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Effect of thiophene substitution on the intersystem crossing of arene photosensitizers

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The effect of the thienyl substitution on the intersystem crossing (ISC) of a few arenes was studied with steady state and time-resolved transient absorption and emission spectroscopies, as well as DFT/TDDFT computations. We found that the phenyl and thienyl substituents generally induce red-shifted absorptions for the chromophores, and the DFT/TDDFT computations show that the red-shifted absorption and emission is due to the increased HOMO and the reduced LUMO energy levels. Nanosecond transient absorption spectra indicate the formation of triplet state, the triplet state lifetime is up to 282 μ s, and the singlet oxygen quantum yields (Φ_{Δ}) are up to 60 %. DFT/TDDFT computation indicate that introducing the thienyl substituent alters the relative singlet/triplet excited state energy levels, and the energy level-matched S₁/T₂ states are responsible for the enhanced ISC of the thienyl compounds. These information are useful for design of heavy atom-free triplet photosensitizers and for study of the fundamental photochemistry of organic compounds.

Introduction

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Intersystem crossing (ISC) and triplet photosensitizers play important roles in photochemistry and photobiology.¹⁻⁶ For instance, triplet photosensitizers are important compounds which have potential applications in the field of photocatalysis,7-9 photodynamic therapy (PDT, which is a promising approach for treatment of tumor),^{10–12} photovoltaics,13 and triplet-triplet annihilation upconversion (TTA-UC).14-19 A good triplet photosensitizer show efficient intersystem crossing (ISC) and long lived triplet excited state, in addition to strong absorption of excitation light. Conventional triplet photosensitizers usually contain heavy atoms like iodo, bromo or metal atoms, Pt, Ir, Ru etc from d and f block of periodic table.^{20,21} The heavy atom effect is beneficial for the flip or rephrase of electron spin due to spin orbit coupling (SOC) process. But toxicity and cost-efficiency are major drawbacks of these photosensitizers. In order to avoid these problems, triplet photosensitizers without heavy atom are highly desired. So far some method, i.e., thermally activated reverse intersystem crossing,22-24 singlet fission spin–orbit charge transfer (SOCT),26 (SF).25 spin convertor,^{22,27,28} doublet excited state,^{29,30} and exciton coupling³¹ to augment ISC of heavy atom free compounds have been developed. But for most of these methods, the molecular structures are synthetically demanding.

Thus new methods to achieve efficient ISC without heavy

atom effect and simple molecular structure profile are desired. Previously, ISC was observed for thiophene oligomers and also for thienyl-containing chromophores.^{32–38} Thienyl groups can be easily introduced to these molecules by cross coupling reaction. Thiophenes are suitable for biological applications, especially as thiophene derivatives are used as food flavouring additives.^{39,40} Moreover, attaching thienyl unit to a chromophore may red-shift the absorption wavelength, which are beneficial for preparation of new triplet photosensitizers. Pyridine attached with thienyl moiety was reported and efficient ISC was observed, but the absorption is in UV range.⁴¹ Previously thiophene moiety was introduced to copolymer Bodipy backbone, ISC was proposed to be responsible for the reduced fluorescence emission of the copolymer, but the triplet state was not studied.42 Thiophene fused Bodipy derivatives were also reported to show ISC, 43,44 but it is clear that more molecular structure diversity needs to be explored.

In order to study the effect of thienyl substitution on the ISC of organic chromophores, herein we selected a few representative arenes for preparation of thienyl compounds (Scheme 1). Perylene (**Per**), naphthalimide (**NI**) and anthracene (**An**) are among the most investigated chromophores, but the effect of thienyl substituents on the ISC of these chromophores was not studied. Such compounds (**Per**, **NI** and **An**) are relevant for biological investigations as they don't show dark toxicity.⁴⁵⁻⁴⁷ Steady state and time resolved transient absorption spectroscopies were used for study of the photophysical properties. The properties of the thiophene-appended arene fluorophores are compared with those of phenyl counterparts. We found that the ISC can be enhanced by introducing thienyl unit to the chromophores.

Experimental section

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General methods

All chemicals used in the synthesis were of analytical grade and were used as received. Solvents were dried and distilled before use for synthesis. Detail of synthesis is given in supporting information (see experimental section).

Nanosecond transient absorption spectroscopy

LP920 laser flash photolysis spectrometer (Edinburg Instruments, UK) equipped with Tektronix TDS 3012B oscilloscope was used for studying nanosecond time—resolved transient absorption spectroscopy. The samples were deaerated with argon for 15 minutes before measurement and flow of gas was kept constant during the measurements. The data was processed by LP920 software.

Singlet oxygen sensitization

Singlet oxygen of compounds were measured with diphenylisobenzofuran (DPBF) as singlet oxygen scavenger. By following the absorption (λ_{max} = 414 nm) of DPBF, the ${}^{1}O_{2}$ production was monitored. For calculation of singlet oxygen quantum yield (\mathcal{D}_{Δ}), the following equation (1) was used:

$$\Phi_{\rm sam} = \Phi_{\rm std} \left(\frac{1 - 10^{-A_{\rm std}}}{1 - 10^{-A_{\rm sam}}} \right) \left(\frac{m_{\rm sam}}{m_{\rm std}} \right) \left(\frac{\eta_{\rm sam}}{\eta_{\rm std}} \right)^2 \tag{1}$$

In above equation, "std" and "sam" stands for standard and sample. η , A, Φ and m stands for refractive index of the solvent, absorbance at excitation wavelength, singlet oxygen quantum yield and slope of the absorbance of DPBF changing with time, respectively. For measurement, optically matched solutions of sample and standard were used. Tetraphenyl

porphyrin (TPP) was used as standard ($\mathcal{D}_{\Delta} = 62\%$ in DCM) for measurement of singlet oxygen (\mathcal{D}_{Δ}) oPMTPEF% \mathcal{DCM} and anthracene was used as standard ($\mathcal{D}_{\Delta} = 70\%$ in Methanol) for measurement of \mathcal{D}_{Δ} of **DT-An**, **MT-NI**, **MP-NI** in methanol.

Results and discussion

Design and synthesis of the compounds

Previously, ISC properties of bodipy derivatives with fused thiophene were reported.^{43,44} Thiophene attached bodipy copolymer were also reported.⁴² It was proposed that the decrease in fluorescence emission is due to ISC process. To explore the effect of thiophene substitution on ISC and triplet state properties, we designed and synthesized different arene compounds attached with thienyl units (Scheme 1).

Perylene is known for its high fluorescence quantum yield. Thus it is feasible to study the effect of thienyl substitution on the ISC of this chromophore. We expect thienyl attachment to the core of perylene will reduce the fluorescence quantum yield (\mathcal{D}_F) of **MT-Per** and increase the ISC ability of compound. **MP-Per** was prepared as a reference compound. Thienyl unit was introduced by Pd (0)–catalyzed Suzuki cross coupling reaction (scheme 1).

NI is a well known chromophore, which is electron deficient. Introducing a thienyl unit results electron push-pull character in **MT-NI**, thus it is expected the that absorption wavelength will be red-shifted. Compounds related to **MT-NI** were previously reported but triplet state properties were not investigated.⁴⁸ It should be pointed out that the pristine **NI**



Scheme 1 Reagents and conditions: (i) 1.2 equivalent of *N*-bromosuccinimide (NBS), DMF, 25 °C, 24 h; (ii) Thiophene-2-ylboronic acid, K₂CO₃, Pd(PPh₃)₄, PhCH₃/Et–OH/H₂O (4/2/1, v/v), refluxed at 90 °C for 8 h, under Ar; (iv) 2-ethylhexylamine, Et-OH, refluxed at 90 °C for 8 h, under Ar; (v) and (viii) the same to (ii); (vi) and (ix) the same to (iii); (vii) Br₂, CHCl₃, stirred at room temperature for 5 h under Ar.

(without any substituents at 4–position) possesses an efficient ISC, but the absorption is in UV range. With introducing phenyl group at 4-position (**MP-NI**), the fluorescence was reported to be 78 %,⁴⁹ i.e., the ISC decreased.

An is with efficient ISC ($\Phi_T = 70$ %).⁵⁰ It was proposed that the T_2 and T_3 states are involved in the ISC of An, T_2 is with similar energy level to that of S_1 state, and $S_1 \rightarrow T_2(T_3) \rightarrow T_1$ was proposed. Substitution on the An may change the relative energy levels of S_1/T_2 states, thus the ISC may be inhibited to large extent given the T₂ state is with higher energy level than S_1 state. The relative energy level of S_1/T_2 state of **An** also dependent on the matrix micro environment, for instance, the solvent polarity. We introduced two thienyl moieties on the An core (DT-An) to study the effect on ISC ability. The photophysical properties of DT-An were reported previously and triplet lifetime is investigated by indirect method,⁵¹ however, triplet properties were not investigated in detail. We did not attempt to induce oligomeric thienyl moiety on to the chromophores, previously it was reported that high oligomeric thiophene may show reduced ISC ability.52-55

UV–Visible absorption spectra

The UV–Vis absorption spectra of compounds were studied and compared with reference compounds (Fig. 1). Both the thienyl and phenyl substituted compounds show bathochromic shift (red shift) as compared to reference compounds. The

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compounds with thienyl substitution show more red-shifted absorption than phenyl substituted compounds. This may be due to the increase in π -conjugation by attaching thienyl moiety to the core of chromophore.

For instance, **Per** shows absorption band at 434 nm, with the attachment of phenyl group, **MP-Per** shows red shift in absorption of about 8 nm while in case of **MT-Per** the absorption is further red shifted (446 nm) due to increase in interaction between thiophene and **Per** core. It is noted that upon thienyl attachment the vibronic progression of compounds become less significant. The effect of thienyl introduction to the core of chromophore is more prominent in case of **NI** where the bathochromic shift in absorption for **MT-NI** is about 27 nm as compared to reference compound (**Br-NI**) (Fig 1b). However, **MP-NI** shows less red—shifted absorption of 9 nm. Also the broad, structure less peak was observed by substitution of either phenyl or thiophene with core of **NI**. This may be due to electron donating ability of thiophene or phenyl to electron deficient **NI** moiety.

The attachment of two thiophenes to the core of anthracene also shows more red-shifted absorption of about 20 nm as compared to the compound with phenyl substitution (16 nm) (Fig.1c). However the effect on vibronic progression with substitution of either phenyl or thiophene is very less.



Fig. 2 Fluorescence emission spectra. (a) MT-Per (λ_{ex} = 397 nm); (b) MT-NI (λ_{ex} = 317 nm); and (c) DT-An (λ_{ex} = 373 nm). Optically matched solutions were used (A = 0.16 for MT-Per, A = 0.09 for MT-NI, A = 0.04 for DT-An). 20 °C.

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Interestingly, the absorptivity of the thionated compound, **DT**-**An**, was enhanced as compared to that of **An**. For instance, $\varepsilon = 1.2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at 376 nm was observed for **DT**-**An**, but the corresponding ε of anthracene is $6.0 \times 10^2 \text{ M}^{-1} \text{ cm}^{-1}$ at the same wavelength. The **DT**-**An** solution ($c = 1.0 \times 10^{-5} \text{ M}$ in toluene, 20 °C) was irradiated at $\lambda_{\text{ex}} = 377 \text{ nm}$ (maximum absorption) with Xe lamp for different time intervals (from 1 minute to 45 minutes). We found the decrease in UV-Visible absorption (see **ESI**⁺ Fig. S39) with prolonged irradiation, which shows that the **DT**-**An** is not very stable if exposed to light for continuous long time.

Fluorescence emission spectra

The emission of all compounds in different solvents was studied (Fig. 2). **MT-Per** show hypsochromic shift (blue shift) (\approx 8 nm) in emission with increased solvent polarity. The fluorescence intensity is also solvent dependent (slightly intensified in polar solvent). In case of **MT-NI** the emission is red shifted ($\lambda_{max} = 454$ nm in toluene to $\lambda_{max} = 496$ nm in methanol) and the intensity of emission increases with increasing polarity of solvent. Bathochromic shift (red shift) was also observed in **DT-An** with increased solvent polarity.

MT-NI is interesting, the emission is intensified in polar solvents (Fig. 2b). This may be due to the change of the S_1/T_n energy gap in different solvents, for instance the $n-\pi^*$ state may change its energy level in different solvents (either singlet

or triplet). Similar results were observed for **MP-NI** (see **ESI** Fig. S23b[†]). Interestingly, the emission wavelength of other compounds is not dependent on solvent polarity.

The emission spectra of compounds were studied and compare with the reference compounds (Fig. 3). **MT-Per** show decreased fluorescence intensity with emission band at 477 nm. This band is red–shifted as compared to emission of **Per** moiety at 445 nm. In case of **MP-Per**, emission band was observed at 461 nm. The red shift in emission band was also observed for **MP-Per** but fluorescence quenching is not significant ($\Phi_F = 94.0$ %, Table 1) when compared with reference compound **Per** ($\Phi_F = 98.0$ % in n–hexane, Table 1).

The effect of thiophene and phenyl substitution on the core of anthracene and naphthalene imide is different from perylene core. By introducing phenyl group to the core of **An**, an increased fluorescence quantum yield ($\Phi_F = 97$ %, Table 1) was observed with emission band at 425 nm (Fig. 3c). In case of **DT-An**, however, the fluorescence quantum yield ($\Phi_F = 2$ %, Table 1) was greatly reduced with red shifting of emission band to 436 nm. The decrease in emission of **DT-An** may be due to some radiation less decay and ISC (See later section for detail).

For **MP-NI**, a broad structure less emission band was observed at 414 nm (Fig. 3b). The emission of the compound (**MP-NI**) significantly increased with phenyl substitution on **NI**



Fig. 3 Fluorescence emission spectra of (a) Per, MT-Per and MP-Per (λ_{ex} = 406 nm), (b) Br-NI, MT-NI and MP-NI (λ_{ex} = 340 nm), (c) An, DT-An and DP-An (λ_{ex} = 344 nm) in toluene, 20 °C.



Fig. 4 Decay traces of the fluorescence of (a) MT-Per (λ_{em} = 475 nm), MP-Per (λ_{em} = 460 nm) and Per (λ_{em} = 445 nm) (b) MT-NI (λ_{em} = 475 nm) and MP-NI (λ_{em} = 445 nm) (c) DT-An (λ_{em} = 445 nm), DP-An (λ_{em} = 430 nm) and An (λ_{em} = 450 nm). MT-Per, MP-Per and Per were excited with a picosecond pulsed laser (407 nm). MT-NI, MP-NI, DT-An, DP-An, and An were excited with a picosecond pulsed laser (340 nm). $c = 1.0 \times 10^{-5}$ M in acetonitrile, 20 °C.

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core. In case of **MT- NI**, the emission band was observed at 455 nm (Fig. 3b). The fluorescence quantum yield of **MT-NI** is 14 % (Table 1) as compared to **MP-NI** compound (Φ_F = 78 %, Table 1), while the reference compound (**Br-NI**) is non-fluorescent. Enhance in fluorescence is due to charge transfer ability of aryl group to the electron deficient **NI**.

The fluorescence lifetimes of the compounds were studied (Fig. 4). For **Per**, fluorescence lifetime of 4.3 ns was determined in acetonitrile. Similar fluorescence lifetime (τ_F = 3.6 ns) was observed for **MP-Per**. For **MT-Per**, however, a short lived luminescence component was observed as 0.58 ns (98 %) / 4.0 ns (2 %). This result indicates that there is an efficient quenching channel for the S₁ state of **MT-Per**. This quenching channel can be attributed to ISC (see later section).

The photophysical parameters of the : to the photophysical parameters of the : to the photophysical parameters of the : to the photophysical parameters of the compounds were determined. The results show that the \mathcal{D}_{Δ} is up to 60 % (**MT-Per**). Moderate singlet oxygen quantum yield was observed for **MT-NI** (\mathcal{D}_{Δ} = 22 %). For **DT-An**, the \mathcal{D}_{Δ} = 13 %, which is much lower than that of **An** (\mathcal{D}_{Δ} = 70 %).

Nanosecond transient absorption spectroscopy: the triplet excited states property of the compounds

In order to confirm the formation of triplet state with thienyl attached chromophores, the nanosecond transient absorption spectra of the compounds were studied (Fig. 5). For **MT-Per**, an excited state absorption (ESA) band at 548 nm was



Fig. 5 Nanosecond time-resolved transient absorption spectra of (a) MT-Per (b) MT-NI (c) DT-An (d) Decay trace of MT-Per at 560 nm, λ_{ex} = 355 nm (e) Decay trace of MT-NI at 560 nm, λ_{ex} = 355 nm (f) Decay trace of DT-An at 397 nm, λ_{ex} = 355 nm (pulsed nanosecond laser), c = 1.0×10⁻⁵ M for MT-Per, and c = 5.0 × 10⁻⁵ M for both MT-NI and DT-An. In deaerated toluene, 20 °C.

Table 1 Photophysic	al parameters o	of the c	compound

	$\lambda_{ m abs}{}^a$ / nm	ε ^b	λ_{em} / nm	$\varPhi_{F}{}^{d}$ / %	λ_{ex^e} / nm	τ_{F}^{f} / ns	<i>τ</i> г ^в / μs	\varPhi_{Δ^h} / %
MT- Per	421, 446	2.81, 3.32	477	15	406	0.6 ^{<i>a</i>} , 0.6 ^{<i>n</i>}	281.8	60
VP-Per	416, 442	1.25, 1.56	461, 489	94	406	3.3ª ,3.6 ⁿ	_ <i>i</i>	_ <i>i</i>
MT-NI	367	1.55	455	14	340	3.2 ^{<i>a</i>} , 3.4 ^{<i>n</i>}	56.7	22
MP-NI	349	1.33	414	78	340	3.4 <i>ª</i> , 3.7 <i>ⁿ</i>	70	21
DT-An	377, 397	1.20, 1.16	447	2	344	1.0 <i>ª</i> , 1.4 <i>ⁿ</i>	5.7	13
P-An	373, 393	0.96, 0.90	430, 409	97 ^{i,48}	344	5.4 <i>ª</i> , 6.0 <i>ⁿ</i>	<i>k</i>	_ <i>i</i>
Per	407, 434	3.47, 4.50	445, 471	98 ^{i,49}	406	3.8 <i>ª</i> , 4.3 <i>ⁿ</i>	_ <i>k</i>	_ <i>i</i>
Br-NI	340, 355	1.74, 1.55	<i>k</i>	_ <i>j</i>	340	_ <i>i</i>	28.4	_ <i>i</i>
٩n	357, 377	0.61, 0.58	453, 426	27 ⁱ	344	3.3 <i>ª</i> , 3.8 ⁿ	64.5	70 ⁱ

^{*a*} In toluene (1.0 × 10⁻⁵ M), ^{*b*} Molar extinction coefficient at absorption maxima, $\varepsilon : 10^4$ M⁻¹ cm⁻¹, ^{*c*} Emission wavelength, ^{*d*} Fluorescence quantum yield in toluene, ^{*e*} Excitation wavelength for measurement of the fluorescence, For **MT-Per** and **MP-Per**, perylene was used as standard ($\Phi_{\rm E} = 98\%$ in n-hexane). For **MT-NI**, **MP-NI**, **DT-An** and **DP-An**, anthracene was used as standard ($\Phi_{\rm E} = 30\%$ in ethanol), ^{*f*} Fluorescence lifetimes in toluene. ^{*n*} Singlet oxygen quantum yield, for **MT-Per** and **MP-Per** in DP-An in methanol, anthracene was used as standard ($\Phi_{\rm A} = 70\%$ in methanol). ^{*f*} Iluerescence lifetimes in toluene. ^{*n*} Singlet oxygen quantum yield, for **MT-Per** and **MP-Per** in DE-An and DP-An in methanol, anthracene was used as standard ($\Phi_{\rm A} = 70\%$ in methanol). ^{*f*} Iluerescence lifetimes in toluene. ^{*n*} Singlet oxygen quantum yield, for **MT-Per** and **MP-Per** in DF-An and DP-An in methanol, anthracene was used as standard ($\Phi_{\rm A} = 70\%$ in methanol). ^{*f*} In acetonitrile.

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observed (Fig. 5a). For **MT-Per**, no significant ground state bleaching (GSB) band was observed. We suppose this is due to the overlap of the GSB and ESA bands. It is noticeable that the ESA band of **MT-Per** (548nm) is red–shifted as compared to that of **per** (450 nm).⁵⁸ It is reasonable because the steady state UV–Vis absorption of **MT-Per** is red–shifted as compared to that of perylene.

The triplet state lifetime of **MT-Per** was determined as 282 μ s, which is close to the previous report of 272 μ s, accessed with the intramolecular triplet photosensitizing method.⁵⁸ It should be pointed out that the triplet state lifetime of **MT-Per** is much longer than **Br-Per** (62.2 μ s), we attribute this to the lack of significant heavy atom effect in **MT-Per**. Heavy atom effect may enhance the T₁ \rightarrow S₀ transition, as such the triplet state life may be reduced. It should be pointed out that the transient observed is not charge separated state (anion **per** should give absorption at 585 nm).⁵⁹ The enhanced ISC in the thienyl compounds may be attributed to the alternation of the excited state energy levels, and the establishment of the energy level matched S₁/T_n states.^{55,60,61}

For **MT-NI**, ESA band at 561 nm was observed upon pulsed laser excitation, a minor GSB band was observed at 360 nm. The ESA band is similar to the previously reported ESA band of **NI** moiety (450–650 nm).⁶² The triplet state lifetime was determined as 56.7 μ s. Similar results were observed for **DT-An** (Fig. 5c). The ESA band at 426 nm is close to the pristine **An** (see ESI⁺, Fig. S29). It is interesting that the triplet state lifetime was determined as 5.9 μ s, much shorter than the triplet state lifetime of **An** (64.5 μ s) (see **ESI** Fig. S29⁺). The reason may be due to the intramolecular rotation of the thienyl substituents, or the vibration induced enhanced coupling between T₁ and S₀ state.

DFT calculation

The molecular geometries of the compounds were optimized









Fig. 6 Selected frontier molecular orbitals of Per, MP-Per and MT-Per calculated with DFT theory at B3LYP/6-31G (d) with Gaussian 09.



Fig. 7 proposed energy levels and frontier molecular orbital diagrams of **MT-Per**. DFT calculation was performed at the B3LYP/6-31G (d) level using Gaussian 09W. Alkyl chains are simplified as methyl groups to reduce the computation time.

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Table 2 Properties of the low-lying electronic excited states of MP-Per and MT-Per. Calculated by TDDFT//B3LYP/6-31G (d), based on the DFT/B3LYP/6-31G(d) optimized ground state geometries.

	States	Electronic transition	Energy / eV/nm ^a	f ^b	Composition ^c	CI ^d
MT-Per	Singlet	$S_0 \rightarrow S_1$	2.57 / 481	0.7304	H→L	0.7061
		$S_0 \rightarrow S_2$	3.51 / 352	0.0001	H−1→L	0.4934
		$S_0 \rightarrow S_3$	3.61/343	0.0012	H→L+2	0.5653
		$S_0 \rightarrow S_4$	3.68 / 336	0.0417	H→L+1	0.5004
	Triplet ^e	$S_0 \rightarrow T_1$	1.43 / 862	0.0000	H→L	0.6951
		$S_0 \rightarrow T_2$	2.67 / 464	0.0000	H−6→L	0.1087
		$S_0 \rightarrow T_3$	3.06 / 405	0.0000	H→L+3	0.4327

^o Only the selected low-lying excited states are presented. ^b Oscillator strengths. ^c Only the main configurations are presented. ^d The CI coefficients are in absolute values.



Scheme 3. Simplified Jablonski diagram illustrating the photophysical processes in (a) MP-Per (b) MT-Per (c) DP-An and (d) DT-An. The excited state energy levels of compounds are derived from spectroscopic data (UV–Vis and fluorescence emission). The triplet excited state energy values were calculated by TDDFT//B3LYP/6-31G (d). In toluene.

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(Scheme 2). For **MT-Per**, the dihedral angle between the thienyl plane and **per** plane is 44.2 °. Interestingly the dihedral angle for **MP-Per** is 52.8 °. These results indicate that the π -conjugation in **MT-Per** is slightly more effective than that in **MP-Per**. Similar results were observed for **MT-NI** and **MP-NI**. For **DT-An** and **DP-An**, interestingly, similar dihedral angles were observed (89.8 ° and 90.5 °, respectively). The frontier molecular orbitals of the compounds were studied base on the optimized ground state geometry (Fig. 6).

The general effect of attaching phenyl and thienyl substituents to the chromophores is the increased energy levels for the occupied orbitals, and the decreased energy levels of the frontier empty orbitals. This trend is responsible for the red-shifted absorption bands of the compounds as compared to the reference compounds. We used DFT/TDDFT to calculate the excited state of the compounds to rationalize the ISC abilities (Fig. 7). The excited states energy levels and the electronic transitions of **MT-Per** are presented. The calculated S₁ state is with a vertical transition energy of 2.57 eV (481 nm), which is very close to the experimental results of the absorption band at 446 nm (Fig. 1a). This agreement rationalized out theoretical computation. The computation also infers that there is no other major absorption band down to 350 nm, which is verified by experimental observation.

The triplet excited states were also computed (Fig. 7). T₁ state (1.44 eV) is well below the S1 state (2.57 eV), however, T2 state (2.67 eV) is with similar energy to S_1 state. Moreover, the electronic configuration of S₁ state is with significant $\pi-\pi*$ feature, for T₂ state, however, the $\pi-\pi*$ feature is predominant. These two characters make the S_1/T_1 states strongly coupled, and we suppose the $S_1 \rightarrow T_2$ ISC is enhanced. Ultrafast internal conversion $T_2 {\rightarrow} T_1$ populates the T_1 state finally. We examined the excited state energy levels of per (see ESI Fig. S36⁺), no T₂ state sharing similar energy with S₁ state was observed. Thus the enhanced ISC in MT-Per can be rationalized by the close-lying S_1/T_2 states. Previously thiophene fused Bodipy was reported to show efficient ISC.⁴³ It was shown that a coupling matrix elements of a few cm⁻¹ is sufficient for efficient ISC. Among the other factors, the heavy atom effect of the sulfur atom is responsible for the ISC.^{37, 38} It was proposed that the $S_1 \rightarrow T_1$ ISC is inhibited given the energy gap between the two states is large. On the other hand, the $S_1 \rightarrow T_2$ ISC becomes possible given the energy gap between the two states is small.^{54, 55} The energy levels of the excited states of a few representative compounds were presented in Scheme 3. For MP-Per, the T_2 state (2.95 eV) is higher than S_1 state (2.80 eV), and the T_1 state (1.48 eV) is well below the S_1 state. Thus we propose the electronic coupling S_1/T_n is weak and the ISC should be poor.

Conclusions

In summary, in order to prepare heavy atom free triplet photosensitizers, thienyl moiety was introduced to the chromophores of perylene, naphthaleneimide and anthracene. The photophysical properties of the compounds were studied with steady-state and time-resolved transient absorption and emission spectroscopies, as well as DFT computations. The UV-Vis absorption of the chromophores is generally red-shifted upon introducing the thienyl moieties. We found that ISC generally enhanced with attaching thienyl moiety on the chromophores, and the singlet oxygen quantum yield is up to 60 %. The triplet state lifetimes are as long as 282 µs. DFT/TDDFT computations on the excited states show that the relative energy levels of the excited state were altered by introducing thienyl substituents, and the energy level matched S₁/T₁ states of the thienyl substituted compounds contribute to the enhanced ISC ability. All these features are beneficial for the compounds to be used as triplet photosensitizers. These works propose new insights in the design of triplet photosensitizers to be used in photophysics and photobiology, and especially in photodynamic therapy.

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Table of Contents Entry:

Effect of thiophene substitution on the intersystem crossing of arene photosensitizers

Farhan Sadiq,^a Jianzhang Zhao,^a* Mushraf Hussai,^a and Zhijia Wang^a

Effect of Thiophene Substitution on ISC					
			s	Φ_{Δ} = 60 % $\Phi_{\rm F}$ = 15% ISC ability	
So	0.03 0.02 0.01 0.00 0.00	T-Per 0 μ ⁶ 1665 μs 1665 μs 0 480 600 720 Wavelength / nm	¹ (F) S₀ ▼	ISC T ₁	

Thiophene substitution gives energy level-matched S_1/T_2 states and the ISC was enhanced, which was not observed with phenyl substitution.