTPyr(Et), the TT unit of one molecule stacks in between two Pyr units of neighbouring molecules, forming infinite columns of π - π stacking fragments

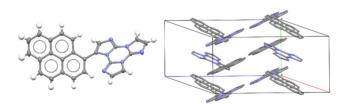


Fig. 23 X-Ray crystal structure of TTPyr(RT). Left: View of a single TTPyr molecule (ellipsoid drawn at 30%); right: view of molecular packing (hydrogen atoms are omitted for clarity). Reproduced with permission from ref. 80. Copyright 2021, John Wiley and Sons.

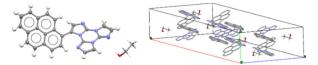


Fig. 24 X-Ray crystal structure of TTPyr(Et). Left: View of a single TTPyr molecule interacting through hydrogen bonds with an ethanol molecule (ellipsoid drawn at 30%, only one model of disordered ethanol molecule is shown); right: view of the molecular packing (hydrogen atoms are omitted for clarity and only one model is shown for ethanol molecules). Reproduced with permission from ref. 80. Copyright 2021, John Wiley and Sons.

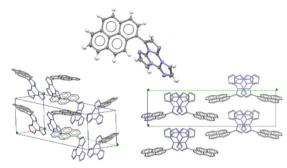


Fig. 25 X-Ray crystal structure of TTPyr(HT). Top center: View of a single TTPyr molecule (ellipsoids are drawn at 30%); bottom: two views of the molecular packing (hydrogen atoms are omitted for clarity). Reproduced with permission from ref. 80. Copyright 2021, John Wiley and Sons.

(Fig. 23 and 24). On the other hand, in TTPyr(HT) the molecules form columns where only the TT fragments are facing each other and the pyrene units of adjacent molecules protrude in opposite directions (Fig. 25).

Crystals of TTPyr(RT) and TTPyr(Et) display a similar excitation dependent photophysical behaviour (Φ about 40%), comprising one fluorescence band (at 490 and 493 nm, respectively) and one phosphorescence band (at 550 and 555 nm, respectively) (Fig. 26) with relative intensity varying with crystallinity of the examined sample.

In agreement with its different disposition of the chromophore inside the structure with respect to the other crystalline forms, TTPyr(HT) displays a macroscopically different photophysics with dual fluorescence (HEF and LEF at 420, 450 nm and 480 nm, respectively) and single phosphorescence (at 550 nm) with relative intensity depending on the excitation energy. For all phases, the phosphorescence feature was assigned to π - π (TT-TT or TT-Pyr interactions) aggregated species. For what concerns fluorescence, DFT/TDDFT calculations on dimeric prototypes of TTPyr(RT) evidenced a blocked conformation with reduced twisting with respect to the isolated molecule and therefore optimized lower energy S1 minimum, resulting in the observed red shifted single fluorescence (monitored in solution). On the other hand, the TTPyr(HT) dimer, where the pyrene moiety is still free to get the two S_0 minima, produces dual fluorescence.

Relatively to TTPyr2 and TTPyr3, showing in powder only one fluorescence band (at 490 and 476 nm, respectively) and one

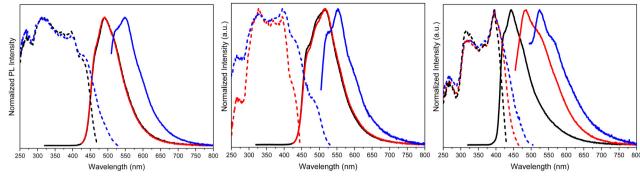


Fig. 26 Normalized PL emission (full line) and excitation (dashed line) spectra at RT. Left: TTPyr(Et) crystals. $\lambda_{exc} = 300$ nm (black line), $\lambda_{exc} = 405$ nm (red line), $\lambda_{\text{exc}} = 495$ nm (blue line); $\lambda_{\text{em}} = 494$ nm (black line); $\lambda_{\text{em}} = 610$ nm (blue line). Middle: **TTPyr(RT)** crystals. $\lambda_{\text{exc}} = 300$ nm (black line), $\lambda_{\text{exc}} = 405$ nm (red line), λ_{exc} = 490 nm (blue line); λ_{em} = 466 nm (red line), λ_{em} = 555 nm (blue line). Right: **TTPyr(HT)** crystals. λ_{exc} = 300 nm (black line), λ_{exc} = 440 nm (red line), $\lambda_{\text{exc}} = 480$ nm (blue line); $\lambda_{\text{em}} = 445$ nm (black line), $\lambda_{\text{em}} = 483$ nm (red line), $\lambda_{\text{em}} = 524$ nm (blue line).

Scheme 16 Chemical structures of TT-HThio and TT-HThio₃.

phosphorescence band (at 528 and 522 nm, respectively), the lack of structural details allowed drawing only qualitative conclusion. In particular, aggregated species were deemed responsible for the long-lived emission appearing at the same wavelength as that of TTPyr LEP.

3.3.5c TT-thiophenes. 3-(4-Hexylthiophen-2-yl)-triimidazo [1,2-a:1',2'-c:1'',2''-e][1,3,5]triazine, **TT-HThio**, and 3,7,11-tri(4hexylthiophen-2-yl)-triimidazo[1,2-a:1',2'-c:1'',2''-e][1,3,5]triazine, TT-(HThio)₃ (Scheme 16), display in DCM dilute solutions at 298 K, a single fluorescence band (at 370 and 380 nm, Φ equal to 11% and 5%, respectively). 86 At 77 K and in PMMA blended films (0.5 wt%, Φ equal to 15% and 17%, respectively) superimposable spectra were obtained (fluorescence at 365 and 370 nm, respectively) as expected for a molecular emission in rigidified media.

TT-HThio crystallizes in the $P\bar{1}$ space group with head-tohead π -stacked aggregates. No single crystals were obtained for TT-(HThio)₃.

Crystals of the former and powder of the latter display crystallization enhanced emission (CEE) through an excitation dependent behaviour comprising one fluorescence band (at 376 and 382 nm, and 400 nm, respectively) and two phosphorescence bands (HEP at 425 and 451 nm, and 428 and 453 nm, respectively; LEP at 497, 530, and 578 nm, and 514 and 550 nm, respectively) (overall $\Phi = 26\%$ and 22%, respectively, Fig. 27). CEE behaviour was confirmed by a decrease in Φ (18%) through grinding crystals of TT-HThio in a mortar. From DFT/TDDFT and X-ray studies, HEP and LEP observed in both solid

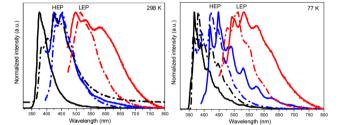


Fig. 27 Normalized PL emission of crystals of TT-HThio: (continuous lines) and of crystalline powders of $TT-(HThio)_3$ (dashed dotted lines) spectra. Left 298 K at $\lambda_{\rm exc}$ = 300 nm (black), \cong 380 nm (blue), 450 nm (red); right 77 K, emission at λ_{exc} = 300 nm (black), 360 nm (blue), \cong 440 nm (red).

compounds were assigned to molecular and aggregated π - π (TT-TT) species.

3.3.5d TT-carbazoles. Carbazole, Cz, and its derivatives have been the subject of numerous investigations aimed at clarifying the mechanisms involved in their RTUP. It was reported that commercially available Cz is mixed with traces of its isomer (1*H*-benzo[*f*]indole), which is involved in the origination of the long lived emission. 118,119 This discovery has further pointed to the well-known issue of using highly purified uncontaminated samples when investigating the luminescence properties of materials but has also stimulated studies on new pure carbazole RTP derivatives. 120-122 With this in mind, we synthesized and deeply investigated three TT-Cz derivatives with the two units differently connected: specifically 3-(9H-carbazol-9-yl)triimidazo[1,2-a:1',2'c:1'',2''-e[1,3,5]triazine, **TT-(N)-Cz**, 3-(9-ethyl-9*H*-carbazol-3-yl)triimidazo[1,2-a:1',2'-c:1",2"-e][1,3,5]triazine, TT-(C)-Cz, and 3-(4-(9H-carbazol-9-yl)phenyl)triimidazo[1,2-a:1',2'-c:1",2"-e][1,3,5]triazine, TT-Ph-Cz (Scheme 17).81,84

Scheme 17 Chemical structures of TT-(N)-Cz, TT-(C)-Cz and TT-Ph-Cz.

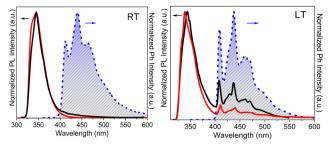


Fig. 28 TT-(N)-Cz normalized emission spectra ($\lambda_{\rm exc}$ = 300 nm). PL of DCM solutions (10^{-6} M, red) at 298 K (left) and 77 K (right) in air. PL of PMMA films (0.5 wt%) in vacuum (black) and delayed spectra (blue dashed; delay 200 µs, window 500 µs at 298 K (left); delay 5 ms, window 10 ms at

3.3.5d.1 TT-(N)-Cz. In dilute DCM solution TT-(N)-Cz shows at room temperature two sets of absorption bands at 280 and 288 nm and 313 and 326 nm and a broad fluorescence band at 345 nm (Φ = 27%). At 77 K, a strong fluorescence band at 339 nm and a much weaker vibrationally resolved phosphorescence band at 411, 439, and 466 nm are observed. Blended PMMA films (TT-(N)-Cz 0.5 wt%, Fig. 28) display at RT in vacuum one fluorescence band at 345 nm (Φ = 28%) and one vibrationally resolved phosphorescence band (maxima at 412, 440 and 462 nm).

TT-(N)-Cz crystallizes in the monoclinic $P2_1/c$ (TT-(N)-CzM) and in the triclinic P1 (TT-(N)-CzT) space groups. In both TT-(N)-Cz polymorphs, TT and Cz are almost orthogonal, with structures dominated by π - π stacking interactions between TT moieties (see Fig. 29).

Crystals of both polymorphs (Fig. 30) revealed quite similar excitation dependent emissive features (Φ = 13 and 16% for TT-(N)-CzT and TT-(N)-CzM, respectively) comprising HEF (349 and 357 nm for TT-(N)-CzT and TT-(N)-CzM, respectively), LEF (in the 380-402 nm interval), HEP (442, 464, and 437 nm, respectively) and LEP (509 and 517 nm, respectively).

The origin of this multicomponent emissive behaviour was disclosed through spectroscopic, structural and computational studies revealing the molecular or the aggregated nature of each contribution. LEF and LEP possess aggregated origin as proven by both their absence in diluted solutions and blended

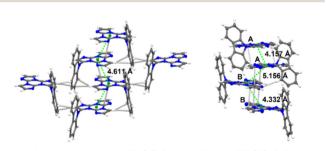


Fig. 29 Crystal packing of TT-(N)-CzM (left) and TT-(N)-CzT (right), showing the shorter distances between triazinic geometrical centroids (green spheres) and intermolecular contacts shorter than the sum of vdW radii (light grey dashed lines). Ellipsoids at 30% probability. Reproduced with permission from ref. 84. Copyright 2023, by Elsevier Ltd.

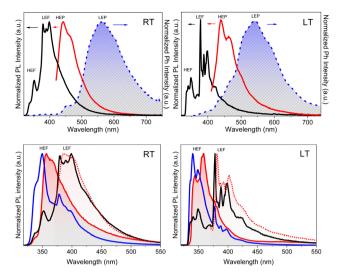


Fig. 30 Normalized emission at 298 K (left) and 77 K (right). Top: TT-(N)-**CzT** crystals: PL spectra (continuous lines): $\lambda_{exc} = 300$ nm (black) and $\lambda_{\rm exc}$ = 400 nm (red); delayed spectra (blue dashed): delay 1 ms, window 5 ms. Bottom: PL emission spectra of: **TT-(N)-CzM** crystals, λ_{exc} = 300 nm (red continuous); λ_{exc} = 355 nm (red dotted); **TT-(N)-CzT** crystals, λ_{exc} = 300 nm, before (black) and after (blue) grinding.

films and their quenching through crystal grinding. In addition, LEP appears in the same spectral region where RTP is observed for TT emitters having columnar or dimeric π - π aggregates. Based on theoretical studies, the LEF origin was as well attributed to strong π - π interactions involving the TT scaffold. In fact, TDDFT calculations performed on the molecule resulted, among the others, in an S1 state of Cz character and an S_3 state of TT character, both having (π,π^*) symmetry. For π - π dimeric prototypes a clear stabilization accompanied by a noteworthy increase in the oscillator strength was calculated only for S₃, which has been therefore identified as the lowest energy excited state in the crystal (SH).

3.3.5d.2 TT-(C)-Cz. In dilute DCM solution, TT-(C)-Cz shows at RT two absorption bands at 239 and 290 nm with a tail at about 330 nm and a broad fluorescence at 380 nm (Φ = 20%). At 77 K, a broad long-lived component at about 500 nm (LEP) is clearly visible in the PL spectrum. PMMA films (TT-(C)-Cz 0.5 wt%, Fig. 31) in vacuum display one fluorescence band at 377 nm and two phosphorescence bands at about 417 nm (HEP) and 515 nm (LEP), which appear to be vibronically resolved at 90 K (at 412, 442, and 500 nm, respectively).

TT-(C)-Cz crystallizes in the Pna2₁ space group with two independent molecules in its a.u., i.e., A and B, having the dihedral angle between TT and Cz units equal to 34.2° (A) and 37.8° (B), indicating partial conjugation. Moreover, differently from the TT-(N)-Cz polymorphs, in TT-(C)-Cz the π - π stacking interactions between TT units are replaced by analogous interactions between TT and Cz.

TT-(C)-Cz crystals (Φ = 28%, Fig. 32) display excitation dependent PL spectra comprising one fluorescence band at 402 nm with shoulder at 420 nm and one phosphorescence band at 460 nm with shoulder at 486 nm (HEP). Moreover, an

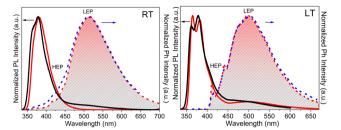


Fig. 31 TT-(C)-Cz normalized emission spectra ($\lambda_{\rm exc}$ = 300 nm). PL of DCM solutions (2 \times 10⁻⁶ M, red continuous) at 298 K (left) and 77 K (right). PL of PMMA films (0.5 wt%, at 298 K, left, and 90 K, right) in vacuum (black) and delayed spectra (blue dashed, delay 0.2 ms, window 0.5 ms; red dashed, delay 50 ms, window 10 ms at 95 K.

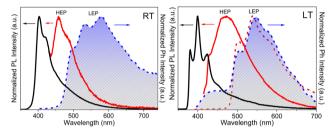


Fig. 32 Normalized emission spectra of TT-(C)-Cz crystals at 298 K (left) and 77 K (right). PL (continuous line) $\lambda_{\rm exc}$ = 300 nm (black) and $\lambda_{\rm exc}$ = 415 nm (red), delayed spectra (dashed line) $\lambda_{\rm exc}$ = 385 nm (298 K, delay 1 ms, window 5 ms; 90 K, blue: delay 0.5 ms, window 0.5 ms; red: delay 10 ms, window 20 ms).

additional phosphorescence band (LEP at 531 and 580 nm and at 500 and 540 nm at RT and 77 K, respectively) was disclosed in delayed spectra.

Supported by DFT/TDDFT calculations, fluorescence and HEP were associated with molecular excited states. They are red shifted with respect to the corresponding ones in TT-(N)-Cz owing to the reduced molecular twisting and the consequently increased electronic communication between TT and Cz. Again, LEP was attributed to a triplet of aggregated origin and its appearance in solutions or blended films was justified by the presence of aggregated forms even at very low concentrations. However, in the present case, less efficacious π - π stacking interactions between TT and Cz moieties result in RTP visible only in delayed experiments and in the absence of LEF.

3.3.5d.3 TT-Ph-Cz. The compound shows at 298 K in dilute DCM solutions four absorption maxima at 236, 293, 310 and 340 nm and a broad, structureless fluorescence band at 370 nm with a shoulder at 350 nm (Φ = 63%). At 77 K, a narrowing of the band (maximum at 353 nm) was observed together with the appearance of a broad phosphorescence band centered at 512 nm. The molecular or aggregate origin of the latter could not be established since, even in dilute solutions, the presence of small aggregates in frozen DCM is possible. 68,85 PMMA films (TT-Ph-Cz 0.5 wt%, Fig. 33) in vacuo display at 298 and 77 K a photophysical behaviour strongly resembling that of frozen solution. In particular, one narrow fluorescence band with

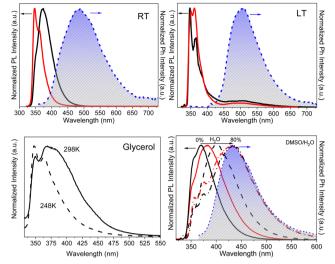


Fig. 33 TT-Ph-Cz. Normalized emission spectra (λ_{exc} = 300 nm). Top: PL in DCM (2 \times 10⁻⁶ M, red lines) at 298 K (left) and 77 K (right) in air. PL of PMMA films (0.5 wt%, at 298 K, left, and 90 K, right) in vacuum (black) and delayed spectra (blue dashed, delay 0.2 ms, window 0.5 ms). Bottom: PL in glycerol (2 imes 10 $^{-6}$ M, right) at 248 K (dashed line) and 298 K (continuous line). PL in DMSO (10^{-6} M) at 298 K (left) with increasing H₂O volume. 0% (black continuous), 20% (red continuous), 50% (black dashed), 70% (red dashed-dotted), 80% (black dashed-dotted). Delayed spectrum (blue dashed, delay 0.2 ms, window 0.5 ms) of the 80% water fraction solution.

vibronic replicas at 347 and 360 nm (Φ = 60.2%) and a broad phosphorescence band (490 or 508 nm, at 298 and 90 K, respectively) were observed. Speculating rigidification effects, spectra of dilute glycerol solution were collected. At 298 K, a broad band centered at 380 nm and a narrow peak at 350 nm were visible. Importantly, disappearance of the 380 nm component was observed by increasing the viscosity of the solution at low temperature. These results suggested dual emission from a Franck-Condon (FC) and a relaxed emitting state of molecular TT-Ph-Cz, as confirmed by theoretical calculations. Intriguingly, using solvent/non-solvent (DMSO/water equal to 20/ 80%) mixtures, RTP (430 nm) nanoaggregates were prepared.

TT-Ph-Cz crystallizes in three phases: TT-Ph-CzM (monoclinic C2/c space group), TT-Ph-CzT (triclinic $P\bar{1}$) and TT-Ph-CzO (orthorhombic Pbca), all characterized by the same TT-Cz columnar aggregates. TT-Ph-CzM includes, in its a.u., one MeOH molecule, which is lost at 393 K, resulting in a singlecrystal-to-single-crystal transition to TT-Ph-CzT and, at 443 K, to TT-Ph-CzO (Fig. 34). Transformation of TT-Ph-CzM into TT-Ph-CzT was found to be reversibly accomplished through grinding and MeOH exposure.

The interconversion among the three phases was followed through thermal analysis, photoluminescence investigations and XRPD measurements.

TT-Ph-CzM crystals display multiple emissions (Fig. 35) comprising at 298 K, HEF (375 and 408 nm), LEF overlapped with HEP (425 nm) and LEP (540 nm, overall Φ = 43%) and, at 77 K, only HEF (373 and 388 nm) and LEP (523 nm). The absence of LEF and HEP at 77 K was interpreted with two possible excited state conformations, with the relaxed one

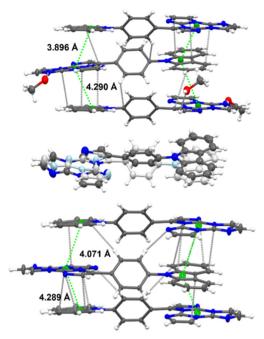


Fig. 34 Crystal structures of TT-Ph-CzM (top), TT-Ph-CzT (middle, showing the two disordered forms by different color gradation) and TT-**Ph-CzO** (bottom). In a and c, the shorter distances between triazinic and pyrrolic geometrical centroids (green spheres) and intermolecular contacts shorter than the sum of vdW radii (light grey dashed lines) are reported. Ellipsoids at 30% probability. Reproduced from ref. 81 under the terms of the Creative Commons CC BY license. Copyright 2023, John Wiley and Sons.

being not accessible at low temperature, in agreement with results obtained in solution. In addition, LEP was associated with π - π stacking interactions among **TT** and **Cz** units.

T-Ph-CzT and TT-Ph-CzO display, as well, multiple emissions but with reduced contribution from LEF/HEP at 298 K. This difference was related to the co-crystallized MeOH in TT-Ph-CzM, forming strong HBs with the TT unit. These, on one hand, provide conformational freedom to the Ph-Cz fragment resulting in LEF and, on the other hand, contribute to

Scheme 18 Chemical structures of TT-2Py and TT-4PyF derivatives.

suppressing non-radiative deactivation channels highly competitive with HEP.

These studies revealed how synergistic and different combinations of TT and a chromophoric fragment (Cz) can result in quite different emissive behaviours due to both molecular reasons and aggregation modes. Crystals of TT-(N)-Cz (both polymorphs), TT-(C)-Cz and TT-Ph-Cz, with or without cocrystallized MeOH, display one LEP band associated with π - π stacking interactions involving only the TT unit or TT and Cz units. Moreover, TT-(N)-Cz and TT-Ph-Cz are characterized by HEF of molecular origin and LEF of different nature in the two compounds: in TT-(N)-Cz LEF derives from the TT-based π - π aggregated species, while in TT-Ph-Cz it is associated with conformational freedom resulting in rigidochromic and multistimuli responsive behaviour.

3.3.5e TT-pyridines. Among TTs, 3-(pyridin-2-yl)triimidazotriazine (TT-2Py), the pyridine derivative with the pyridinic nitrogen atom in the ortho position with respect to TT (Scheme 18) is characterized by multifaceted emissive properties particularly difficult to rationalize.85 In fact, the partial rotational freedom of the pyridine ring is responsible for different metastable states, which result, in the crystalline phase, in the formation of three polymorphs and in excitation dependent emission comprising multiple fluorescence and RTP bands even in blended films. In particular, TT-2Py photoluminescence is characterized by two fluorescence components (HEF and LEF) and four phosphorescence components (HEP, MEP, two LEPs and DRP) related to the physical state of the sample.

In dilute DCM and ACN solutions at 298 K, TT-2Py displays absorption bands at about 235 and 290 nm and one emission

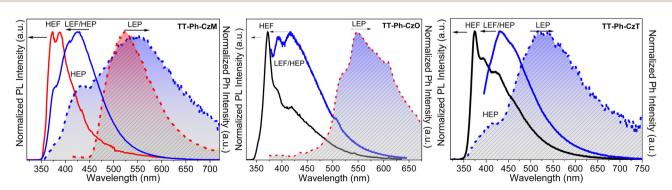


Fig. 35 Normalized PL (full lines) and delayed (dashed lines) spectra. Left: TT-Ph-CzM crystals (λ_{exc} = 300 nm) at 298 K (blue, blue dashed: delay 0.2 ms, window 0.5 ms) and 77 K (red, red dashed: delay 1 ms, window 5 ms). Middle: **TT-Ph-CzO** crystals at 298 K (black: λ_{exc} = 300 nm; blue: λ_{exc} = 370 nm; red: $\lambda_{\rm exc}$ = 360 nm, delay 1 ms, window 5 ms). Right: TT-Ph-CzT crystals at 298 K (black: $\lambda_{\rm exc}$ = 300 nm; blue full: $\lambda_{\rm exc}$ = 375 nm; blue dashed: $\lambda_{\rm exc}$ = 300 nm, delay 0.2 ms, window 0.5 ms.

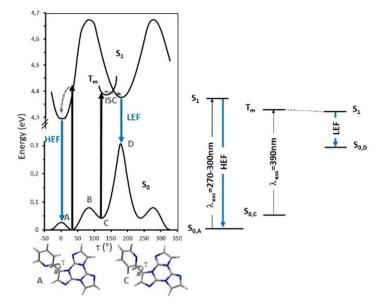


Fig. 36 Left: scans of the relaxed potential energy surfaces of S_1 and S_0 of TT-2Py along the $N_{py}-C_{py}-C_{TT}-C_{TT}$ torsion angle, τ , at the (TD)- ω B97X/6-311++G(d,p) level of theory. T_m represents a generic triplet level, A and C denote minima on S_0 and B is the barrier between the two minima. Energies are relative to the S_0 state equilibrium geometry. Right: simplified Jablonski diagram of the fluorescence components of TT-2Py

band at 350 nm ($\Phi \cong 17\%$). Detailed investigation of delayed spectra of deareated solutions and solvent-nonsolvent mixtures indicated the presence of different long-lived emissions. In particular, HEP and MEP at 345 and 380-420 nm, respectively, and two LEPs in the 490-560 nm interval, were observed.

TT-2Py crystallizes as three different polymorphs (A, Pbcn; H, $P2_1/c$ and X, $P2_1/c$ space group) depending on the recrystallization solvent (CH₂Cl₂/CH₃OH, CH₃CN/H₂O or CH₃CN, respectively). All of them display, in their crystal structure, π - π stacking interactions among TT moieties, characterized by slightly different intermolecular distances and slippage features. The TT units are further anchored to each other by several short C-H···N HBs in the plane roughly perpendicular to the stacking axis. On the other hand, the pyridinic ring is involved only in weak interactions, resulting in slightly different tilting with respect to TT (41.47, 43.7 and $37.6/39.6^{\circ}$ in A, H, and the two independent molecules of X, respectively).

According to an extensive spectroscopic, structural and theoretical investigation, LEP and DRP were attributed to dimeric or columnar π - π interactions among TT units, respectively. Noteworthily, while DRP was observed only for crystals of the polymorph with the strongest π - π interaction, the LEP components are present in all phases, including dilute solutions, where the presence of aggregated species cannot be totally excluded. The remaining emissions, namely HEF, HEP, MEP and LEF, were associated with molecular electronic states: HEF to S₁, HEP to a high energy T_n, MEP to T₁ and LEF to S₁ of a different conformer. In more detail, HEP anti-Kasha emission is due to the difficult IC from T_n to T_1 having different characters ($(\sigma/\pi,\pi^*)$ and (π,π^*) , respectively). LEF is associated with the presence, in the TT-2Py ground state (Fig. 36 left), of a local minimum (C) where the pyridinic N atom faces the TT

unit rather than on the opposite side, as found in the minimum energy geometry (A). Although conformer C is not observed in any of the TT-2Pv polymorphs, its minority presence cannot be excluded in any of the examined phases (solution, blended films and, as defects, in the crystal phase), with the two minima being separated by a low ($\cong 2$ kcal mol⁻¹) barrier (B). The two observed fluorescence components are therefore associated with radiative decay from S₁ of relaxed conformers A (HEF) and C (LEF), with the latter emission being detectable only by excluding the stronger HEF. The mechanism proposed to explain LEF, requiring population of a triplet T_m of low energy followed by ISC to S1, has been supported by pump-probe experiments.

To deepen the comprehension of the mechanisms involved in TT-2Py photophysical behaviour, blended PMMA films were exposed to acidic vapors to give TT-2PyH⁺, where a proton is added to the pyridinic nitrogen atom. According to DFT scan calculations, the conformation of the protonated species was predicted to be locked due to the formation of a strong N-H⁺···N intramolecular hydrogen bond, accessible after rotation around the TT-pyridine bond by about 180° with respect to the neutral form. Such blocked structure predicted the suppression of LEF. Moreover, all computed transitions (both singlet and triplet states) were found to be red shifted with respect to the neutral form and to possess (π,π^*) character, therefore excluding the possible presence of anti-Kasha HEP. In agreement with this finding, for TT-2PyH⁺/PMMA blended films, only one fluorescent band (at 412 nm) was observed (Fig. 37), together with a weak phosphorescent band, both at lower energy with respect to the corresponding ones of TT-2Py.

3-(2-Fluoropyridin-4-yl)triimidazo[1,2-*a*:1',2'-*c*:1",2"-*e*][1,3,5]triazine, TT-4PyF (Scheme 18), displays in dilute ACN solution at 298 K two absorption maxima at 227 and 291 nm and an

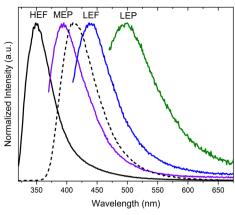


Fig. 37 Photophysical properties of TT-2Py in PMMA (TT-2Py/PMMA 10% wt) before (solid lines) and after (dashed line) HCl exposure. PL emission spectra λ_{exc} = 300 nm (black lines), λ_{exc} = 350 nm (violet), λ_{exc} = 390 nm (blue), and λ_{exc} = 450 nm (green).

intense fluorescence band at 358 nm (Φ = 50%).⁸² At 77 K, an additional long-lived contribution is present at 454 nm. Similarly, fluorescence (at 348 nm) and green phosphorescence (at 415 and 436 nm) are observed at 298 K in PMMA blended films (w/w 6%).

The compound crystallizes in the $P\bar{1}$ space group with columnar π - π (TT-TT) aggregates. Crystals of TT-4PvF are characterized by fluorescence (at 373 nm) and dual phosphorescence (HEP at 403, 424 and 446 nm, and LEP at 547 nm, Fig. 38) with overall Φ = 25%. Based on structural and

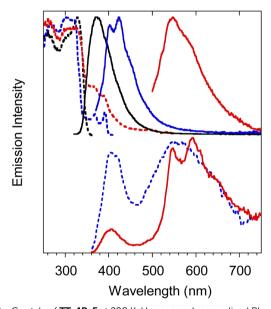


Fig. 38 Crystals of TT-4PyF at 298 K. Upper panel: normalized PL emission ($\lambda_{\rm exc}$ = 300 nm, black solid line; $\lambda_{\rm exc}$ = 360 nm, blue solid line; $\lambda_{\rm exc}$ = 480 nm, red solid line) and excitation (λ_{em} = 373 nm, black dashed line; λ_{em} = 425 nm, blue dashed line; λ_{em} = 570 nm, red dashed line) spectra. Bottom panel: Normalized phosphorescence spectra (λ_{exc} = 300 nm; delay 200 μs, window 1 ms, blue dashed line; delay 5 ms, window 20 ms, red solid line). Reproduced from ref. 82 under the terms of the Creative Commons CC BY license. Copyright 2019 by the authors. Licensee MDPI, Basel, Switzerland

computational studies, HEP has been assigned to a molecular triplet while LEP has been ascribed to π - π aggregates. The presence of a single high energy fluorescence in TT-4PvF having only one conformer further supports the hypothesis of a different conformer at the origin of LEF in TT-2Py.

3.3.6 TTs as ligands in hybrid inorganic/organic derivatives. Metal containing compounds are usually characterized by short lifetimes of their triplet states due to the strong SOC associated with the presence of the heavy metal atom, which favors both ISC and radiative deactivation through otherwise spin-forbidden paths. This heavy-atom effect is larger when the metal orbitals are involved in the luminescence transition and this is the reason why solid-state afterglow emission is extremely rare in coordination compounds.

In this regard, an additional interesting feature of TT derivatives is the presence, at the vertexes of a regular triangle, of three nitrogen atoms potentially available for coordination, leading to various metal complexes and coordination polymers especially with filled-shell d¹⁰ systems, which lack low lying ligand-field excited states and offer an opportunity to observe other excited states.

3.3.6a TT as a ligand. By reacting TT with different metal salts, either TT coordination compounds or complexes where TT molecules are cocrystallized were obtained.

In particular, four coordination compounds, namely $[Zn_3(CH_3COO)_6(H_2O)_2](TT)_2$, $[Cd(H_2O)_6](ClO_4)_2(TT)_2$, $[Cd(H_2O)_6] (BF_4)_2(TT)_2$ and $[Zn(H_2O)_6](BF_4)_2(TT)_2$, accommodating TT as a guest in their crystal lattice, were isolated and investigated to clarify the extrinsic heavy metal effect on the chromophore's photophysics.

In crystals of $[Zn_3(CH_3COO)_6(H_2O)_2](TT)_2$ the TT moieties are organized in π - π stacked columns similar to those found in TT itself (Fig. 39). 123

In agreement with this finding, crystals of [Zn₃(CH₃COO)₆-(H₂O)₂](TT)₂ display at 298 K both fluorescence (at about 400 nm) and RTUP (at about 555 nm, Fig. 40); the latter is associated with the presence of the observed stacking interactions. By comparison between the metal complex and TT, the external heavy atom effect in the intensification of the RTUP emission was disclosed.

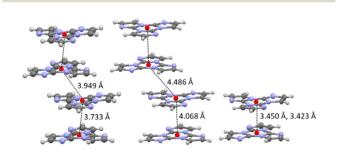


Fig. 39 Motifs of chromophore's aggregation in TT (left); [Zn₃(CH₃COO)₆- $(H_2O)_2](TT)_2$ (centre); $[Cd(H_2O)_6](ClO_4)_2(TT)_2$, $[Cd(H_2O)_6](BF_4)_2(TT)_2$ and $[Zn(H_2O)_6](BF_4)_2(TT)_2$ (right) with distances between centroids equal to 3.450 Å for the former and to 3.423 Å for the latter two. Reproduced with permission from ref. 123. Copyright 2019, John Wiley and Sons.

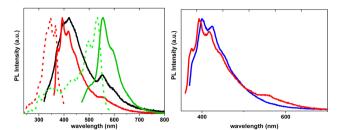


Fig. 40 Normalized PL spectra. Left: crystals of [Zn₃(CH₃COO)₆- $(H_2O)_2](TT)_2$. Emission (full lines) at λ_{exc} = 300 nm (black), λ_{exc} = 340 nm (red), λ_{exc} = 450 nm (green), and excitation (dashed lines) at λ_{em} = 416 nm (red) and λ_{em} = 600 nm (green). Right: Emission spectra of $[Zn_3(CH_3COO)_6(H_2O)_2](TT)_2$ ($\lambda_{exc} = 340$ nm, red) and TT ($\lambda_{exc} = 350$ nm,

In the three isostructural compounds, $[Cd(H_2O)_6](ClO_4)_2(TT)_2$ $[Cd(H_2O)_6](BF_4)_2(TT)_2$ and $[Zn(H_2O)_6](BF_4)_2(TT)_2$, TT molecules form stacked dimers instead of columns.

Crystals of [Cd(H₂O)₆](ClO₄)₂(TT)₂ display at 298 K a broad, featureless emission band comprising one fluorescence band (at 421 nm) and one RTUP band (at about 550 nm), which were associated with the π - π dimers. The fluorescence/RTUP intensity ratio is higher in [Cd(H₂O)₆](ClO₄)₂(TT)₂ than [Zn₃(CH₃COO)₆-(H2O)2](TT)2, indicating that RTUP is more sensitive to the supramolecular organization of the chromophores themselves (columns vs. dimers) rather than to the extrinsic heavy atom

The different heavy atom effect exerted by Cd vs. Zn was by comparing $[Cd(H_2O)_6](BF_4)_2(TT)_2$ $[Zn(H_2O)_6](BF_4)_2(TT)_2$ both showing one fluorescence band (at 383 and 370 nm, respectively) and one RTUP band (at 441 and 469 nm and 394 and 422 nm, respectively). The latter possesses a shorter triplet lifetime in the cadmium complex compared to zinc (τ = 125 ms and 542 ms, respectively), indicating higher SOC in the former.

The observed emission red-shift of $[Cd(H_2O)_6](ClO_4)_2(TT)_2$ with respect to the two other isostructural compounds was associated with the different counter ions through DFT and TDDFT calculations on TT·ClO₄ and TT·BF₄ interacting units. In fact, while HOMOs of TT·BF₄ are essentially localized on TT, those of TT·ClO₄ are delocalized on both interacting units, suggesting in the latter case charge transfer character for the S₀-S₁ transition. The CT character of emissive levels of [Cd(H₂O)₆](ClO₄)₂(TT)₂ was therefore deemed responsible for the observed red shift of its emissions.

 $Zn(\pi)$ and $Cd(\pi)$ coordination compounds with **TT** have also been obtained, in particular the cationic [Zn(TT)(NO₃)(H₂O)₃]- (NO_3) and the neutral $[Cd(TT)_2(NO_3)_2(H_2O)_2]$ complexes where TT ligands form infinite stacking columns with TT-TT distances much shorter in the former (the distance between triazine geometric centroids equal to 3.85 Å vs. 4.88-4.94 Å). 124

Crystals of the zinc complex display an intense fluorescence band (at 439 nm) with a long-lived tail (at about 550 nm) (overall $\Phi = 1\%$), which was assigned, due to crystallographic considerations, to π - π aggregates of the ligand. Comparison of the photophysical parameters (quantum yields and lifetimes) of [Zn(TT)(NO₃)(H₂O)₃](NO₃) with those of TT itself and the [Zn₃(CH₃COO)₆(H₂O)₂](TT)₂ cocrystal, having a similar organization of TT inside the structure, allowed us to conclude that the presence of Zn(II) facilitates depopulation of S₁ through ISC to a triplet level with $k_{\rm r} < k_{\rm nr}$, with the intrinsic (coordination) effect being more pronounced than the extrinsic (cocrystal) one.

Crystals of $[Cd(TT)_2(NO_3)_2(H_2O)_2]$ at 298 K show one fluorescence band (at 430 nm) and one phosphorescence band (at 505 nm), which, again based on crystallographic considerations, were identified as ligand-centered emissions.

The versatility of TT as a coordinating ligand is also manifested in the isolation of several Cu(I) and Ag(I) coordination polymers (CPs), ranging from 1D chains to 3D coordination networks, in which TT is either a monodentate or bi- and tridentate bridging ligand. 125,126 Among these, two Cu and three Ag CPs were obtained with the required high purity grade for reliable photophysical measurements. In particular, 1D doublestranded stair $[MI(TT)]_n$ and 3D $[MCI(TT)]_n$ (M = Cu, Ag) isostructural polymers and a 3D Ag(I) derivative, namely $[Ag_3(TT)_4]_n(NO_3)_{3n} \cdot 6nH_2O$, were isolated and characterized. $[MI(TT)]_n$ crystallized in the monoclinic $P2_1/c$ space group forming double-stranded stairs of $[MI]_n$ composition, decorated on both sides with monodentate TT ligands. The TT ligands on both sides of the chains are all parallel and superimposed allowing π - π stacking interactions.

Crystals of $[MI(TT)]_n$ display an excitation dependent emissive behaviour. For crystals of [AgI(TT)]_n at 298 K one fluorescence band at 385 nm and three phosphorescence bands (HEP at 411 and 445 nm, MEP at 446, 476 and 509 nm, and LEP at 494, 530, 575, 620 and 680 nm) were visible (overall Φ equal to 19%). For $[CuI(TT)]_n$ at an appropriate excitation wavelength three phosphorescence bands were observed (Φ = 18%). Two of them (MEP at 431, 460 and 487 nm and LEP at 536, 582 and 623 nm) fall in the same spectral range as that of [AgI(TT)]_n, while the third one (at 568 nm), activated only by exciting at high energy ($\lambda_{\rm exc}$ < 390 nm), is specific for [CuI(TT)]_n and assigned to a 3XMLCT state. Based on structural considerations, LEP was associated with π - π stacking interactions between TT units and MEP was associated with I···C intermolecular electronic coupling, also in view of its similarity, in both position and shape, with that observed in 1I and TT-**DITFB.**⁷¹ The structures of these four compounds are in fact characterized by comparable I···C contacts between adjacent stairs (in $[MI(TT)]_n$), helices (in 1I) and chains (in $TT \cdot DITFB$). The similarity of LEP and MEP in the two isostructural $[MI(TT)]_n$ polymers was a clear indication that the metal plays a secondary role in these emissions and can be therefore referred to as an "external" perturber. Ag(I) HEP was interpreted as due to deactivation of a ligand centered triplet state as supported by the energy spacing (about 1300–1550 cm⁻¹) of its vibrational components, which can be associated with a vibronic progression involving imidazole ring modes. The absence of fluorescence and HEP in $[CuI(TT)]_n$ was justified, through theoretical studies, with the greater metal contribution to the intramolecular emissive behaviour of copper resulting in the

suppression of fluorescence through easy ISC to close triplets and activation of the XMLCT phosphorescence. 127

3D coordination polymers $[MCl(TT)]_n$ crystallize in the cubic space group $Pa\bar{3}$. Unlike $[MI(TT)]_n$ polymorphs, the TT ligand uses the nitrogen atoms of all of its three imidazole moieties to coordinate the metal atoms. Moreover, the ligands are also involved in π - π stacking interactions. At 298 K, crystals of [AgCl(TT)]_n display an excitation-dependent emission spectrum comprising one fluorescence band (at 448 nm) and two superimposed phosphorescence bands (in the 530-615 nm range), one of molecular origin and the other assigned to TT-TT π - π dimers. For $[CuCl(TT)]_n$ only two long-lived emissions (at 515) and 560 nm) were observed, with the lowest energy one assigned as well to π - π dimers and the other to a molecular triplet. Again, the presence of fluorescence for the Ag(I) polymorph was interpreted as due to a reduced metal contribution of Ag(I) with respect to Cu(I) in the emitting states. 127

The 3D coordination polymer $[Ag_3(TT)_4]_n(NO_3)_{3n} \cdot 6nH_2O$ crystallizes in the cubic space group I43d with each silver atom coordinated to four TT molecules in a distorted tetrahedral environment and no stacking interactions between TT molecules. Its crystals display at 298 K (Φ equal to 7.5%) excitationdependent emissions comprising a broad fluorescence band (at 404 nm) and two phosphorescence bands (at 454 and 556 nm), which were related, according to DFT/TDDFT calculations, to triplet states of different nature indicating anti-Kasha behaviour.

3.3.6b TT-COOH as a ligand. Functionalization of TT with a carboxylic group provides additional sites for metal coordination. Therefore, TT-COOH was reacted with different metal salts resulting in isostructural complexes, namely [M(TT- $COO_2(H_2O_2)$ (M = Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II)).⁸⁹ They crystallize in the triclinic $P\bar{1}$ space group where the deprotonated TT-COO residue coordinates in an N,Obidentate chelate coordination mode forming a rare-met seven-membered metallochelate ring giving an extended Hbonded layer. Adjacent layers stack in a zip-like mode with partial overlap of coordinated luminophores.

Crystals of zinc and cadmium complexes, the only emissive in this series (Φ = 9 and 1.4%, respectively), display a photophysical behaviour quite similar to that of free TT-COOH. This suggests an external role of the metal (whose evidence is limited to a lower quantum yield in metal containing derivatives) as supported by DFT-TDDFT calculations. In fact, similarly to TT-COOH, two molecular fluorescence components (HEF at 338 and 352 nm for Zn and Cd, respectively; LEF at 382, 405 and 430 for both compounds) and phosphorescence components (HEP at 452 nm, MEP at 490 and 523 nm, respectively) with anti-Kasha behaviour were observed for the two complexes (Fig. 41). Moreover, an additional LEP (at 556 and 577 nm, respectively) of π - π stacked origin was present in the PL spectrum of the compounds.

3.3.6c TT-Py as a ligand. The coordination properties of TT can also be enhanced by insertion of pyridinic moieties (TT-Pys) through appropriate coupling reaction starting from nBr. This leads to the engineering of new extended hybrid

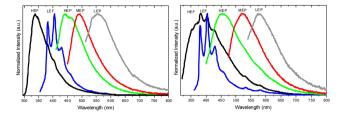


Fig. 41 Normalized PL emission spectra at RT. Left: crystals of [Zn(TT- $COO_2(H_2O)_2$] λ_{exc} = 280 nm (black); 340 nm (blue); 390 nm (green); 435 nm (red) and 493 nm (grey). Right: crystals of [Cd(TT-COO)₂(H₂O)₂] $\lambda_{\rm exc}$ = 300 nm (black); 340 nm (blue); 390 nm (green); 454 nm (red) and

supramolecular systems in which TT-Pys can act as mono-, biand tri-dentate ligands.

A series of Cu(II) coordination compounds with pyridinesubstituted derivatives, namely 3-(pyridin-2-yl)triimidazo[1,2a:1',2'-c:1'',2''-e[[1,3,5]triazine (TT-2Py) and 3-(pyridin-4-yl)triimidazo[1,2-a:1',2'-c:1",2"-e][1,3,5]triazine (**TT-4Py**), were reported. 128 In particular, a mononuclear complex [Cu(NO₃)₂- $(H_2O)_2(TT-4Pv)_2$ $\cdot 2H_2O$, a binuclear one $[Cu_2(CH_3COO)_4(TT-4Pv)_2]$ $2Py_2$, and a 1D coordination polymer $[Cu(NO_3)_2(TT-2Py)]_n$ where luminophores coordinate to the metal ion as either monodentate terminal ligands or bidentate-chelate ones, were obtained. In spite of the rich variety of structural patterns, accommodating both hydrogen bonds and $\pi \cdots \pi$ stacking interactions with different overlapping areas of the stacking ligands, the compounds are scarcely emissive in agreement with the paramagnetic character of the Cu(II) ion.

The ability of TT-2Py to act as a chelating ligand giving a seven-membered metallacycle through the nitrogen atom of the pyridinic ring and the other on the imidazolic unit, as observed in $[Cu(NO_3)_2(TT-2Py)]_n$, was exploited for the preparation of other coordination compounds. In particular, TT-2Py was reacted with Re(1) and Cu(1) further evidencing its versatility in adopting different coordination modes.

With Re(1), a mononuclear ([ReCl(CO)₃(TT-2Py)]) and a hexanuclear species ([{Re(μ -Cl)(CO)₃(μ -TT-2Py)}{Re₂(μ -Cl)₂(CO)₆}]₂) were isolated. 129 In the mononuclear complex the rhenium atom attains an octahedral geometry and bears three terminal carbonyl ligands in a facial arrangement, one terminal chloro ligand and two nitrogen atoms of the chelating TT-2Py ligand (Fig. 42), namely the nitrogen atom of the pyridyl substituent and the nitrogen atom of the triimidazotriazine moiety, similarly to what is observed in $[Cu(NO_3)_2(TT-2Py)]_n$. The hexanuclear species contains two [ReCl(CO)₃(TT-2Py)] moieties with geometry quite similar to the one of the mononuclear complexes, which bridge two additional [Re₂(µ-Cl)₂(CO)₆] fragments through the chloro ligand and a nitrogen atom of the triimidazotriazine moiety (Fig. 43).

The absorption and emission spectra of the two complexes were recorded in dilute DCM and toluene solutions, respectively. The mononuclear derivative shows two broad absorption bands at 247 and 301 nm both of which, based on DFT/TDDFT calculations, are assigned to MLCT + XLCT states. Moreover, for the lower energy transition, an additional ILCT contribution

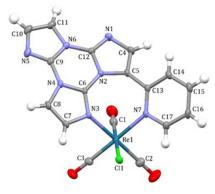


Fig. 42 View of the rhenium complex [ReCl(CO)₃(TT-2Py)] as found in its crystal structure, with a partial labelling scheme. Ellipsoids are drawn at the 50% probability level. Reproduced from ref. 129 under the terms of the Creative Commons license and with permission from the Royal Society of Chemistry. Copyright 2023.

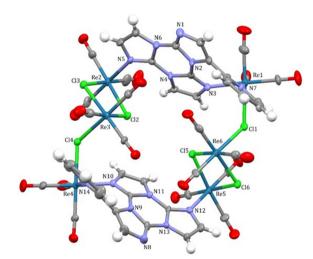


Fig. 43 View of the rhenium complex ${Re(\mu-Cl)(CO)_3(\mu-TT-2Py)}{Re_2(\mu-Cl)_2(CO)_6}_2$ as found in the crystal structure of its n-hexane solvate, with a partial labelling scheme. Ellipsoids are drawn at the 50% probability level. Reproduced from ref. 129 under the terms of the Creative Commons license and with permission from the Royal Society of Chemistry. Copyright 2023.

was predicted from calculations. The hexanuclear species displays absorption bands at 234, 264 and 320 nm, with a shoulder at 346 nm with not clearly established origin.

Upon excitation at 365 nm, the two compounds display a broad unstructured phosphorescence band (at 583 and 597 nm, Φ = 0.4 and 0.01%, for the mono- and the hexanuclear species, respectively). In the solid state, both derivatives maintain the structureless profile with a concomitant important hypsochromic shift of the phosphorescence maxima (532 and 563 nm, respectively) and increase in the photoluminescence quantum yield (12 and 2.5%, respectively). Such AIE features were attributed to restriction of the vibrational motions.

By mixing copper iodide with TT-2Py in ACN at 298 K in a 2:1 molar ratio, an orange emissive solid, namely $[Cu_2I_2(TT-2Py)]_n$, was obtained. ¹³⁰ This Cu(1) CP, crystallizing in the $P2_1/n$

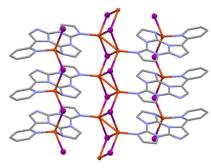


Fig. 44 View of a single monodimensional chain of $[Cu_2I_2(TT-2Py)]_n$ showing the central double stranded stair and the two lateral single zigzag structural motifs bridged by the ligand. Reproduced from ref. 130 under the terms of the Creative Commons CC BY license. Copyright 2023 by the authors. Licensee MDPI, Basel, Switzerland.

space group, is characterized by a quite rare crystal structural motif, comprising a double-stranded (CuI)₂ stair and a single CuI zig-zag chain (Fig. 44), which, among copper(1) halide based compounds, was reported in the literature only once previously (CSD Refcode GAJBEB¹³¹).

Powders of $[Cu_2I_2(TT-2Py)]_n$ display at 298 K an orange broad excitation independent emission of XMLCT character centered at 588 nm (quantum yield, Φ , equal to 7%; $\tau = 1.33 \,\mu s$) shifted to 580 nm ($\tau = 17.89 \,\mu s$) at 77 K (Fig. 45). Based on the one order of magnitude increase of lifetime upon cooling (from 298 to 77 K) and on the presence of a triplet almost isoenergetic with S_1 , a TADF mechanism at the origin of the single emission of $[Cu_2I_2(TT-2Py)]_n$ was not fully excluded.

To further investigate the coordination ability of the TT ligands, the tri-pyridinic substituted derivative, namely 3,7,11-tri(pyridin-4-yl)triimidazo[1,2-a:1',2'-c:1",2"-e][1,3,5]triazine, hereafter TT-4Py₃, having three pyridyl groups with nitrogen atoms in the *para*-position with respect to TT and oriented with a trigonal symmetry, was synthesized and reacted with Ag(I), Cd(II) and Cu(I). Three layered CPs, [Ag{(TT-4Py₃){SO₃CF₃)]_n· LancH₂Cl₂, [Cd{TT-4Py₃}(NO₃)₂(EtOH)]_n and [(Cu₂I₂)₃{TT-4Py₃}_n· xn(H₂O,EtOH) were obtained and characterized by SCXRD, XRPD, IR and photoluminescence spectroscopies and their emissive

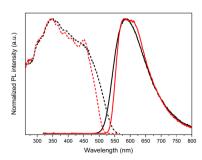


Fig. 45 Normalized excitation (dashed) and PL emission (continuous) spectra of crystalline powders of $[\mathbf{Cu_2}]_{\mathbf{z}}(\mathbf{TT-2Py})]_n$ at 298 K (black, $\lambda_{\rm em} = 588$ nm; $\lambda_{\rm exc} = 300$ nm) and 77 K (red, $\lambda_{\rm em} = 580$ nm; $\lambda_{\rm exc} = 300$ nm). Reproduced from ref. 130 under the terms of the Creative Commons CC BY license. Copyright 2023 by the authors. Licensee MDPI, Basel, Switzerland.

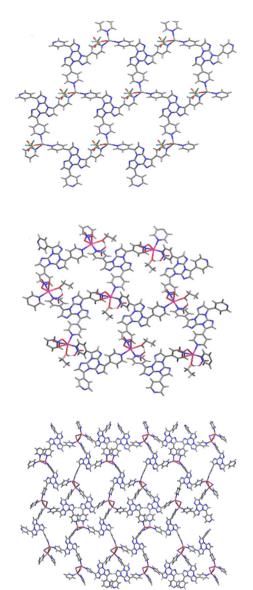


Fig. 46 Crystal structures of [Ag{(TT-4Py₃)(SO₃CF₃)]_n $\frac{1}{2}$ nCH₂Cl₂, [Cd{TT- $4Py_3$ { NO_3 }₂(EtOH)]_n and [(Cu₂I₂)₃{TT-4Py₃}₄]_n: $xn(H_2O,EtOH)$: views of a single molecular layer down the [1, 1, -1], [1, 0, -2] and [1, 0, 1] directions for [Ag{(TT-4Py₃}(SO₃CF₃)]_n $\frac{1}{2}$ nCH₂Cl₂ (top), [Cd{TT-4Py₃}(NO₃)₂(EtOH)]_n (middle) and $[(Cu_2l_2)_3\{TT-4Py_3\}_4]_n \cdot xn(H_2O,EtOH)$ (bottom). Adapted with permission from ref. 132. Copyright 2024, John Wiley and Sons.

properties were interpreted with the aid of DFT/TDDFT calculations.

 $[Ag\{(TT-4Py_3\}(SO_3CF_3)]_{n-\frac{1}{2}}nCH_2Cl_2 \text{ and } [Cd\{TT-4Py_3\}(NO_3)_2-1]_{n-\frac{1}{2}}nCH_2Cl_2$ (EtOH)]_n crystallize, respectively, in $P2_1/c$ and $P\overline{1}$ space groups to give very similar 2D coordination motifs, where the ligand acts as a trigonal donor through the pyridyl nitrogen atoms bridging three different metal ions, so that each metal is coordinated to three different ligands (Fig. 46). [(Cu_2I_2)₃{TT- $4Py_3$ ₄_n·xn(H₂O,EtOH) crystallizes in the $P2_1/c$ space group without significant inter-layer interactions between aromatic fragments except for a short distance (3.735 Å) between the triazinic centroids of two TT-4Py3 ligands belonging to two

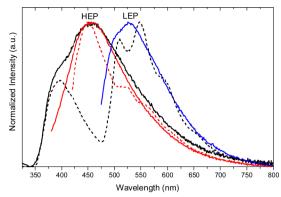


Fig. 47 Normalized PL emission spectra of [Ag{(TT-4Py₃)(SO₃CF₃)]_n· $\frac{1}{2}$ nCH₂Cl₂ crystals at 298 K (full lines) and 77 K (dashed lines); $\lambda_{\rm exc}$: 300 nm (black lines); 358 nm (red full line); 400 nm (red dashed line) and 460 nm (blue line). Adapted with permission from ref. 132. Copyright 2024, John Wiley and Sons

parallel neighboring layers (Fig. 46), according to quite strong $I \cdots \pi$ halogen bonds. ^{133–138} Powders of **TT-4Py**₃ and crystals of $[Ag\{(TT-4Py_3\}(SO_3CF_3)]_{n-\frac{1}{2}}nCH_2Cl_2$ and $[Cd\{TT-4Py_3\}(NO_3)_2-1]_{n-\frac{1}{2}}nCH_2Cl_2$ $(EtOH)_n$ display excitation dependent emissive behaviour while those of $[(Cu_2I_2)_3\{TT-4Py_3\}_4]_n \cdot xn(H_2O,EtOH)$ are characterized by a single, broad, excitation independent emission. In more detail, TT-4Py₃ shows at 298 K and an appropriate excitation wavelength, one fluorescence band (at 365 nm) and two phosphorescence bands (at 458 and 549 nm). Similarly, crystals of $[Ag\{(TT-4Py_3\}(SO_3CF_3)]_{n-\frac{1}{2}}nCH_2Cl_2$ show at 298 K one fluorescence band (at 390 nm) and two phosphorescence bands (at 460 and 530 nm) (overall $\Phi \cong 1\%$, Fig. 47). At 77 K the three emissions are still visible in slightly different positions (at 395 nm; 450 nm; 510, 548, 592 and 655 nm, respectively) but with different relative intensities with respect to that observed at room temperature suggesting different deactivation paths at the two temperatures.

Crystals of $[Cd{TT-4Py_3}(NO_3)_2(EtOH)]_n$ display at 298 K and an appropriate excitation wavelength (Fig. 48), one fluorescence band (at about 405 nm) and two phosphorescence bands (at about 455 and 550 nm, overall $\Phi\cong$ 15%), slightly shifted and better vibronically resolved at 77 K (at 346, 365, 381, 403 and 421 nm; 450 nm; 498 and 536 nm, respectively).

Interestingly, in both $[Ag\{(TT-4Py_3\}(SO_3CF_3)]_n \cdot \frac{1}{2}nCH_2Cl_2$ and $[Cd{TT-4Py_3}(NO_3)_2(EtOH)]_n$, the presence of the metal results in a red shift of the fluorescence with respect to that observed for the free ligand, while it does not affect the phosphorescence emission maxima. The latter were assigned to molecular (HEP) and supramolecular (LEP) contributions (π - π stacking arrangement of the ligands).

DFT/TDDFT calculations on both the isolated ligand and discrete models of the two compounds, comprising the metal ion and its full coordinating sphere, revealed that the set of singlet and triplet excited states display an alternation of pure (π,π^*) and mixed $(\sigma/\pi,\pi^*)$ levels, with the σ contribution mainly located on the pyridine moieties. While for TT-4Py3 the lower energy singlet states have mixed ${}^{1}(\sigma/\pi,\pi^{*})$ (S₁) or pure ${}^{1}(\sigma,\pi^{*})$ character ($S_2 \div S_4$), and T_1 is a ${}^3(\pi,\pi^*)$ state, coordination to the

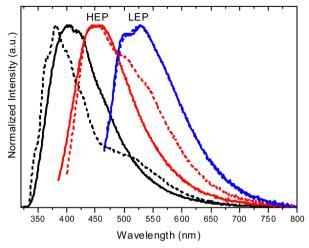


Fig. 48 Normalized PL emission spectra of [Cd{TT-4Py₃}(NO₃)₂(EtOH)]_n crystals at 298 K (full lines) and 77 K (dashed lines); λ_{exc} : 300 nm (black lines); 370 nm (red full line); 380 nm (red dashed line) and 450 nm (blue lines). Adapted with permission from ref. 132. Copyright 2024, John Wiley and Sons

Ag(I) and Cd(II) ions results in stabilization of the (π,π^*) singlets, which are located at lower energy with respect to the almost unvaried ${}^{1}(\sigma/\pi,\pi^*)$ and ${}^{1}(\sigma,\pi^*)$ ones. The low energy triplets, instead, remain almost unperturbed. This explains the observed red shift of the fluorescence emission, differently from HEP which remains energetically unaffected by complexation. Moreover, inspection of the orbitals mainly involved in the transitions revealed that in both compounds LUMOs and HOMOs are essentially ligand-centered. Only for [Ag{(TT- $4Py_3$ { SO_3CF_3] $_n$ $\frac{1}{2}nCH_2Cl_2$, however, a partial, non-negligible delocalization on the metal was calculated, resulting in a modest MLCT contribution. The absence of a metal contribution in the transitions of $[Cd{TT-4Py_3}(NO_3)_2(EtOH)]_n$ explained its much higher quantum yield compared to that of [Ag{(TT- $4Py_3$ { SO_3CF_3] $_n$ $\frac{1}{2}nCH_2Cl_2$, due to the reduction, in the former, of the 'detrimental' (from this point of view) path towards the phosphorescence emission.

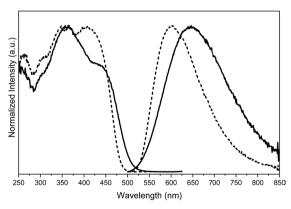


Fig. 49 Normalized PL emission (λ_{exc} : 360 nm) and excitation spectra of $[(Cu_2I_2)_3(TT-4Py_3)_4]_n \cdot xn(H_2O,EtOH)$ crystals at 298 K (full line) and 77 K (dashed lines); (λ_{em} : 645 nm full line, 602 nm dashed line). Reproduced with permission from ref. 132. Copyright 2024, John Wiley and Sons.

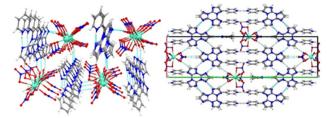


Fig. 50 Left: crystal structure of (TT-2PyH)[Eu(NO₃)₄(H₂O)₂]: fragment of the H-bonded layer. Right: crystal structure of (TT-4PyHTT-4Py)2[Eu(NO3)5(H2O)]-(CH3CN)2: fragment of crystal packing with indication of stabilising short contacts. Adapted with permission from ref. 139. Copyright 2024, American Chemical Society.

The single broad phosphorescence (at about 650 and 606 nm at RT and 77 K, respectively) observed for crystals of $[(Cu_2I_2)_3\{TT-4Py_3\}_4]_n \cdot xn(H_2O,EtOH)$ was associated with multiple contributions mainly related to the ligand itself on the basis of its long lifetime (τ = 6.36 and 34.47 ms at 298 and 77 K, respectively, Fig. 49) and DFT/TDDFT calculations, providing low energy triplet states with prevalent ILCT character.

Reaction of TT-2Py, TT-4Py and TT-4Py₃ with europium nitrate afforded two salts, namely (TT-2PyH)[Eu(NO₃)₄(H₂O)₂] and $(TT-4PyHTT-4Py)_2[Eu(NO_3)_5(H_2O)]\cdot(CH_3CN)_2$, where the protonated ligands are accommodated as guests in the crystal lattices, and a neutral complex, [Eu(NO₃)₃(H₂O)₂(TT-4Py₃)]. 139

(TT-2PyH)[Eu(NO₃)₄(H₂O)₂] shows a significant planarization of the (TT-2PyH)+ cation provided by intramolecular NH···N HBs resulting in supramolecular chains with an alternation of organic and inorganic motifs within the HB layers (Fig. 50 left). The twisted protonated TT-4Py ligands in (TT-4PyHTT-4Py)₂[Eu(NO₃)₅(H₂O)]·(CH₃CN)₂ form packed HB layers with channels accommodating the bulky inorganic anions (Fig. 50 right).

Differently, in [Eu(NO₃)₃(H₂O)₂(TT-4Py₃)], a direct coordination between one of the N-pyridine binding sites of TT-4Py₃ and the Eu(III) metal centre is present (Fig. 51).

Photoluminescence investigation of (TT-4PyHTT-4Py)₂[Eu(NO₃)₅- (H_2O)]· $(CH_3CN)_2$ and $[Eu(NO_3)_3(H_2O)_2(TT-4Py_3)]$ revealed a broad unstructured triazinic ligand-based emission with very small Eu(III) contribution for the former and an efficient ligand-metal energy transfer for the latter, as manifested by its bright red emission comprising only the characteristic emissive features of Eu(III).

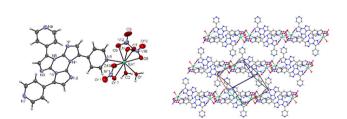
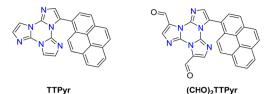


Fig. 51 Crystal structure of [Eu(NO₃)₃(H₂O)₂(TT-4Py₃)]. Left: The molecule of $[Eu(NO_3)_3(H_2O)_2(TT-4Py_3)]$ with the partial numbering scheme. The thermal ellipsoids are shown at the 50% probability level. Right: fragment of the H-bonded layer. Reprinted with permission from ref. 139. Copyright 2024, American Chemical Society.



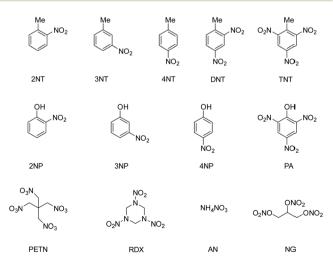
Scheme 19 Chemical structures of TTPyr and (CHO)₂TTPyr

3.4 Applications of TTs

3.4.1 TTs as sensors for explosive detection. The detection of explosives is one of the major concerns in global security and, in the past few decades, great efforts have been devoted to developing fluorescent sensors for rapid and reliable detection of low amounts of energetic hazardous chemicals and their precursors. Fluorescence-based methods have been extensively studied due to their promising advantages such as high sensitivity, selectivity and low costs; moreover, they are user-friendly and can be easily incorporated into handheld devices. 140,141

In this scenario, two emissive pyrene derivatives of TT, namely TTPyr and (CHO)2TTPyr (Scheme 19), were proposed as single-molecule fluorescent probes for the detection of various nitroaromatic energetic hazardous materials.88 The two sensors were investigated by means of fluorescencequenching titrations in solution through the incremental addition of analytes, comprising a large number of highly energetic molecules and explosives (Scheme 20). A strong attenuation of the emission intensity was observed for both compounds in the presence of nitroaromatics (phenols and toluenes) while negligible effects were recorded with aliphatic or inorganic energetic

Fluorescence quenching titrations were analysed through the Stern-Volmer (SV) equation: $I_0/I = 1 + K_{SV}[Q]$, where I_0 and Iare the emission intensities before and after addition of the quencher, respectively, [Q] is the quencher concentration and K_{SV} is the SV constant. For those analytes absorbing in the blue region (e.g. nitrophenols) and thus overlapping and affecting



Scheme 20 List of explosives tested with TTPyr and (CHO)₂TTPyr probes.

Table 1 List of the Stern-Volmer constants and LODs obtained from intensity data at 420 nm for TTPyr and at 565 nm for (CHO)₂TTPyr, (λ_{exc} = 350 nm). For the data set of TTPyr with PA, 3NP and 2NP data are calculated on the emission intensity at 490 nm while for 4NP at 500 nm in order to minimize the secondary inner filter effect

	TTPyr		(CHO) ₂ TTPyr	
Explosive	$K_{\rm SV} \left({\rm M}^{-1} \right)$	LOD (µM)	$K_{SV} (M^{-1})$	LOD (µM)
RDX	$2.30 \times 10^{+2}$	113	$1.66 \times 10^{+2}$	164
PETN	$1.74 \times 10^{+2}$	114	$-1.15 imes 10^{+1}$	_
NG (dynamite)	$2.00 \times 10^{+2}$	126	$2.17 \times 10^{+1}$	880
AN	$1.89 \times 10^{+2}$	120	$1.54 \times 10^{+2}$	146
2NT	$1.71 \times 10^{+3}$	18.15	$4.70 \times 10^{+2}$	41.62
3NT	$2.57 \times 10^{+3}$	17	$5.34 \times 10^{+2}$	30.5
4NT	$9.75 \times 10^{+2}$	28.41	$5.79 \times 10^{+2}$	29.57
DNT	$1.31 \times 10^{+3}$	18.46	$1.06 \times 10^{+3}$	31.76
TNT	$2.17 \times 10^{+3}$	8.2	$1.45 \times 10^{+3}$	10.27
2NP	$3.48 \times 10^{+3}$	12.56	$4.86 \times 10^{+3}$	3.66
3NP	$1.81 \times 10^{+3}$	24.13	$4.90 \times 10^{+3}$	7.58
4NP	$8.99 \times 10^{+3}$	4.87	$1.12 \times 10^{+4}$	2.53
PA	$1.46 \times 10^{+4}$	2.85	$1.25 \times 10^{+4}$	2.76

the 420 nm TTPvr emission according to the secondary inner filter effect, the red-shifted fluorescence of (CHO)2TTPyr at 565 nm represented a valid alternative. Evaluation of the interaction strength between probes and analytes, by means of K_{SV} and limit of detection (LOD) calculations, provided values that are quite comparable for both TT probes (Table 1), according to the following order: aliphatic and inorganic explosives < nitrotoluenes < nitrophenols, with the strongest response in the case of picric acid (PA).

Moreover, time-resolved measurements in the absence and in the presence of increasing concentration of PA or TNT were performed on TTPyr with the aim to discriminate between static or dynamic quenching. The results showed constant excited state lifetimes even at very high quencher concentration, suggesting a static quenching with formation of a non-emissive dark-complex between the probe and the analyte in the ground state. Such evidence was further supported by the isolation and characterization by SCXRD of a TTPyr/PA adduct with 2:1 stoichiometry.

In the panorama of highly energetic molecules, TT was used as a stabilizer of all-carbon-nitrated azoles, usually suffering from drawbacks such as poor thermal stability, frictional and impact sensitivities, deliquescence and hydrolysis. 142,143 By exploiting the donor properties of the electron-rich TT scaffold, three cocrystals with electron-poor acceptors, namely 5nitrotetrazole (HNT), 3,5-dinitro-1,2,4 triazole (HDNT) and 3,4,5-trinitropyrazole (TNP), were prepared (Fig. 52). 144 All

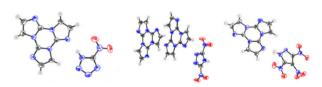


Fig. 52 Crystal structures of: (left) 1:1 TT/HNT cocrystals, (middle) 2:1 TT/HDNT cocrystals and (right) 1:1 TT/TNP cocrystals. Displacement ellipsoids are shown at the 50% probability level. Adapted with permission from ref. 144. Copyright 2022, American Chemical Society

cocrystals exhibited better performances, in terms of thermal stability and mechanical sensitivity, with respect to the pure azole components. By means of SCXRD and theoretical calculations it was suggested that the combination of strong hydrogen bonds (N-H···N, C-H···N, and C-H···O) and weak $NO_2 \cdots \pi$ and π -stacking interactions encountered in the highly energetic adducts could be responsible for their significantly improved performances.

3.4.2 TTs as ligands for bioimaging. The AIE and RTP features displayed by several TTs represent an intriguing starting point for the development of organic luminescent materials for screening, diagnosis and treatment in biomedical applications. In fact, AIE allows exploiting a wide range of molecules, including polyaromatic hydrocarbons, usually showing great photoemissive properties but low solubility in biological media. 145,146 RTP, owing to its unique long-lived signals, is particularly suitable for advanced bioimaging since it allows minimizing or even fully removing the background interference due to autofluorescence from endogenous fluorophores in biological tissues. Moreover, due to triplet exciton population, RTP probes can play an active role in phototheranostics thanks to singlet oxygen and ROS generation. 95,147

To this scope, TTPyr was selected as the test compound due to its luminescence properties such as long-lived emission, tunable emission range and high quantum yields both in solution and as a solid phase.80 Evaluation of TTPyr emissive behaviour in DMSO by adding increasing amounts of a nonsolvent (water) showed a gradual increase and a concomitant blue shift of the emission from 420 to 400 nm by increasing the water content up to 70% in volume (Fig. 53 left). Further water addition resulted in an attenuation of this emission with appearance of an additional low energy fluorescence component (associated with aggregated species) at 480 nm, the wavelength suitable for bacteria and cell imaging studies. Staining experiments with eukaryotic (HeLa and HLF) and prokaryotic (S. aureus and E. coli) cells revealed, through confocal laser scanning microscopy, that TTPyr can enter both type of cells at low concentration in an appropriate time window, locating at cytoplasm level (Fig. 53 right). In addition, MTT assays pointed out the good biocompatibility properties of TTPyr, characterized by distinct cytotoxicity towards cancer cells rather than normal cells. These findings provide useful

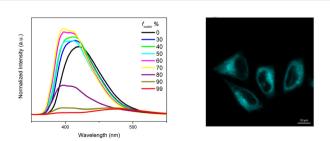
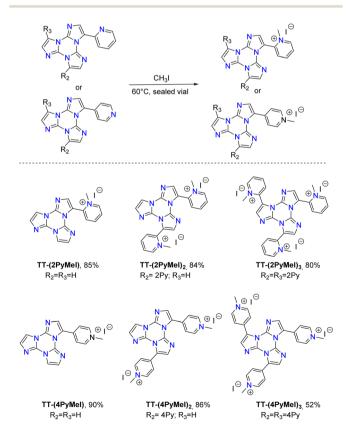


Fig. 53 Left: PL emission spectra of TTPyr (10⁻⁵ M) in DMSO/H₂O mixtures with different water fractions (f_{water}) at RT (λ_{exc} = 340 nm). Right: HeLa cell co-staining experiment (TTPyr 10 μM). Adapted with permission from ref. 80. Copyright 2021, John Wiley and Sons.

insights and indications to further expand the TT family aiming at the development of probes for the intracellular environment sensing to be potentially applied as luminescent drugs for anticancer and phototheranostic studies.

3.4.3 TTs as ligands for G-quadruplex structures. There is an extensive and ongoing research on the development of 1,3,5triazine derivatives for their biological activity in different fields spanning from anticancer, antimalarial, antibacterial, antifungal to antiviral applications. 16,148 In this regard, TT derivatives represent promising candidates to be investigated as DNA stabilizing agents, since they share certain structural features with known G-quadruplex binding ligands.

G-Ouadruplexes (G4) are non-canonical secondary structures of DNA or RNA nucleic acids that self-folds in regions rich in guanine bases organized in planar layers of four guanines (Gquartets), which are repeated inside the biopolymer sequence. 149,150 Intriguingly, it has been reported that putative G4-forming sequences are present in genomic regions and they are involved in several pathologies, such as cancer or viral infections, where they can promote or rule the genetic information transfer. Additionally, they are found to have a role in DNA repair and maintenance, 151,152 and hence there is interest in targeting G4s as an appealing and novel promising antitumor strategy. 150,153,154 There is rich literature on G4 ligands, which are characterized by some common structural features such as the presence of large planar aromatic systems, able to stack with the planar G-quartets, and the presence of polar or positively charged tails, which interact with the negatively



Scheme 21 Preparation of TT-(2PyMeI)_n and TT-(4PyMeI)_n

Scheme 22 Preparation of TT- Gn_x (x = 1-3)

charged phosphate DNA backbone and the grooves and loops of G4s. 155-157 Based on these observations, the flat aromatic TT was appropriately functionalized by the introduction of polar and hydrophilic groups. In particular, $TT-2Py_n$ and $TT-4Py_n$ series were methylated on the pyridinic nitrogen, resulting in water soluble salts with the positive charge at different distances from the central core (Scheme 21).78

In parallel, a family of polar guanyl hydrazones TT- Gn_x (x =1-3) were synthesized through imination of the corresponding formyl-TT-(CHO) $_x$ with aminoguanidine hydrochloride (Scheme 22). 158,159

The methyl pyridinium and guanyl hydrazone TTs were tested as G4 stabilizers by using sequences from the oncogene promoter regions of BCL-2, c-KIT, c-MYC (BCL2 G4, c-KIT2 G4 and c-MYC G4, respectively) and a 26-mer truncation of the human telomeric DNA sequence (Tel26 G4). A biophysical in vitro screening of the ligands was carried out by circular dichroism (CD) analysis and CD-melting experiments, to evaluate the ability of the synthesized compounds to interact and stabilize the G4 targets. The results revealed a noteworthy G4stabilizing effect for most of the tested compounds even at low concentrations, with stabilization increasing with the number of substituents on the TT core (Table 2). Moreover, a comparison of ligand-G4s affinity for the TT-(2PyMeI)_n and TT-

Table 2 Compound-induced thermal stabilization of the investigated G4s measured by CD melting experiments. $\Delta T_{\rm m}$ is the difference between the $T_{\rm m}$ of DNA in the presence (2 molar equiv.) and absence of compounds. $T_{\rm m}$ values in the absence of compounds are: Tel26 = 44.6 (\pm 0.1) °C; BCL2 = 61.7 (\pm 0.1) °C; c-KIT2 = 59.0 (\pm 0.1) °C and c-MYC = 67.9 (\pm 0.1) °C. All experiments were performed in duplicate, and the reported values are the average of two measurements

	$\Delta T_{ m m}$ (°C)	$\Delta T_{ m m}$ (°C)								
Compounds	BCL2	c-KIT2	c-MYC	Tel26						
TT-(2PyMeI)	-1.6	1.9	0.8	0.9						
TT-(2PyMeI) ₂	0.2	1.0	4.7	2.1						
TT-(2PyMeI) ₃	6.4	4.3	8.1	5.0						
TT-(4PyMeI)	3.2	7.0	2.1	6.6						
TT-(4PyMeI) ₂	13.7	15.3	3.8	16.6						
TT-(4PyMeI) ₃	>30	22.0	2.1	22.0						
TT-Gn ~~	7.2	11.0	6.2	2.3						
TT-Gn ₂	>30	27.8	10.8	8.4						
TT-Gn ₃	>30	27.7	16.9	11.7						

 $(4PyMeI)_n$ series revealed better interaction for the parasubstituted one, highlighting the importance of the positive charge distance from the central scaffold.

Förster resonance energy transfer (FRET) melting assays on the three best performing ligands, namely TT(4PyMeI)3, TT-Gn2 and TT-Gn₃, supported the remarkable stabilizing ability of the three candidates and provided evidence for better performances of guanyl hydrazone derivatives (rather than the pyridinium ones) probably due to higher flexibility of the peripheral fragments allowing more effective interactions with the grooves/loops of G4s. On the other hand, in order to estimate the ligands' selectivity for G4 over duplex DNA, FRET melting and microscale thermophoresis (MST) experiments were carried out, 160,161 overall suggesting the need for improving their selectivity toward G4 structures by an appropriate molecular design.

4. Conclusions

The present perspective comprehensively gathers studies on a promising family based on the cyclic triimidazole scaffold, a small, rigid, planar, N-rich system with excellent π - π stacking ability and with moderate electron withdrawing character. Fascinating observations have already been made by inspection of multiemissive properties and coordination potentialities of different members of the family, including the TT prototype, and the results are here analytically reported according to different classes.

Excitation dependent short and long-lived photoluminescence of molecular and supramolecular origin resulting in AIE features has been frequently disclosed. TT's multifaceted emissive behaviour, including dual fluorescence and phosphorescence, RTP from aqueous aggregates, mechanochromism and vapochromism, confirms TT as a powerful building block for designing high-performance single-component luminescent materials.

Intriguingly, some compounds possess anti-Kasha fluorescence (namely 1-3X (X = Cl, Br) and TT-Benzo) or phosphorescence (TT-2Py and $[Ag_3(TT)_4]_n(NO_3)_{3n} \cdot 6nH_2O$) or both (TT-COOH, $[Zn(TT-COO)_2(H_2O)_2]$ and $[Cd(TT-COO)_2(H_2O)_2]$). Some others possess dual fluorescence due to emission from different conformers (TT-2Py, TTPyr and TT-Ph-Cz). Finally, all compounds, except Iso-A, display π - π stacking induced phosphorescence. Interpretation of the mechanisms involved in the photophysical behaviour has been achieved through experimental, structural and computational studies. Discrimination between molecular and supramolecular features has been provided by the comparison of photoluminescence in solution and low loaded blended film with respect to crystalline phases. Further proof has been given by mechanochromism associated with supramolecular components and, when possible, comparison among polymorphs.

Preliminary applications of TTs in sensing and bio-medicine open avenues for further studies in these fields and exciting results in a plethora of applications are expected by using TT as a building block for molecular, macromolecular and supramolecular systems.

Table 3 Photophysical properties of TTs

		298 K	298 K				77 K			
Compound		$\overline{\Phi}$ (%)	Origin	λ _{em} (nm)	$ au_{\mathrm{av}}$	Origin	λ _{em} (nm)	τ_{av}	Ref.	
N	DCM	2	S ₁ -S ₀	400	7.09 ns	$\begin{array}{c} S_1 S_0 \\ T^H S_0 \end{array}$	435	14.31 ns		
$N \setminus N$	pwd	18	S_1-S_0	425	9.89 ns	S_1-S_0	500 430	0.927 s 12.32 ns		
	•	20	$T^H - S_0$	520	0.555 s	$T^H - S_0$	520	0.963 s	100	
N N N	cryst	30	S_1-S_0 T^H-S_0	400 525	7.67 ns 0.970 s	S_1-S_0 T^H-S_0	403 510	8.96 ns 1.075 s	106	
T N										
NNN	cryst	13	$S_1 - S_0$	415	2.98 ns	S ₁ -S ₀	420	14.41 ns	106	
Iso-A			S_n - S_0	333, 348	0.77 ns	S_n-S_0	333, 349	1.22 ns		
CI			$S_1 - S_0$	350	1.02 ns	$S_1 - S_0$	367, 378, 383	4.76 ns		
N N			T_1-S_0 T^H-S_0	405, 428 510	269.74 μs 25.99 ms	T_1-S_0 T^H-S_0	406, 429, 450 487, 515	1.66 ms 778.44 ms		
NNN	cryst	24				T^{σ} – S_0	558	11.92 ms	68	
1Cl N			$S_n - S_0$	329	n.d.	S_n-S_0	329, 339, 348	n.d.		
CI			S_1-S_0 T_1-S_0	397 434	1.41 ns 1.33 ms	S_1-S_0 T_1-S_0	362, 380, 401 436	1.48 ns 4.38 ms		
			$T^{H}-S_0$	481, 512, 552	49.13 ms	$T^H - S_0$	483, 515, 554	530.56 ms		
NNN	cryst	12				T^{σ} – S_0	549	12.68 ms	68	
CI										
26										
CI N			S_n-S_0	327, 341, 349	n.d.	S_n-S_0	318, 332	n.d.		
CI			$S_1 - S_0$ $T_1 - S_0$	373 416, 438	0.65 ns 13.66 ms	$S_1 - S_0$ $T_1 - S_0$	358, 380 416, 439	0.96 ns 516.60 ms		
N			$T^{H}-S_0$	492, 523	142.45 ms	$T^H - S_0$	490, 521	700.58 ms		
NNN	cryst	9				T^{σ} – S_0	550	11.22 ms	68	
201										
3CI N	DCM	3	S_n-S_0	328, 342, 358	0.68 ns	$T_1 - S_0$	580	0.276 ms		
N N Br	pwd	< 0.1	S_n-S_0	326, 345, 365, 382	0.89 ns	S_n-S_0	344, 365, 378	0.86 ns		
N N			S_1-S_0	426, 530	5.52 ns	S_1-S_0 T_1-S_0	457, 492, 530 573	2.54 ns 0.274 ms	69,70	
N N						1 0			,	
1Br N—	DCM	< 0.1	C _C	380	5.22 ns	T ₁ -S ₀	575	0.288 ms		
Br	pwd	14	S_n - S_0 S_n - S_0 T^{Br} - S_0	395, 419, 443	0.91 ns	S_n - S_0 T^{Br} - S_0	409, 434, 462	1.96 ns		
N N			$T^{Br}-S_0$ T^H-S_0	470 553, 600, 646	1.07 ms 28.85 ms	$T^{Br}-S_0$ T_1-S_0	433, 461, 484 558	4.05 ms 0.302 ms		
NNN			1 50	300, 000, 040	20.00 1113	11 00		3.002 III3	69,70	
Br D									•	
Br										
2Br										

Table 3 (continued)

		298 K 77 K							
Compound		Φ (%)	Origin	λ _{em} (nm)	τ_{av}	Origin	λ _{em} (nm)	τ_{av}	Ref.
Br N Br	DCM pwd	<0.1 <0.1	$S_n - S_0$ $S_n - S_0$ $S_1 - S_0$ $T^H - S_0$	370 394, 418, 444 415, 437 555, 605, 656	10.91 ns 1.02 ns n.d. 18.42 ms	$\begin{array}{c} {\rm T_1-S_0} \\ {\rm S_n-S_0} \\ {\rm S_1-S_0} \\ {\rm T^H-S_0} \\ {\rm T^{Br}-S_0} \\ {\rm T_1-S_0} \end{array}$	585 392, 417, 440 414, 440 545, 596, 650 490 590	0.263 ms 1.51 ns n.d. n.d. 18.11 ms 0.200 ms	69
3Br N N N	DCM cryst	<0.1	$S_1 - S_0$ $T^H - S_0$ $T_1 - S_0$	476 517, 563, 612 630	1.37 ns 63.69 ms 0.53 μs	$T_{1}-S_{0}$ $S_{1}-S_{0}$ $T^{I}-S_{0}$ $T^{H}-S_{0}$ $T_{1}-S_{0}$	630 458 460, 495, 530 511, 526, 558, 573, 610 640	27.27 μs 2.77 ns 34.85 ms 66.47 ms 23.66 μs	71
N N N	cryst	7	$S_1 - S_0 \\ T^H - S_0 \\ T_1 - S_0$	443 625 680	1.23 ns 9.47 ms 3.47 ms				71
2I N F F F	cryst	5	S_1 – S_0 T^H – S_0	410 496, 528, 566	2.56 ns 21.48 ms	$S_{1} - S_{0}$ $T^{I} - S_{0}$ $T^{H} - S_{0}$ $T_{1} - S_{0}$	440 463, 497, 537 490, 527, 560 720	3.41 ns 14.65 ms 20.01 ms 6.83 μs	71
TT-DITFB	DCM PMMA	2 3	$S_{1}\text{-}S_{0} \\ S_{1}\text{-}S_{0} \\ S^{H}\text{-}S_{0} \\ T_{1}\text{-}S_{0} \\ T^{H}\text{-}S_{0} \\ S_{1}\text{-}S_{0} \\ S^{H}\text{-}S_{0}$	363 342 383 439 522 314, 326, 338 354, 367, 377	n.d. 0.99 ns 1.46 ns 0.16 ms 6.9 ms n.d. 1.05 ns	$S_1 - S_0 \\ S^H - S_0$	310, 327, 337 354, 364, 383	n.d. 1.47 ns	87
TT-CCH NCOOH TT-COOH	DMSO cryst	3.8 26	$\begin{array}{c} T_1 - S_0 \\ T^H - S_0 \\ S_2 - S_0 \\ S_1 - S_0 \\ S_2 - S_0 \\ S_1 - S_0 \\ T_1 - S_0 \\ T_1 - S_0 \\ T^H - S_0 \end{array}$	396, 420 545 327, 343 404 342 386, 408, 432 445 487 549, 590, 642	0.25 ms 4.66 ms n.d. 3.55 ns 2.32 ns 2.75 ns 3.64 ms 5.58 ms 117 ms	$\begin{split} & T_1 - S_0 \\ & T^H - S_0 \end{split}$ $& S_2 - S_0 \\ & S_1 - S_0 \\ & T_2 - S_0 \\ & T_1 - S_0 \\ & T^H - S_0 \end{split}$	395, 419 489, 523 326, 341 385, 408, 435 457 505 549, 590, 642	6.39 ms 44.84 ms 2,51 5,51 117 ms 526 ms 1.1 s	89
N N N N N N N N N N N N N N N N N N N	DCM pwd	17 18	$S_{2}-S_{0} \\ S_{2}-S_{0} \\ S_{1}-S_{0} \\ T^{H}-S_{0}$	327, 341, 359 335, 350, 366 387, 407, 429 497, 536, 623	3.24 ns 2.61 ns n.d. 0.339 s	S_2-S_0 S_2-S_0 S_1-S_0 T^H-S_0	338, 352, 373 339, 352, 370 394, 413, 437 504, 537, 621	5.06 ns 1.93 ns n.d. 0.573 s	70
TT-Benzo									

Table 3 (continued)

		298 K				77 K			
Compound		Φ (%)	Origin	λ_{em} (nm)	$ au_{ m av}$	Origin	λ _{em} (nm)	$ au_{ m av}$	Ref.
TT-Pyr	DMSO cryst TT-Pyr(Et) TT-Pyr(RT) TT-Pyr(HT)	92 53 20 21	$\begin{array}{c} S_1 – S_0 \\ S_1 – S_0 \\ T^H – S_0 \\ S_1 – S_0 \\ T^H – S_0 \\ S_1' \\ S_1 - S_0 \\ T^H – S_0 \end{array}$	420 493 555 490 550 422, 443 483 524, 563	2.76 ns 2.97 ns 4.95 ms 1.85 ns 4.62 ms 0.62 ns 1.99 ns 23.4 ms	$\begin{array}{c} S_1 – S_0 \\ T^H – S_0 \\ S_1 – S_0 \\ T^H – S_0 \\ S_1' \\ S_1 – S_0 \\ T^H – S_0 \end{array}$	463, 493, 520 553, 596 463, 492, 520 556, 599 413, 450 478 553, 590	4.17 ns 5.37 ms 2.66 ns 5.61 ms 1.56 ns 2.91 ns 26.2 ms	79,80
	DMSO pwd	78 40.2	$S_1-S_0 S_1-S_0 T^H-S_0$	419 490 528	9.22 ns 4.64 ns 20.54 ms				79
TT-Pyr ₂	DMSO pwd	74.4 36.9	$S_1 - S_0$ $S_1 - S_0$ $T^H - S_0$	422 476 522	11.16 ns 5.12 ns 40.62 ms				79
TT-Pyr ₃	DMSO	3	$S_1 - S_0$	565	2.76 ns				88
CHO)2-11Fyr N N N N N N TT-HThio	DCM PMMA cryst Ground cryst	11 15 26	$\begin{array}{c} S_1 – S_0 \\ S_1 – S_0 \\ S_1 – S_0 \\ T_1 – S_0 \\ T^H – S_0 \\ S_1 – S_0 \\ T_1 – S_0 \\ T^H – S_0 \end{array}$	370 365 376 425, 451 497, 530, 578 376 428, 441 500	0.81 ns 0.72 ns 1.15 ns 5.91 ms 50.22 ms 1.11 ns 5.20 ms 29.81 ms	$S_{1}-S_{0}$ $S_{1}-S_{0}$ $T_{1}-S_{0}$ $T^{H}-S_{0}$ $S_{1}-S_{0}$ $T_{1}-S_{0}$ $T^{H}-S_{0}$	365 368 420, 448 494, 553, 577 375 423, 443 492, 513	1.71 ns 1.48 ns 10.61 ms 132.01 ms 1.91 ns 9.56 ms 60.84 ms	86
H ₁₃ C ₆	DCM PMMA pwd	5 17 22	$S_1-S_0 \\ S_1-S_0 \\ S_1-S_0 \\ T_1-S_0 \\ T^H-S_0$	380 372 382, 400 428, 453 514, 550	1.17 ns 0.90 ns 0.42 ns 15.10 ms 41.51 ms	$S_{1}-S_{0} \\ S_{1}-S_{0} \\ S_{1}-S_{0} \\ T_{1}-S_{0} \\ T^{H}-S_{0}$	370 364, 381 423, 447 478, 512, 544	1.42 ns 1.23 ns 153.42 ms 327.16 ms	86
TT-HThio₃									
N N N N N N N N N N N N N N N N N N N	DCM PMMA	27	$S_1 - S_0$ $S_1 - S_0$ $T_1 - S_0$	337, 345 333, 345 412, 440, 462	3.47 ns 9.58 ns 319.3 ms	S_1-S_0 T_1-S_0 S_1-S_0 T_1-S_0	339 411, 439, 466 345 411, 439, 466 ^b	5.69 ns 2.75 s 10.25 ns 82.87 ms	84
TT-(N)-Cz	cryst TT-(N)-CzT TT-(N)-CzM	13	$\begin{array}{c} S_1 – S_0 \\ S^H – S_0 \\ T_1 – S_0 \\ T^H – S_0 \\ S_1 – S_0 \end{array}$	350 379, 390, 398 442, 464 509 357, 367	2.37 ns 28.02 ns 23.36 ms 247.78 ms 3.66 ns	$S_{1}-S_{0} \\ S^{H}-S_{0} \\ T_{1}-S_{0} \\ T^{H}-S_{0} \\ S_{1}-S_{0}$	329, 343, 352 377, 385, 394 440, 465 495, 516 344, 358	4.30 ns 52.13 ns 82.87 ms 1.14 s 6.34 ns	04

Table 3 (continued)

		298 K				77 K			
Compound		Φ (%)	Origin	λ _{em} (nm)	τ_{av}	Origin	λ _{em} (nm)	τ_{av}	Ref
			$S^H - S_0$	386, 391, 402	15.39 ns	$S^H - S_0$	381, 394, 402	27.31 ns	
			T_1-S_0	437	20.04 ms	T_1-S_0	436	71.35 ms	
_			$T^{H}-S_{0}$	517	0.17 s	$T^{H}-S_{0}$	519	0.13 s	
N-1	DCM	20	S_1-S_0	380	5.55 ns	$S_1 - S_0$	365, 381	5.80 ns	
		22	0 0	2==	0.00	$T^H - S_0$	500	0.88 s	
N N	PMMA	33	$S_1 - S_0$	377	9.98 ns	S_1-S_0	361, 379	10.49 ns	
			T_1 - S_0 T^H - S_0	417	46.51 ms	T_1-S_0 T^H-S_0	412, 442	1.65 s	
$N \sim N \sim N$	oract	20		515	134.6 ms		500	0.24 s	84
	cryst	28	S_1-S_0	402, 420 460, 486	6.74 ns 57.80 ms	S_1-S_0	380, 400, 422 471	8.45 ns 0.12 s	
			T_1 - S_0 T^H - S_0	531, 580	0.12 s	T_1-S_0 T^H-S_0	500, 540	1.17 s	
TT-(C)-Cz			1 50	331, 360	0.12 3	1 50	300, 340	1.17 3	
	DCM	63	$S_1 - S_0$	350, 370	2.86 ns	$S_1 - S_0$	353	5.60 ns	
	DCM	03				$T^{H}-S_{0}$	512	935 ms	
N-	PMMA	60	$S_1 - S_0$	347, 360	7.70 ns	$S_1 - S_0$	350 (90 K)	8.79 nsb	
			$T^H - S_0$	490	246.8 ms	$T^{H}-S_{0}$	508	601.0 ms	
N	cryst TT-Ph-CzM	43	$S_1 - S_0$	375, 408	2.16 ns	S_1-S_0	373, 388	3.45 ns	
			$T_1 - S_0$	425	20.72 ms				
M N N		22	$T^{H}-S_{0}$	540	60.94 ms	$T^H – S_0$	523	684.47 ms	81
	TT-Ph-CzT	22	S_1-S_0	374, 394	3.41 ns				
			T_1 – S_0 T^H – S_0	432	3.03 ms				
TT-Ph-Cz	Transla C. C.	0.2		510	10.61 ms				
	TT-Ph-CzO	23	S_1-S_0	373	3.49 ns 15.04 ms				
			T_1 - S_0 T^H - S_0	416	62.16 ms				
				550 251		c c	205 245	0.20 nc	
	DCM	17	S_1-S_0	351	0.62 ns	S_1-S_0	325, 345	2.32 ns 13.16 ms	
	DCM	17	T_n - S_0	408	10.2 ms 11.01 ms	T_n-S_0 T_1-S_0	375 393	13.10 1118	
	PMMA		T_1-S_0 S_1-S_0	350	1.18 ns	1 ₁ -5 ₀	393		
	1 14114171		$T_1 - S_0$	394	13.73 ms				
			$S'_1 - S'_0$	440	3.47 ns				
N			$T^{H}/-S_0$	530	15.70 ms				
	cryst TT-2Py-A	52		370	698 ms				
	ciyst 11-2Py-A	52	T_n - S_0		0.29 ms				
// N N			T_1-S_0	418 450	0.29 IIIS —				
			$S_1'-S_0'$ $T^{H}'-S_0$						0.5
N N N	TTD OD II			510, 570, 608	2.09 ms				85
	TT-2Py-H		T_n - S_0	374	20.38 ms				
			T_1-S_0	408	0.47 ms 1.91 ns				
TT-2Py			$S_1'-S_0'$	450					
,			$T^{H}'-S_0$	500	18.25 ms				
	TT OD. V		тс	528, 562, 610	5.98 ms 91.83 ms				
	TT-2Py-X		T_n - S_0	362					
			T_1-S_0	402	1.31 ms				
			$S_1' - S_0'$	466	4.13 ns				
			$T^{H}/-S_0$	524	9.38 ms				
N			$T^H - S_0$	636, 695, 767	111.1 ms				
N			S_1-S_0	365	1.25 ns				
\\			T_1 - S_0 T^H - S_0	458 549	6.31 ms				
			1 -30	349	66.41 ms				
N=\N									
., N	pwd	_							132
N /									
N~									
TT-4py ₃									
N ~	ACN	50	$S_1 - S_0$	358	4.26 ns	$S_1 - S_0$	344	4.04 ns	
		30				$T_1 - S_0$	454	1.63 s	
N. N	PMMA		S_1-S_0	348	1.89 ns				
			$T_1 - S_0$	415, 436	3.09 ms	_			0.0
N N F	cryst	25	S_1-S_0	373	4.77 ns	S_1-S_0	385	16.42 ns	82
			$\begin{matrix} \mathbf{T_1}\text{-}\mathbf{S_0} \\ \mathbf{T^H}\text{-}\mathbf{S_0} \end{matrix}$	403, 424, 446	11.64 ms	T_1-S_0	401, 425, 457	12.95 ms	
			$T^{-1}-S_0$	546, 592	419.08 ms	$T^{H}-S_{0}$	549	1.93 s	
TT-4PyF									

Table 3 (continued)

		298 K				77 K			
Compound		$\overline{\Phi}$ (%)	Origin	λ _{em} (nm)	$ au_{ m av}$	Origin	λ _{em} (nm)	$ au_{\mathrm{av}}$	Ref.
Hybrid inorganic/organic derivative	s								
$[Zn_3(CH_3COO)_6(H_2O)_2](TT)_2$	cryst	7	$S_{1}-S_{0}$	375, 395, 418	6.75 ns	$S_1 - S_0$	416	8.45 ns	123
		40	$T^H - S_0$	555	0.650 s	$T^{H}-S_{0}$	554	1.303 s	400
[Cd(H2O)6](ClO4)2(TT)2	cryst	10	S_1-S_0 T^H-S_0	421 549	5.17 ns	S_1-S_0 T^H-S_0	440	5.50 ns	123
[Cd(H ₂ O) ₆](BF ₄) ₂ (TT) ₂	cryst	16	$S_1 - S_0$ $S_1 - S_0$	383	0.110 s 17.16 ns	$S_1 - S_0$ $S_1 - S_0$	550 390	0.585 s 18.63 ns	123
	crysc	10	$T^H - S_0$	441, 469	0.293 s	$T^H - S_0$	441, 471	0.753 ms	120
$[Zn(H_2O)_6](BF_4)_2(TT)_2$	cryst	9	$S_1 - S_0$	370	3.52 ns	$S_1 - S_0$	371	5.66 ns	123
- , , , , , , , , , ,			$T^{H}-S_{0}$	394, 422	0.542 s	$T^{H}-S_{0}$	397, 422	1.29 s	
[Zn(TT)(NO3)(H2O)3](NO3)	cryst	1	S_1 - S_0 T^H - S_0	439	4.36 ns	S_1-S_0 T^H-S_0	430	5.93 ns	124
[Cd(TT) ₂ (NO ₃) ₂ (H ₂ O) ₂]	cryst		$S_1 - S_0$ $S_1 - S_0$	550 430	67.70 ms 0.61 ns	$S_1 - S_0$ $S_1 - S_0$	498 430	534.63 ms 2.15 ns	124
[Cu(11)2(NO3)2(112O)2]	Clyst		$T^H - S_0$	505	32.69 ms	$T^H - S_0$	500	240.96 ms	124
$[Ag(TT)I]_n$	cryst	19	S_1-S_0	385, 400	2.15 ns	S_1-S_0	386, 395	2.31 ns	126
			T_1-S_0	411, 445	$<$ 50 μs	T_1-S_0	425, 446	$421.03~\mu s$	
			$T^{1}-S_{0}$	446, 476, 509	2.84 ms	$T^{I}-S_{0}$	440, 470, 506,	5.67 ms	
			TT. C	404 520 575	20.76	т с	541	44.54	
			T_H – S_0	494, 530, 575, 620, 680	39.76 ms	T_H-S_0	490, 528, 576, 631, 701	44.51 ms	
[Cu(TT)I]n	cryst	18	$T_1 - S_0$	568	32 μs	$T_1 - S_0$	568	47.14 μs	125,
[(-)]	Jan		$T^{I}-S_{0}$	431, 460, 487	_ '	$T^{I}-S_{0}$	430, 460, 494,	•	126
							538		
F. (-) -77			T_H-S_0	536, 582, 623	302.12 μs	T_H-S_0	529, 580, 627	1.03 s	
$[Ag(TT)Cl]_n$	cryst		S_1-S_0	448	4.45 ns				126
			T_1 - S_0 T_H - S_0	520 526, 565, 615	— 47.7 ms				
$[Cu(TT)Cl]_n$	cryst	4	$T_1 - S_0$	515	6.24 μs				125,
[()]n	,	_	$T_H - S_0$	560	3.56 ms				126
$[Ag_3(TT)_4]_n(NO_3)_{3n} \cdot 6nH_2O$	cryst	7.5	$S_1 - S_0$	404	1.49 ns	$S_1 - S_0$	391	1.76 ns	126
			T_n - S_0	454	3.41 ms	T_n-S_0	471	32.69 ms	
[7. (TT COO) (T O)]		0	T_1-S_0	556	1.04 ms	$T_1 - S_0$	565	33.36 ms	00
$[Zn(TT-COO)_2(H_2O)_2]$	cryst	9	S_2 - S_0 S_1 - S_0	338 382, 405, 430	0.88 ns 1.94 ns				89
			$T_2 - S_0$	452	1.42 ms				
			$T_1 - S_0$	490	4.3 ms				
			$T^H - S_0$	566	478 ms				
$[Cd(TT-COO)_2(H_2O)_2]$	cryst	1.4	$S_2 - S_0$	352	0.77 ns				89
			S_1-S_0	382, 405, 430	1.59 ns 2.04 ms				
			$T_2 - S_0$ $T_1 - S_0$	452 523	10.4 ms				
			$T^{H}-S_{0}$	577	116 ms				
[ReCl(CO) ₃ (TT-2Py)]	Tol	0.4	T_1-S_0	583	483 ns				129
	pwd	12	$T_1 - S_0$	532	100 ms				
[Re3Cl3(CO)9(TT-2Py)]2	Tol	0.01	T_1-S_0	597	500 ns				129
$[Cu_2I_2(TT-2Py)]_n$	pwd	2.5	T_1-S_0	563	40 ms	тс	500	17.00 ms	120
$ \begin{bmatrix} Cu_2I_2(TT-2Py)]_n \\ [Cu_2I_2(TT-2Py)]_2 \end{bmatrix} $	cryst	7.3 44	T_1-S_0 T^I-S_0	588 515	1.33 ms 9.35 μs	T_1-S_0 T^I-S_0	580 513	17.89 ms 27.93 μs	130
	crysc		$T^H - S_0$	598	19.07 μs	$T^H - S_0$	596, 645	1.73 ms	
$[Ag{(TT-4Py_3)(SO_3CF_3)]_{n-\frac{1}{2}}nCH_2Cl_2}$	cryst	1	$S_1 - S_0$	390	1.66 ns	$S_1 - S_0$	395	1.96 ns	132
- · · · · · · · · · · · · · · · · · · ·			$T_1 - S_0$	460	0.836 ms	$T_1 - S_0$	450	1.35 ms	
			$T^H - S_0$	530	4.912 ms	$T^{H}-S_{0}$	510, 548, 592,	262 ms	
[Cd(TT 4Dy)(NO) (EtOH)]	oract	15	e e	405	0 F4 ng	6 6	655	2.60 pc	120
$[Cd{TT-4Py3}(NO3)2(EtOH)]n$	cryst	15	S_1-S_0	405	2.54 ns	S_1-S_0	346, 365, 381, 403, 421	2.69 ns	132
			$T_1 - S_0$	455	12.62 ms	$T_1 - S_0$	450	73.88 ms	
			$T^H - S_0$	550	74.63 ms	$T^H - S_0$	498, 536	1.86 s	
$[(Cu2I2)3{TT-4Py3}4]n·xn(H2O,EtOH)$	cryst	≈ 1	$T^H - S_0$	650	6.36 ms	$T^H - S_0$	606	34.47 ms	132
$(TT-4PyHTT-4Py)_2[Eu(NO_3)_5(H_2O)]$	cryst		$S_1 - S_0$	450					139
$(CH_3CN)_2$	orust		${}^{5}D_{0} - {}^{7}F_{2}$	618	202				120
[Eu(NO3)3(H2O)2(TT-4Py3)]	cryst		$^{5}D_{0}-^{7}F_{2}$	618	283 μs				139

 T^{σ} : triplet of (π, σ^*) symmetry, T^{Br} : triplet located on the Br halogen bond; T_n : high energy triplet; S_n : high energy singlet; T^I : triplet associated with the extrinsic I effect, S'_0, S'_1 : S_0 , S_1 from a second conformer; S^H : singlet from π - π aggregates; T^H : triplet from π - π aggregates; T^H : triplet from π - π aggregates; T^H : triplet from T^H : trip

A close control of the excited-state energy, which is essential for the development of triplet exciton-harvesting organic emitters, such as those with TADF and RTP, is far from being reached and needs further investigations through appropriate functionalization of the TT core with donor groups. 57,58 When compared with other fused nitrogen-rich heterocycles, TT enables the preparation of asymmetric scaffolds: brominated derivatives have been revealed as convenient starting materials in C-C and C-N cross-coupling reactions, and therefore, donor-acceptor groups can be introduced on the core by properly reacting 1-2Br.

The presence of three exo-oriented nitrogen atoms on the TT scaffold, its relatively simple functionalization with coordinating groups and the possibility to prepare mono-, di- and trisubstituted systems make TTs particularly attracting in view of their further exploitation in coordination chemistry and isolation of porous metal-organic frameworks (MOF). In addition, tri-substituted TTs with C_3 symmetry represent appealing building blocks for the production of covalent organic frameworks (COF), as reported for other π -extended conjugated multiazine or H-bonded organic frameworks (HOF), by fine tuning pendant groups around the central core. Moreover, because of their octupolar character, appropriately functionalized tri-substituted TTs represent suitable candidates for NLO applications and as chromophores for multiphoton absorption.

Due to their planar and prochiral nature, TTs can be exploited for the development of self-organized homochiral two-dimensional nanostructures on different surfaces to be used, for example, in the preparation of graphene-like structures.

A further challenge regarding this family is the application of iso-A, the TT isomer, in the preparation and characterization of molecular and supramolecular materials analogous to those of TT. Moreover, iso-A utilization in the preparation of carbene compounds (through salification of the asymmetric nitrogen and subsequent reaction with metals) as preliminarily reported in the literature⁶⁴ deserves further investigation.

Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this perspective.

Conflicts of interest

There are no conflicts to declare.

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