Searching Building Blocks with Large Excited-State Gaps in Five-memebered Heterocyclic Rings by Aromaticity Strategy

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Keywords: triplet energy gap, five-membered rings, ultrafast spectroscopy, singlet fission, hot exciton

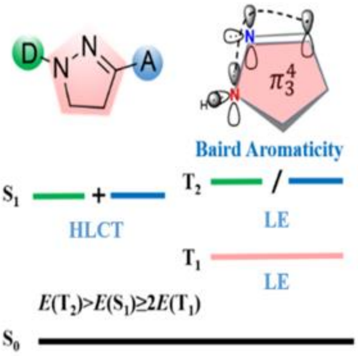


Table of Contents: We have proposed a facile strategy to achieve large triple gap by manipulating the aromaticity and the transition properties of the low-lying excited states, then theoretically designed and experimentally verified a series of donor-bridge-acceptor based on partially conjugated five-memebered rings with high aromaticity in T_1 state to meet the harsh energy conditions of large triplet energy gap between T_2 and T_1 ($\Delta E_{T_1T_2}$) for hot exciton materials and $E(T_2)>E(S_1)\geq 2E(T_1)$ for singlet fission materials.

Abstract: Organic molecules with large gap between the excited singlet/triplet states can be applied in hot exciton emission and singlet fission to beat the spin statistics limit in optoelectronic devices. Herein, a novel strategy is proposed for achieving large triplet-triplet gap ($\Delta E(T_1T_2)$) and singlet-triplet gap ($\Delta E(S_1T_1)$) by manipulating the aromaticity of the low-lying excited states. Partially conjugated five-membered heterocyclic rings are found to naturally have low $E(T_1)$ owing to high aromaticity obeying Baird's Rule. Utilizing such ring (pyrazoline) as a bridge and selecting various donor and acceptor moieties, numbers of derivatives have been theoretically designed with tunable emission colors, significantly large $\Delta E(T_1T_2)$ and $\Delta E(S_1T_1)$, and satisfying $E(T_2)>E(S_1)\geq 2E(T_1)$. The ultrafast spectroscopy and sensitization measurements for one of them with blue fluorescence (named TPA-DBPrz) confirm the calculated prediction. This work opens a new avenue and provides molecular units to develop high-efficiency optoelectronic materials.

1. Introduction

Organic light-emitting diodes (OLEDs) have been successfully commercialized on displays and solidphase lighting due to their advantages.[1-4] There has been a long-standing challenge to beat 25% statistical limit[5] in the electroluminescence devices. Recently, nearly 100% IQE has been obtained in the thermally-activated delayed fluorescence (TADF) materials for electrofluorescence.[6-7] For TADF materials, efficient reverse intersystem crossing (RISC) is essential to convert triplet states to singlet manifold for fluorescence, which usually requires a significantly small singlet-triplet energy gap (ΔE_{ST}).[6]

It is well known that such small ΔE_{ST} can be generated by separating the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) in space, which concurrently leads to very weak oscillator strength, quite small emissive cross section and considerably long fluorescence lifetime.[6, 8] The hybrid locally-excited charge transfer (HLCT) materials based on the hot exciton mechanism put forth by Ma and Yang are expected to make up for the deficiency, because more local excitation (LE) feature produces larger oscillator strength for fluorescence and RISC between higher excited singlet and triplet manifolds is more efficient without serious time delay.[9] In this mechanism, the triplet excition is utilized through the RISC from higher triplet state to the singlet state. Thus, a large triplet-triplet gap $\Delta E(T_1T_2)$ is indispensable to efficiently suppress the nonradiative internal conversion from T_2 to T_1 which is a extremely harsh condition for organic compounds.

Very recently, the singlet fission (SF) materials are promising candidates for organic photovoltaics and electroluminescence because two low-energy triplet excited states (T_1) are generated from one high-energy singlet excited state (S_1), overcoming the 34% Shockley-Queisser efficiency limit in solar cells[10] and the 25% exciton utilization efficiency in OLED[11]. An efficient SF process basically requires the energy of S_1 larger than twice that of T_1, $E(S_1) \geq 2E(T_1)$.[12] At the same time, the energy condition of $E(T_2) > E(S_1)$ should also be met to avoid the intersystem crossing (ISC) from S_1 to T_2 and the recombination of T_1 excitons.[13] Overall, the HLCT and SF materials have similar energy requirements (see **Figure 1**), i.e., large $\Delta E(T_1T_2)$ and $\Delta E(S_1T_1)$. However, it is a formidable challenge to design molecules with large $\Delta E(T_1T_2)$ or $\Delta E(S_1T_1)$, let alone both.

In this work, we first demonstrate that some triplet-stabilized five-membered heterocyclic rings (i.e., pyrazoline) naturally have low $E(T_1)$ owing to high aromaticity in T_1 obeying Baird's Rule[14], and large energy gaps $\Delta E(T_1T_2)$ and $\Delta E(S_1T_1)$ due to the different transition properties among the S_1, T_1 and T_2 states. A series of donor-bridge-acceptor (D-B-A) systems are then designed based on pyrazoline ring as a bridge via introducing different donor or acceptor moieties (see **Scheme 1**). For the constructed pyrazoline derivatives, the low $E(T_1)$ is consistently maintained because the transition density of T_1 is still localized in pyrazoline ring and the high $E(T_2)$ is generated via a transition over substituted donors or acceptors, which results in a large $\Delta E(T_1T_2)$. With that, a novel series of full-color emitters with large $\Delta E(T_1T_2)$ and $\Delta E(S_1T_1)$ are predicted through theoretical calculations and proved by transient absorption spectroscopy spectra of TPA-DBPrz, which, to the best of our knowledge, has not been previously reported.

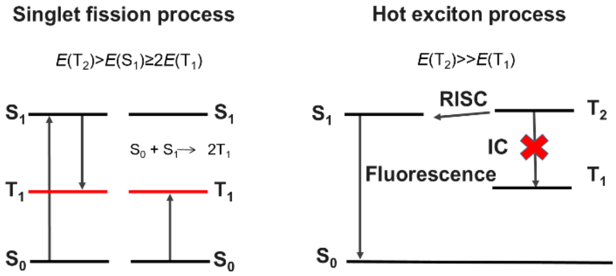
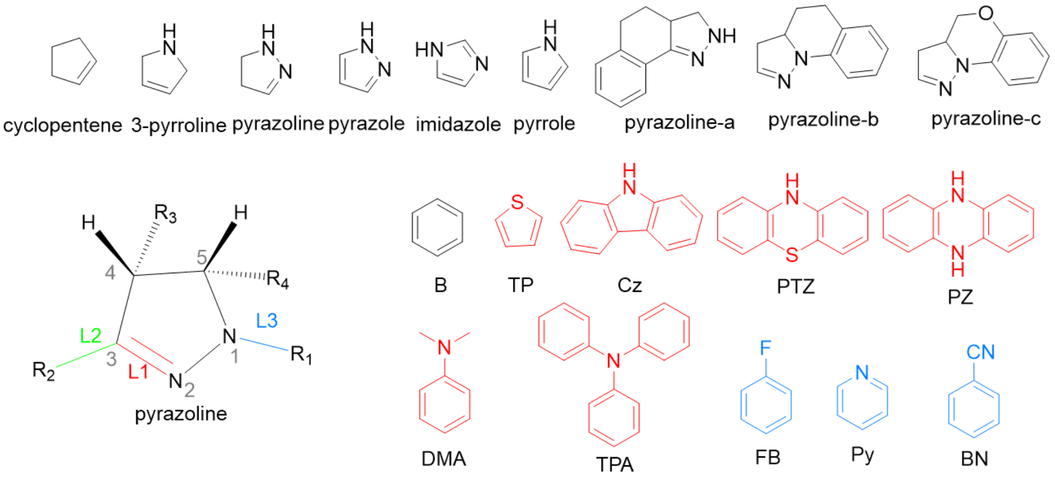


Figure 1. Schematic diagram of energy levels for the SF and HLCT materials.



Compound	R₁	R₂	R₃	R₄	Compound	R₁	R₂	R₃	R₄	Compound	R₁	R₂	R₃	R₄
1	B	FB	H	H	**10**	FB	B	H	H	**19**	B	FB	B	H
2	TP	FB	H	H	**11**	H	B	H	FB	**20**	B	FB	DMA	H
3	TP	Py	H	H	**12**	H	FB	H	B	**21**	B	FB	Py	H
4	Cz	Py	H	H	**13**	H	FB	B	H	**22**	B	FB	H	B
5	Cz	BN	H	H	**14**	H	B	FB	H	**23**	B	FB	H	DMA
6	PTZ	Py	H	H	**15**	FB	H	B	H	**24**	B	FB	H	Py
7	PTZ	BN	H	H	**16**	B	H	FB	H	TPA-DBPrz	B	B	H	TPA
8	PZ	B	H	H	**17**	B	H	H	FB					
9	PZ	BN	H	H	**18**	FB	H	H	B					

Scheme 1. Chemical structures of five-membered rings and constructed molecules in this work (red: donor; blue: acceptor).

2. Results and Discussion

2.1. Five-membered heterocyclic rings with large triplet-triplet and singlet-tripelt gaps.

The conjugated five-membered rings are frequently used as fundamental units in luminous molecules, such as cyclopentene, 3-pyrroline, pyrazoline, pyrazole, imidazole and pyrrole as shown in **Scheme 1**. The effects of molecular conjugation on the emissive spectra and efficiencies from S_1 have been widely investigated in organic systems.[15] However, the effects of molecular conjugation on the porperty and energy of triplet states have rarely been explored. We here systematically investigate the energy orders of low-lying excited triplet and singlet states of the five-membered rings with different degree of conjugation, including olefinic rings (cyclopentene), antiaromatic rings (3-pyrroline and pyrazoline) and aromatic rings (pyrazole, imidazole and pyrrole).

We optimize the geometrical structures via SA4-CASSCF/cc-PVTZ with active space (10e, 10o) and calculate the electronic structures via MS4-CASPT2/cc-PVTZ for the low-lying triplet and singlet states of these five-numbered rings, and the results are shown in **Figure 2** and **Table 1**. It is seen in **Figure 2**a that cyclopentene, 3-pyrroline and pyrazoline are partially conjugated with transition densities mainly localized on double bond and lone-pair electrons, while pyrazole, imidazole and pyrrole are fully conjugated with transition density delocalized over the whole rings. Furthermore, it is found from **Table 1** that the partially conjugated cyclopentene, 3-pyrroline and pyrazoline rings have low $E(\mathrm{T}_1)$, which naturally meet the energy condition of $E(\mathrm{T}_1)<<E(\mathrm{T}_2)$ as required for HLCT materials and $2E(\mathrm{T}_1)\leq E(\mathrm{S}_1)<E(\mathrm{T}_2)$ as needed for SF materials; while the fully conjugated pyrazole, imidazole and pyrrole rings possess high $E(\mathrm{T}_1)$ and relatively small $\Delta E(\mathrm{T}_1\mathrm{T}_2)$. Such energy orders are closely related to the natrue of the geometrial structures and electronic transition properies in the excited states. Upon excitation, the double bonds are elongated to a greater extent in cyclopentene (0.130 Å), 3-pyrroline (0.158 Å) and pyrazoline (0.184 Å) than those (ca. 0.100 Å) in pyrazole, imidazole and pyrrole as shown in **Figure 2**b and S1, which largely weaken the coupling between the two p-orbitals of the former, leading to low $E(\mathrm{T}_1)$. These results are also consistent with Baird's Rule, in which the aromaticity is always changed upon triplet excitation and the aromatic triplet states are more stable with lower energy.[14, 16-17] Especailly, pyrazoline (π_3^4) is a [4n] electron system, which is typically aromatic in T_1. The anisotropy of the induced current density[18] (AICD) which can character the molecular aromaticity is calculated and plotted in **Figure 2**c. The clockwise ring currents in **Figure 2**c of cyclopentene, 3-pyrroline and pyrazoline rings indicate them to be aromatic while the anticlockwise ring currents in pyrazole, imidazole and pyrrole prove them to be antiaromatic in T_1. Thus, according to Baird's Rule, cyclopentene, 3-pyrroline and pyrazoline retain stabilized T_1 states with low energy. Furthermore, the orbitals are energetically well-separated in these rings as shown in **Figure 2**d, especially, the energy gap between HOMO and HOMO-1 is very large. The T_1 states are dominated by the transition from HOMO to LUMO while the T_2 states stem from the transition from deeper occupied orbitals to LUMO or higher unoccupied orbitals, which results in large $\Delta E(\mathrm{T}_1\mathrm{T}_2)$. All these results indicate cyclopentene, 3-pyrroline and pyrazoline are expected to be good triplet-stabilized candidates for ultra-large $\Delta E(\mathrm{T}_1\mathrm{T}_2)$. The similar conclusion can be obtained by the TDA-DFT approach as shown in supporting information (SI).

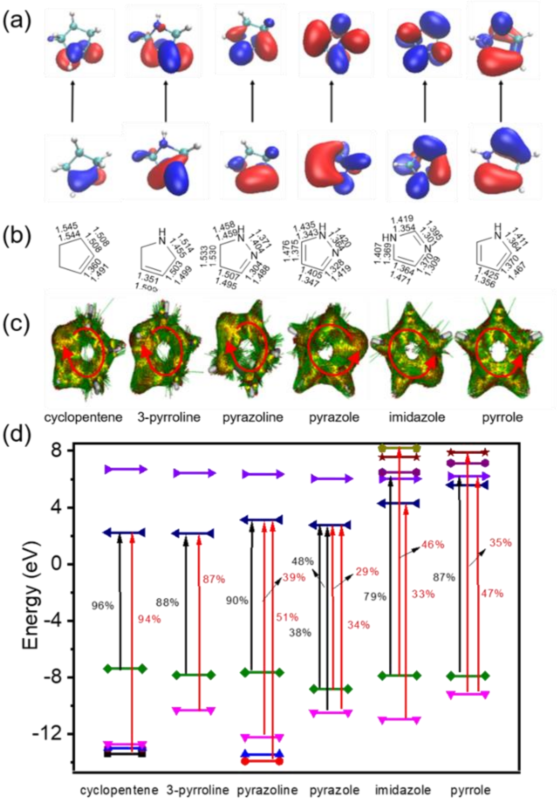


Figure 2. a) Nature transition orbitals (NTOs) of T_1 at T_1-geometry; b) Optimized bond lengths (Inside: S0-geometry; Outside: T_1-geometry); c) AICD plots of six five-numbered rings in T_1 state in which the induced current density vectors denoted by the arrows; and d) frontier orbitals energies and transitions of T_1 (black) and T_2 (red) states.

Table 1. Vertical excitation energies (Unit: eV) of six five-numbered rings at T_1-geometry.

Compound	$E(T_1)$	$E(T_2)$	$E(S_1)$	$2E(T_1)$	$\Delta E(T_1T_2)$
cyclopentene	1.01	6.04	3.77	2.02	5.03
3-pyrroline	1.26	4.09	3.56	2.52	2.83
pyrazoline	1.54	4.68	3.55	3.08	3.14
pyrazole	2.84	4.43	4.97	5.68	1.59
imidazole	3.44	5.10	5.44	6.88	1.66
pyrrole	3.35	4.84	5.34	6.70	1.49

We further calculate the low-lying excited states of the extended systerms (pyrazoline-a, pyrazoline-b and pyrazoline-c in **Scheme 1**) based on pyrazoline ring at TDA/LC-ωPBE*/6-31G(d) level. They all exhibit much lower energy of T_1 than those of S_1 and T_2 (Table S3) because the T_1 mainly originates from pyrazoline ring (Figure S3a), while T_2 and S_1 are significantly changed by the introduced chemical groups. These results further demonstrate the partly conjugated rings can serve as triplet-stabilized moieties for the HLCT and SF materials.

2.2. Construction of pyrazoline derivatives with large triplet-triplet and singlet-triplet gaps.

Pyrazoline derivatives have been investigated as hole-transport materials[19], fluorescent sensor[20] and medicine[21] owing to high stability and wonderful photophysical properties. Very few cyclopentene and 3-pyrroline derivatives have been reported in the literature, let alone their applications in the materials science. Hence, in this work, pyrazoline ring is used as a bridge (B) to construct 25 compounds by introducing different donor (D) and acceptor (A) groups, namely, D-B-A type compounds (see **Scheme 1**). Among them, the electron-withdrawing ability of the acceptors becomes stronger from FB, Py to BN owing to lower LUMO energies, and the electron-donating ability of the donors becomes stronger from TP, Cz, PTZ to PZ due to higher HOMO energies (Table S4).

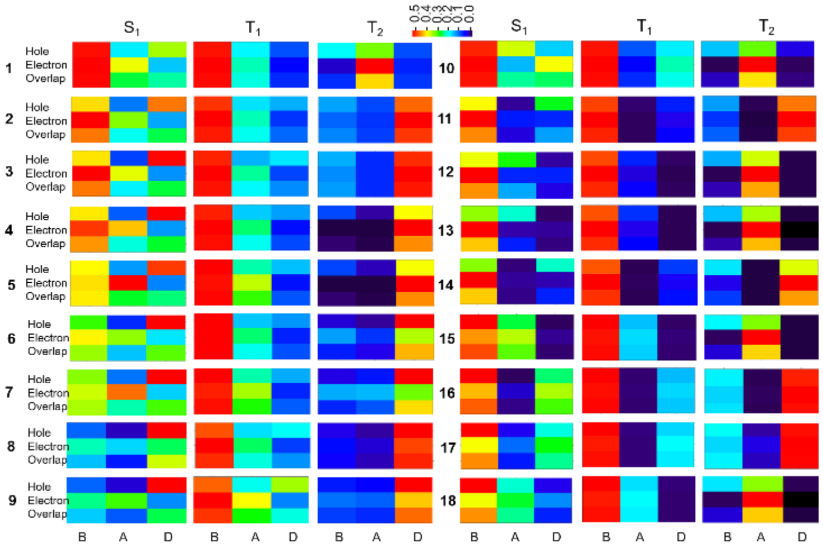


Figure 3. Hole-electron distribution heat maps of **1-18**.

Compounds **1-9** with different D or A at the same substituted 1- and 3-positions all possess with nearly coplanar conformations with high rigidity. Upon excitation, significant modifications occur on three bond lengths rather than angles and dihedral angles, as seen in Table S5. These three bond lengths are C=N in pyrazoline ring (L_1), the bond linking B and A (L_2) and the bond linking B and D (L_3), respectively, as illustrated in **Scheme 1**. From S_0-geometry to T_1-geometry, L_1 is considerably elongated by 0.081-0.136 Å, which is similar to the change of single pyrazoline ring, while L_2 and L_3 are slightly shortened by 0.002-0.07 Å as seen in Table S5. The hole-electron analyses are carried out to unravel the transition nature of the low-lying excited states through hole-electron distribution heat maps [22] and natural transition orbitals (NTOs) as plotted in **Figure 3** and Figure S4, respectively. It is seen from two figures that for all the molecules T_1 is a locally excited (LE) state originating from pyrazoline ring, which results in their $E(T_1)$ very close to that of single pyrazoline ring, namely, ca. 1.50 eV, as shown in **Figure 4**a. T_2 is a LE state mainly stemming from either acceptor or donor group, which has much wider energy-gap than that of pyrazoline ring. Thus, $E(T_1)$ is much smaller than $E(T_2)$. By contrast, S_1 acquires a delocalized transition with partial charge-transfer (CT) character. The resultant $E(S_1)$ is smaller than $E(T_2)$ as seen in

Figure 4a. Furthermore, the difference in the nature of electronic configuration between T_2 and S_1 states can give rise to large spin-orbit coupling (SOC), which facilitates the mutual conversion between them. Overall, the nine compounds all meet the energy conditions of $E(T_1) << E(T_2)$ and $2E(T_1) \leq E(S_1) < E(T_2)$, indicating them to be good candidates for HLCT or SF molecules. In addition, while retaining large $\Delta E(T_1T_2)$ and $\Delta E(S_1T_1)$, the emissive wavelengths vary in a wide visible region of 2.30~3.27eV (Table S6), which enriches the HLCT or SF systems with multicolor emission light.

Among the nine compounds, compound **1** has the largest $\Delta E(T_1T_2)$ (2.19 eV) with the substituents BF and B. Hence, we change the substituted position of BF and B (compounds **10-18** in Scheme 1) to investigate the position dependence of the substituents on the properties of the low-lying excited states in **Figure 4**b. It can be seen that (i) the energy relationship of $E(T_1) << E(T_2)$ is still maintained with $\Delta E(T_1T_2)$ larger than 1.91 eV, which is independent on the positions of BF and B in the pyrazoline ring; (ii) the $2E(T_1) \leq E(S_1) < E(T_2)$ is well held except for **11** and **14** with B at the 3- site and BF at the 4- or 5- sites of pyrazoline ring; (iii) relative to compound **1** and **10**, the $E(S_1)$ and $E(T_2)$ are raised while the $E(T_1)$ fluctuates between 1.30 and 1.71 eV for compounds **11-18**. Thus, it can be predicted that among these systems, compounds **12**, **15** and **18** would be excellent HLCT materials because of large $\Delta E(T_1T_2)$ that blocks the internal conversion from T_2 to T_1 and small $\Delta E(S_1T_2)$ that facilitates the intersystem crossing from T_2 to S_1; and Compounds **10**, **16** and **17** would act as excellent SF materials owing to not only $2E(T_1) \leq E(S_1)$ but also large $\Delta E(S_1T_2)$. The reason of large $\Delta E(T_1T_2)$ in **10-18** is the same with that in **1-9** (**Figure 3** and Figure S4).

The effect of the number of substituents on the excited-state property are further studied through adding donor or acceptor at 4- or 5-site of pyrazoline ring when B and BF are fixed at 1- and 3-site, respectively (compounds **19-24** in **Scheme 1**), and the resultant excitation energies and NTOs are given in Table S6 and **Figures 4**c, S4. The $E(S_1)$, $E(T_1)$, $E(T_2)$ of these compounds **19-24** are all similar to those of compound **1**, which suggests the substituents linked to the sp^3 hybridized carbon atom of the pyrazoline (R_3 and R_4) have no effect on the excited-state properties while the ones at the conjugated part of the pyrazoline ring play important roles. Therefore, it is declared that the low-lying excited-state properties can be tuned by changing R_1 and R_2 at 1- and 3- sites of pyrazoline ring, and other physical properties such as crystallization ability, glass-transition temperature etc. can be controlled via adding R_3 or R_4 at 4- and 5-sites. Thus, excellent HLCT or SF materials can be properly designed for optoelectronic devices.

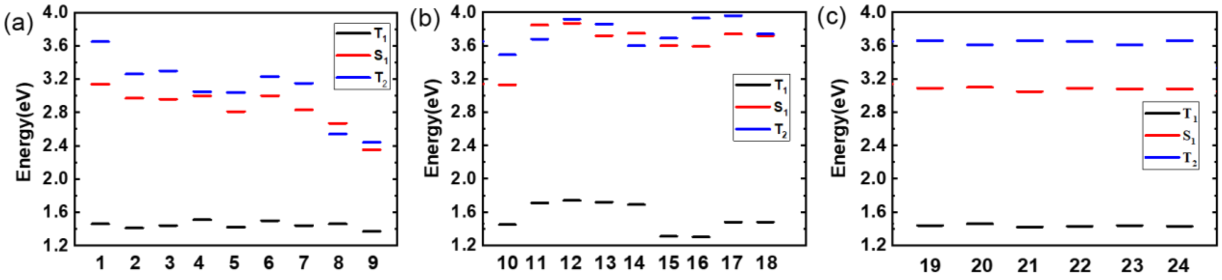


Figure 4. Excitation energies of the compounds at T1-geometry at TDA/LC-ωPBE*/6-31G(d) level.

2.3. Experimental validation of theoretically designed TPA-DBPrz molecule.

Keeping the above design strategy in mind, we build a compound named as TPA-DBPrz with R_1=B, R_2=B, R_3=H and R_4=TPA, which has properly large molecular weight to meet the requirement for the application in optoelectronic devices. The low-lying excited states are calculated at MS4-CASPT2(8,8)/cc-PVDZ level and the results are given in **Figure 5**a, including energy levels, transition properties and involved frontier orbitals. The S_1 state has a hybrid transition character with LE on pyrazoline and CT from 1-site phenyl to 3-site phenyl ring. The T_1 state stems from LE on pyrazoline ring, as well as a marginal contribution from two phenyl rings. The T_2 state comes from the electron transition on TPA moiety. The resultant $E(S_1)$, $E(T_2)$ and $E(T_1)$ are 2.68, 1.55, and 3.23 eV based on T_1-goemetry, respectively, leading to large $\Delta E(T_1T_2)$ of 1.68 eV. In addition, the oscillator strength (*f*) of $T_1 \rightarrow T_2$ transiton is a significant value (*f*=0.0007), which indicates the effective absorption from T_1 to T_2. To prove our theoretical predictions, we synthesized TPA-DBPrz compound and measured its photophysical properties. The synthetic route of TPA-DBPrz is shown in Scheme S1 and it is unambiguously characterized by ^{1}H NMR, ^{13}C NMR, high resolution mass spectrometry and elemental analysis as given in SI. The ultraviolet-visible absorption and photoluminescence (PL) spectra of TPA-DBPrz in chloromethane (DCM) solution are plotted in **Figure 5**b. The PL shows a blue emission with a emission maximum at 453 nm, very close to the theoretical value. Femtosecond transient absorption spectroscopy (fs-TA) of TPA-DBPrz in dichloromethane (DCM) is performed upon excitation at 400 nm and it is found that there appear two types of features: short-lived excited state absorption (ESA) band at about 582 nm, and two gradually increasing ESA bands at both 527 nm and 830 nm (see **Figure 5**d-e, S5). The long-lived component dominates the spectrum after 250 ps and lasting for several ns. It is seen that (i) the excited state corresponding to 582 nm firstly generates upon excitation and then disappear rapidly, which can be attributed to the transition of $S_1 \rightarrow S_n$; (ii) the transient species corresponding to 527 nm and 830 nm is populated from the S_1 state, which can be hypothetically assigned to the transition from T_1 to T_n state. In order to confirm this assignment, we further obtain the sensitized T_1 state of the TPA-

DBPrz using a phosphorescence dye $\mathrm{Ru(bpy)_3Cl_2}$ with a $E(\mathrm{T_1})$ (2.1 eV).[23] (detailed in Figure S7). It is shown that the sole $\mathrm{Ru(bpy)_3Cl_2}$ show no ESA band at 527nm and 830nm while $\mathrm{Ru(bpy)_3Cl_2}$&TPA-DBPrz exhibit a long-lived absorption band (Figure S6) at 830nm (1.49eV) and a strong and long-lived ESA band (**Figure 5**c) at 527nm, corresponding to the lowest excited state of TPA-DBPrz ($\mathrm{T_1}$) sensitized by $\mathrm{Ru(bpy)_3Cl_2}$. This is coincident with the calculated energies of the $\mathrm{T_1 \rightarrow T_2}$ (1.68 eV) and $\mathrm{T_1 \rightarrow T_n}$ transitions of TPA-DBPrz mentioned above. The rate constant for intersystem crossing from $\mathrm{S_1}$ to $\mathrm{T_1}$ can be determined from the rise evolution of 830-nm curve, yielding the k_{ISC} of 103 ps^{-1}. These results confirm that the theoretically designed TPA-DBPrz possesses large $\Delta E(\mathrm{T_1T_2})$, potentially important for HLCT and SF application.

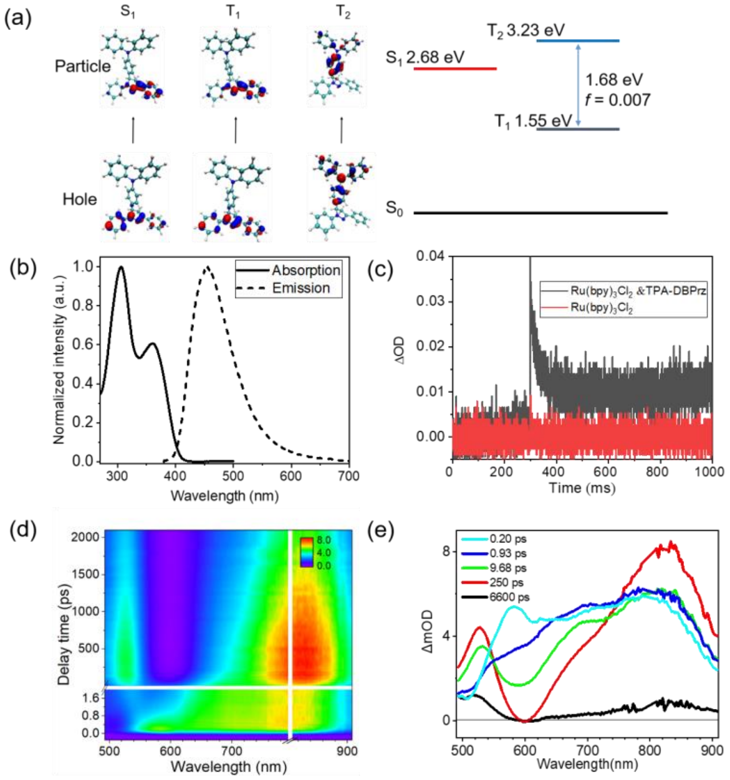


Figure 5. a) Nature transition oribtals (NTOs), energy levels and the oscillator strength (*f*) of TPA-DBPrz based on $\mathrm{T_1}$-goemetry. b) Normalized UV-vis and PL spectra in DCM solution; c) ns-TA measurement of $\mathrm{Ru(bpy)_3Cl_2}$ (20 uM) and $\mathrm{Ru(bpy)_3Cl_2}$ (20 uM) &TPA-DBPrz (1 mM) in DCM monitored at 527 nm. d) and e) fs-TA spectra and corresponding dynamics curves of TPA-DBPrz in the DCM solution (10 μM).

3. Conclusion

To conclude, we propose an excited-state aromaticity strategy to design the compounds with large triplet-triplet and singlet-triplet gaps which are of potential application in SF and hot exciton materials. We first investigate the energy orders in the low-lying excited states of a seires of typical five-membered rings with different degree of conjugation using the state-of-the-art quantum chemistry approaches. It is found that the partly conjugated five-membered heterocyclic rings are expected to be good triplet-stabilized candidates because of elongated double bond (by 0.130~0.184 Angstrom) and high aromaticity in T_1. Then, we choose pyrazoline ring as a bridge and design 25 molecules of donor-bridge-acceptor (D-B-A) type through substituting donors and acceptor at different site positions. The calculated results indicate that T_1 is a locally excited state originating from pyrazoline ring, which maintains low $E(T_1)$ (very close to that of single pyrazoline ring, ca. 1.50 eV), T_2 is a locally excited state mainly stemming from either acceptor or donor moiety, which generates high $E(T_2)$, while S_1 is a hybrid excited state with local excitation and charge transfer character. Consequently, the $E(T_2)$ is much higher than T_1 and the $E(S_1)$ is slightly smaller than $E(T_2)$, which result in large $\Delta E(T_1T_2)$, and $\Delta E(S_1T_1)$ and meeting $2E(T_1) \leq E(S_1) < E(T_2)$. Finally, we synthesize a designed TPA-DBPrz molecule and investigate its photophysical properties by theoretical calculations and experimental measurements. The fs-TA spectra of TPA-DBPrz in DCM and the ns-TA spectra of TPA-DBPrz&Ru(bpy)$_3$Cl$_2$ in DCM both show the absorption from T_1 to T_2 at 830nm (1.49eV), which fully proves the theoretically predicted $\Delta E(T_1T_2)$ of 1.68eV.

In summary, using reliable quantum chemistry methods, we have successfully identified five-membered heterocyclic rings which can naturally stabilize triplet state, based on which we have designed 25 compounds that all exhibit large $\Delta E(T_1T_2)$ and $\Delta E(S_1T_1)$ and thus serve as promising candidates for hot exciton and SF materials. This work will provide a new route and a number of novel molecular cores for designing high-performance hot exciton and SF materials in practice.

Acknowledgements

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Author contributions

ZS, QP and QS conceived the project. QS designed molecules and carried out the calculations. QO, DH, and LW helped with the calculation process and provided inspiring suggestions for improvement. YC and YW synthesized the molecule. CG, YW and LH conducted the ultrafast spectroscopy and sensitization measurements. All authors contributed to data analysis and write the paper.

Competing interests

The authors declare no competing interests.

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