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Crystal Engineering of Room Temperature Phosphorescence in Organic Solids

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Abstract: We report a series of highly emissive azatriangulenetrione (TANGO) solids in which the luminescent properties are controlled by engineering the molecular packing by adjusting the steric size of substituents. The co-alignment of 'phosphorogenic' carbonyl groups within the π -stacks results in an almost pure triplet emission in HTANGO, TCTANGO, TBTANGO and TITANGO, while their rotation by ~60° in the sterically hindered *t*BuTANGO leads to an almost pure singlet emission. Despite strong π -interactions, aggregation-induced quenching and triplet-triplet annihilation are avoided in HTANGO and TCTANGO which display efficient phosphorescence in the solid state. To our knowledge, HTANGO with the solid-state phosphorescence quantum yield of 42% at room temperature is the most efficient phosphor composed of the 1st/2nd raw elements only.

There is a rapidly growing interest in organic room temperature phosphorescent (ORTP) dyes as alternatives to traditional inorganic/metalorganic phosphors.^[1] Their potential applications includes time-gated biological imaging/sensing,^[2] anticounterfeiting and data encryption,^[3] high-efficiency light-emitting diodes,^[4] improving charge generation in photovoltaic devices,^[5] phosphorescence nanowire lasing^[6] and amplified upconversion emission.^[7] ORTP emitters carry several potential advantages over their heavy metal containing counterparts such as lower toxicity, and environmental footprint, longer lifetimes, low-cost processing, and vast opportunities for tuning their photophysical properties.^[3b, 8]

Phosphorescence is a spin-forbidden radiative decay of the lowest-energy triplet state T₁ which can be formed from a singlet excited state (S1) via intersystem crossing (ISC). However, in most organic materials the ISC is very slow and generally cannot compete with fluorescence and non-radiative decays. A common approach to design phosphorescence in organic compounds is the incorporation of heavy atoms such as Br, I, S, Te which enhance the spin orbit coupling (SOC).[9] Another strategy to enhance the SOC is coupling $n-\pi^*$ and $\pi-\pi^*$ transitions with different angular momentum, that can be realized in carbonyl (C=O) containing derivatives.^[2, 3b, 8a, 9e, 10] Apart of efficient ISC, achieving ORTP also requires suppressing the competing nonradiative decay, usually realized through embedding phosphorescent molecules in a rigid (polymer^[10c, 11] or crystal^[9b]) matrix. A dilute concentration of the phosphor in such solid solutions is generally required to avoid their deactivation via triplet-triplet annihilation.

In the last few years, several pure ORTP solids have been reported.^[8b, 9a, 10b, 10d] With few exceptions,^[12] their molecular design is based on non-planar flexible structures that limit π - π interactions in the solid state resulting in 'aggregation-induced emission'. The pioneering B.Z. Tang's work explicitly cites "carbonyl group, halogen atom and nonplanar conformation" as the key for the design of ORTP solids.^[10b, 13] Several other groups have found ORTP in the crystals of similar nonplanar molecules, although in most cases the overall emission is still dominated by fluorescence.^[3b, 8a, 10a, 14]

The role of molecular packing in defining the singlet/triplet exciton dynamics in the solids is widely acknowledged but still poorly understood. W. Huang, X. Lui and coworkers proposed H-aggregation as a design principle for stabilization of triplet excitons. The authors have indeed achieved an ultralong (>1 s) phosphorescence in various carbazole derivatives, although in all cases the fluorescence channel still dominated the emission.^[14a,b] Bryce and coworkers proposed that the ISC is enhanced by intermolecular electronic coupling of the " π " (carbazole) and "n" (carbonyl or sulfonyl) moieties, and demonstrated that pure (fluorescence-free) ORTP (PLQY ~5%) can be achieve in such organic solids when substituted with bromine.^[16] Several groups have further studied the effect of solid state structure on phosphorescent properties through permutation of substituents in the molecule.^[2a, 8a, 14c, 15] However, predictability of the induced changes and the generality of the deduced structure-properties relationships are limited by the complexity of the crystal packing of these low-symmetry molecules. The rational control of the solid-state packing and crystal engineering of ORTPs to design efficient organic phosphors is still missing in the field.

To address this problem, we synthesized a family of planar carbonyl-bridged D_{3h} symmetric triphenylamine derivatives (azatriangulenetriones (TANGOs,^{a)} Scheme1) that display efficient luminescence in the solid state. By adjusting the size of substituents, we can control the molecular orientation within the π -stacks and switch from an almost pure fluorescence to pure phosphorescence. The parent unsubstituted TANGO (HTANGO) shows phosphorescence quantum yields of $42 \pm 2\%$ (in air) and lifetime of 28.6 ms. This is among the highest efficiencies reported for ORTP in pure solids without a heavy atom effect, i.e. made of only light atoms (H, C, N, O). We investigated the effects of the molecular structure and crystal packing on the luminescence of different TANGO derivatives and carried out time dependent density functional theory calculations (TD-DFT) to shed light on the observed relationships.

The TANGO derivatives were synthesized from substituted triphenylamine derivatives 1-3 (Scheme 1) and purified by Soxhlet extraction followed by multiple vacuum sublimations (performed until the solid-state emission spectra remain unchanged). TGA analysis of all TANGO derivatives shows a remarkable thermal stability (T_{dec} > 400 °C in air, Figure S1). With exception of *t*BuTANGO, TANGO derivatives are scarcely soluble in organic solvents. Solutions with µM concentrations can be also prepared in chloroform for HTANGO and TCTANGO (but not TBTANGO and TITANGO). Solution UV-Vis absorption of HTANGO shows a strong vibronically structured π - π^* absorption band at λ^{abs}_{max} = 408 nm which slightly red-shifts in TCTANGO (429 nm) and tBuTANGO (422 nm) (Figure 1a-c). Upon UV excitation all three solutions reveal a deep blue emission with relatively low photoluminescence quantum yields (PLQY) of 1%, 5% and 13% for HTANGO, TCTANGO and *t*BuTANGO, respectively. The emission maxima ($\lambda^{F}_{max} = 422$, 445 and 440 nm for HTANGO, TCTANGO and tBuTANGO, respectively) follows the same trend as the absorption, with similar small Stokes shift of ~0.13 eV.



Figure 1. a-c) Absorption (blue) and emission (steady state at room temperature, black; 0.2 ms delayed at 77 K, green) of HTANGO, tBUTANGO and TCTANGO in chloroform solutions. d-h) Solid state absorption (blue), steady state (black) and delayed (red) emission of TANGO solids at room temperature and i) corresponding phosphorescence lifetime. The arrows in (d-h) show Stokes shifts.

Scheme 1. Synthesis of TANGO derivatives: a1) NCS, MeCN; a2) PyH+Br3-, EtOH/benzene; a₃) l₂, Ag₂SO₄, EtOH; b) FeCl₃, t-BuCl; c) KOH, MeOH/H₂O; d) SOCI₂/DMF, SnCI₄, CH₂CI₂.



Their emission shows a monoexponential decay with the lifetime τ^{F} = 3.5 ns (HTANGO), 3.9 ns (TCTANGO) and 0.9 ns (tBuTANGO) indicating the fluorescence nature of the emission (Figure S4). No detectable delayed (>0.1 ms) emission was observed in these solutions at room temperature and their emission spectra were not affected by the presence of air oxygen. Nevertheless, the ISC does take place in all three derivatives, as expected in aromatic ketones.^[18] In frozen solutions at 77K, the delayed emission can be detected by a naked eye (Figure S5) and the emission spectra show vibronically structured phosphorescence bands at λ^{P}_{max} =461 nm (τ^{P} = 145 ms), λ^{P}_{max} = 487 nm (τ^{P} = 91 ms) and λ^{P}_{max} = 498 nm (τ^{P} = 464 ms) for HTANGO, TCTANGO and tBuTANGO, respectively. A broad shoulder in the HTANGO spectrum at ~550-600 nm (not observed for TCTANGO and tBuTANGO) might be due to partial aggregation upon freezing.

In the solid state HTANGO shows a significantly red-shifted emission with λ^{P}_{max} = 538 nm and lifetime of τ^{P} = 28.6 ms (Figures 1d, i). Its total emission ($t_d = 0$ ms) and delayed emission ($t_d = 0.2$ ms) spectra are nearly superimposable, showing the dominance of the phosphorescence pathway (Figure 1d). The PLQY was found to be 42 \pm 2% for the single crystals of HTANGO (25 \pm 3% for vapor deposited films). TCTANGO solid displays a similar photoluminescence behavior: a red-shifted emission with λ^{P}_{max} = 560 nm and τ^{P} = 6.7 ms (PLQY of 26%). The shorter phosphorescence lifetime of TCTANGO comparing to HTANGO is likely attributed to the heavy atom effect. Indeed, the lifetime further decreases for the heavier TBTANGO (τ^{P} = 2.8 ms; λ^{P}_{max} = 570 nm) and TITANGO (τ^{P} = 0.8 ms; λ^{P}_{max} = 589 nm), albeit with low PLQY (~1.5% for TBTANGO, ~1% for TITANGO).

A completely different behavior, however, was observed in the solid state of tBuTANGO which displays a less pronounced redshift vs solution (λ^{F}_{max} = 495 nm) and same fast radiative decay $(\tau^{F} = 10.0 \text{ ns})$ revealing an almost ^{b)} pure fluorescence with PLQY = 11% (Figures 1f and S4d). The striking difference between the luminescence lifetimes of the TANGOs was visualized with a highspeed camera (SI video) which reveals a progressively diminishing afterglow in the order $\tau_{HTANGO} >> \tau_{TCTANGO} > \tau_{TBTANGO}$ τ_{TITANGO}. Such behavior of TANGO derivatives coupled with their remarkable environmental stability could find applications in pigments for advanced encrypted codes (which use specific delay time and wavelength for decryption).^[3a] The observed differences in the solid-state emission of the TANGO derivatives cannot be fully attributed to molecular effects. All three soluble TANGO derivatives showed similar photoluminescence properties in solution, with mild red-shifts of $\lambda^{\text{F}}_{\text{max}}$ due to CI and tBusubstituents and comparable lifetimes (~1-4 ns). We have performed TD-DFT calculations (B3LYP/6-31G(d)) for optimized molecules in gas phase in both singlet and triplet states and carried out natural transition orbital (NTO) and spin-orbit coupling (SOC) analysis (Figures S6, S7). According to El-Sayed's rules, the ISC is favored for transitions between ${}^{1}n\text{-}\pi^{*}$ and ${}^{3}\pi\text{-}\pi^{*}$ ${}^{[18]}$



Figure 2. Crystal structure of TANGOs showing molecular orientation within π -stacks, in the top (a) and side view (b), and in theadjacent stacks (c). The arrows in (a) show molecular displacement in the stacks, along the O=C...N axis. The red balls in (b) represent the oxygens highlighting the eclipsed (HTANGO, TCTANGO, TBTANGO, TITANGO) and staggered (TBuTANGO) packing; the arrows show interplanar distances. The arrows in (c) show Br...O and I...O halogen bonds

NTO analysis indeed predicts ${}^{1}n-\pi^{*}$ to ${}^{3}\pi-\pi^{*}$ transition for HTANGO and TITANGO, but pure $\pi-\pi^{*}$ singlets and triplets are predicted for all other TANGOs. The resulting high SOC_{S1→T1} for HTANGO (45 cm⁻¹) and TITANGO (88 cm⁻¹) can indeed contribute to efficient ISC of these two compounds but leaves unexplained the observed trend of the phosphorescence efficiency: HTANGO > TCTANGO >> TBTANGO > TITNAGO and almost complete lack of phosphorescence in *t*BuTANGO solid state.

In order to understand the effects of molecular packing on the photoluminescence of TANGOs, their single crystals were grown via physical vapor deposition. X-ray crystallographic analysis reveals that all TANGO derivatives are nearly planar (out of plane deviation <0.33 Å) and pack in one-dimensional slipped π -stacks with interplanar distances of 3.40-3.46 Å (Figure 2). According to crystal structures of TANGOs, the major difference in their packing relates to the alignment of the transition dipoles (N...C=O $\leftrightarrow N^+...C-O^-$) within the stack. These dipoles are co-parallel in all TANGO derivatives except for tBuTANGO, where the steric hindrance of t-butyl group forces the adjacent molecules to rotate 60° versus each other to maintain the π - π interactions. Accordingly, the absorption (i.e. $S_0 \rightarrow S_1$ transition) of *t*BuTANGO in the solid state shows a large bathochromic shift (0.27 eV) vs that in solution, while only a small ~0.1 eV shift was observed for HTANGO and TCTANGO (Figure S2). This difference is reminiscent of J-/H-aggregation in dipolar fluorescent dyes, where the J-aggregation results in large red-shift of the absorption /emission wavelength (versus those of the individual dye molecules in solution) enhancing the oscillator strength of the S₀ \leftrightarrow S_1 transition and H-aggregation causes the opposite effect resulting in optically inactive "dark" singlet excited state.[19]

To shed further light on the role of crystal packing on the excited state properties , TD-DFT calculations were performed for the π -stacked TANGO dimers with varied dihedral angle α between their N...C=O dipoles representing the different rotation of the molecules within π -stacks (Figure 3). The $S_1 \rightarrow S_0$ oscillator strength is zero for α = 0° (corresponding to HTANGO packing) but it increases to 0.063 for α = 60° (corresponding to tBuTANGO packing). As a result, the singlet excited state of tBuTANGO undergoes a fast (fluorescence) decay ($\tau^{\rm F}$ = 10 ns), while the optically inactive singlet excitons in HTANGO (and TCTANGO/TBTANGO/TITANGO) persist for sufficiently long times for ISC.

The reason for the lower phosphorescence quantum yield of TBTANGO and TITANGO comparing to HTANGO and TCTANGO is less obvious. The larger halogen atoms lead to more slipped π -stacks: the displacement along the O=C...N axis increases from 1.86 Å for HTANGO and 1.89 Å for TCTANGO, to 2.02 Å for TBTANGO and 2.46 Å for TITANGO (Figure 2a). These changes can affect the coupling of triplet excitons in terms of transition from a phosphorescence-promoting H-aggregation to Jaggregation.^[14a] The previous work has have attributed solid state phosphorescence in bromobenzaldehyde derivatives to halogen bonding between the bromine and carbonyl groups.[9e] In our case, the halogen bonding interactions have been observed in TBTANGO (O...Br = 3.18 Å) and TITANGO (O...I = 3.05 Å) (Figure 2c) but their phosphorescence is much weaker than that of HTANGO and TCTANGO which lack such interactions. The inconsequential role of the halogen bonds is probably explained by the weak exciton coupling between the stacks (N...N distances 9.40-14.20 Å), comparing to that within the stacks (N...N distances 3.52-4.15 Å). However, we cannot exclude the possible role of defects, particularly for TITANGO with weak C-I bonds.



Figure 3. TD-DFT calculated oscillator strength of TANGO π -dimers as a function of their rotational alignment ($\alpha = 0^{\circ}$ and 60° correspond to crystal packing of HTANGO and *t*BuTANGO, respectively).

In summary, we introduced a new class of emissive azatriangulenetrione pigments whose crystal packing can be designed by tuning the bulkiness of substituent. Using X-ray crystallography we showed that all derivatives pack in columnar

 π -stacks with the relative molecular orientation controlled by the size of the substituent: the t-butyl group causes 60° rotation resulting in almost pure fluorescence (*t*BuTANGO, PLQY = 11%) while smaller side groups (H, Cl, Br, I) lead to co-aligned π -stacks and these derivatives display pure phosphorescence emission at room temperature with PLQY of up to 42% (for HTANGO). The latter sets a new record of efficiency of room temperature phosphorescence in pure organic solids in the absence of the heavy atom effect. Achieving efficient phosphorescence in densely packed solids with strong π - π interactions is particularly impressive as triplet-triplet annihilation and extended exciton diffusion is generally thought to lead to exciton quenching. These results may open new opportunities for design of solid state phosphorescent lasers,[6] electroluminescent devices,^[20] upconverting materials for light harvesting and related applications.[21]

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Notes

^{a)} HTANGO was reported previously.^[22] However, only solution fluorescence in trifluoroacetic acid was reported. Supramolecular assemblies of some TANGO derivatives are also known.^[23] No solid emission or phosphorescent properties have been described for any of the derivatives.

^{b)} The weak shoulder in *t*BuTANGO solid state emission at 550–650 nm was found to be an extremely weakphosphorescence with a lifetime of τ^{P} = 0.6 ms (Figure 1c).

Keywords: Organic Room Temperature Phosphorescence, Crystal engineering, Azatriangulene, J/H-aggregation, π -Stacking

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Table of Contents graphic



Solid state packing in a series of azatriangulenetrione (TANGO) derivatives controls their luminescence properties. Co-alignment of transition dipoles in π -stacks leads to efficient room temperature phosphorescence while their 60° rotation caused by sterically hindering *t*-butyl groups results in an almost pure fluorescence. The phosphorescence quantum yield of 42% is achieved for pure HTANGO crystals without heavy atoms (1st/2nd row elements only).