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Supporting Information

Aggregation-Induced and Polymorphism-Dependent Thermally Activated Delayed Fluorescence (TADF) Characteristics of an Oligothiophene: Applications in Time-Dependent Live Cell Multicolour Imaging

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Experimental Section

Materials and general methods:

Thiophene, CBr₄ and PPh₃ were purchased from Spectrochem Chemicals (India). Pd(PPh₃)₄ was purchased from Sigma-Aldrich (USA). DMF and NBS were purchased from SD Fine Chemicals (India), n-BuLi was purchased from Avra Chemicals (India). CDCl₃ was purchased from Merck (Germany). Standard Schlenk technique was used for reactions requiring inert nitrogen atmosphere. CH₂Cl₂ was dried over CaH₂ and distilled under N₂ atmosphere from appropriate drying agents prior to use. DMF was dried over Na₂SO₄ for overnight and distilled out at reduced pressure and stored over 3Å molecular sieves. THF and Et₂O were dried over sodium. Commercially available reagents were used without further purification unless otherwise stated. All reactions were monitored by thin-layer chromatography.

NMR spectra were recorded on Bruker Advance 400 (400 MHz for ¹H and 100.62 MHz for ¹³C) NMR spectrometer. ¹H NMR and ¹³C NMR Spectra were referenced internally to the solvent signals. High resolution mass spectra were obtained from Q-TOF instrument by electrospray ionization (ESI). Electronic absorption spectra were recorded on a Perkin Elmer LAMBDA 750 UV/visible spectrophotometer. Solution were prepared using a microbalance ($\pm$ 0.1mg) and volumetric glassware and then charged in quartz cuvettes with sealing screw caps. Fluorescence emission studies were carried out on a Horiba JOBIN YVON Fluoromax4 spectrometer and Edinburgh instrument FLS980 model. Photo luminesce lifetime is measured the integrated device in Edinburgh instrument FLS980 model. Single-crystal X-ray diffraction studies were carried out with a Bruker SMART APEX diffractometer equipped with 3-axis goniometer. The crystals were kept under a steady flow of cold dinitrogen during the data collection. The data were integrated using SAINT, and an empirical absorption correction was applied with SADABS. The structures were solved by direct methods and refined by full matrix least-squares on F² using SHELXTL software.¹ The quality of the single crystals of polymorph **1a** was not good as a result the refinement is slightly poor. We tried several crystallization methods to obtain better quality crystals, however, we repeatedly end up with similar quality crystals. With all our effort this is the best quality data we could get for **1a**. The hybrid B3LYP functional² has been used in all calculations as incorporated in *Gaussian 09* package,³ mixing the exact Hartree-Fock-type exchange with Becke's exchange functional⁴ and that proposed by Lee-Yang-Parr for the correlation contribution.⁵ The 6-31G(d) basis set was used for all the atoms which provides reasonably high-quality results in moderate timescales. The ground state geometry optimizations were followed by subsequent frequency test to ascertain stationary points. TD-DFT energy calculations on ground state optimized structures were performed to simulate UV-Visible absorption spectra of the compounds.

Cell Imaging:

Materials: DMEM (Dulbecco's Modified Eagle Medium-High glucose), DPBS (Dulbecco's phosphate buffered saline), Fetal Bovin Serum (FBS), MTT (Thiazolyl blue tetrazolium Bromide), and Penicillin–Streptomycin (Penstrep).

Cell lines used: HeLa cells

Methods:

1. Culturing of cells:

HeLa cells were maintained in aseptic conditions. The cells were cultured in DMEM with 10 % FBS and 1 % Penstrep at 37 °C in a humidified chamber which maintains 5 % CO₂ level.

2.Sub-Culturing of cells:

An 80 % confluent T25 cell culture plate was washed with DPBS to remove dead cells. The attached cells treated with 1 or 2 ml of 1X-Trypsin-EDTA at 37°C. The cells became round and detached from flask after trypsinisation. The trypsin was deactivated by adding 3-4 ml of 10 % FBS. A single cell suspension was made by gentle aspiration with p-1000 tips. The cells were seeded in fresh flask with 1:3 ratios.

3. Freezing and thawing cells:

Actively proliferating cells were trypsinized and suspended in 5 ml of growth medium. The cells were centrifuged for 3 minutes at 100-150 x g using a bench top centrifuge. The cell pellet was suspended in fresh growth medium. The cells were aliquot drop-wise into cryo vials containing an equal volume of pre-chilled 2X freezing mixture consisting of 15% of DMSO in growth medium. The cells were gently mixed and incubated on ice for 30 minutes and then transferred to -70°C for 48-72 h and finally to liquid nitrogen.

In order to revive the cells, a vial of frozen cells from liquid nitrogen was taken out and allowed to thaw in water bath at 37°C. The cells were transferred into a 15 ml centrifuge tube containing 10 ml of growth medium and centrifuged at 100-150 x g for two minutes. The cell pellet was suspended in fresh growth medium and plated in a T-25 flask. Fresh medium was added every alternate day till the cells becomes confluent and could be sub-cultured.

4. Solubility of compounds:

Compound **1** is soluble in cell culture grade DMSO. The stock solution of the compound **1** was made in cell culture grade DMSO (5 mg/ml) for various biological experiments.

5. Cytotoxicity assay (MTT assay):

MTT assay is a standard colorimetric assay used for determining the cytotoxicity of reagents in cells.^[6] Yellow MTT (3-(4, 5-Dimethylthiazol-2-yl)-2, 5-diphenyltetrazolium bromide) is reduced to purple formazan in the mitochondria of living cells. Formazan is dissolved in Dimethyl Sulfoxide (DMSO). The absorbance of formazan solution can be quantified by spectrophotometer by monitoring the intensity of peak at 570-590 nm. The reduction of MTT takes place only when mitochondrial reductase enzymes are active. Therefore, conversion of MTT to formazan is directly correlated to the number of viable cells. The optical density (OD) values of formazan formed in presence of reagents were compared with untreated cells to plot bar graphs.

Scheme S1. Compound **1** showed MTT to formazan conversion by a mitochondrial reductase

In a 96-well tissue culture plate 8000 cells per well were plated and allowed to grow the cells for 24 h. Compound **1** was added to these cells by varying concentrations (200 μM to 3.125 μM) in 0.2 % FBS medium. Three hours before the stipulated time, 20 μl of 5 mg/ml MTT solution was added to each well and incubated further three hours to form formazan crystals. The culture medium was aspirated by pipette and 200 μl of DMSO was then added in each well to dissolve the crystals. The intensity of the purple color produced was estimated by determining the absorbance at 590 nm against DMSO blank using a spectrophotometer (BIO-RAD Model1680, MICROPLATE READER).

6. Confocal microscopy studies:

Approximately 3×10^5 cells were seeded on round cover slips. The cells were allowed to grow for 24 h. These cells were treated with compound **1** (10 μM) for 30 minutes. After treatment with compound **1**, the cells were washed twice with DPBS and mounted on glass plate with antifade. These cover slips were subjected to confocal Zeiss LSM880(Airyscan) microscopy. The images were analyzed on Zen software. The fluorescent intensity was measured with Image J software.

Synthesis and characterization:

Compound **1** was synthesized by palladium metal mediated cross coupling between 2,5-bis(2,2-dibromovinyl)thiophene and thiophene-2-boronic acid. The crude product was washed with brine solutions, water and ethyl acetate. The combined organic layer was concentrated under reduced pressure gave crude compound **1**. Analytically pure **1** was obtained after column chromatography [silica gel, ethyl acetate/ n-hexane (1:03)]. Yield: 0.210 g, 39.7%. ^1H NMR (400 MHz, CDCl_3 , δ in ppm) 6.74 (d, 2H), 6.76 (s, 2H), 6.91(d, 2H), 6.93(d, 2H), 7.08 (d, 2H), 7.17(s, 4H), 7.48 (d, $J=5.18$, 2H); ^{13}C NMR (100 MHz, CDCl_3 , δ in ppm) 122.9, 125.2, 126.3, 126.5, 127.8, 127.9, 128.9, 129.5, 138.2, 142.51, 147.4; ESI-MS (positive ion mode): calcd for $\text{C}_{24}\text{H}_{16}\text{S}_5$ 463.9856, observed 463.9856 (M^+). Anal. Calcd for $\text{C}_{24}\text{H}_{16}\text{S}_5$: C, 62.03%; H, 3.47%; S, 34.5%. Found C, 62.05%; H, 3.45%, S, 33.95%

Figure S1. ^1H NMR spectra of **1** in CDCl_3 .

Figure S2. ^{13}C NMR spectra of compound **1** in CDCl_3 .

Figure S3. HRMS of compound **1** in Methanol.

Optical Characteristics of **1**

Figure S4. (a) UV-Vis (left) and (b) emission(right) spectra of **1** (concentration 10^{-5} M) in solvents with polarity.

Figure S5. (a) Normalized UV-Vis (left) and (b) normalized emission(right) spectra of **1** (concentration 10^{-5} M) in in solvents with polarity.

Figure S6. (a) Excitation dependent emission of **1** in DMSO (left) and (b) Emission dependent excitation spectra of **1**(right) (concentration 10^{-5} M) in various solvents.

Figure S7. 3D plot of Excitation dependent emission spectra of **1** (concentration 10^{-5} M) in DMSO.

Table ST1. Crystal data and structure refinement for 1a: CCDC 1882867

Empirical formula	$C_{24}H_{16}S_5$	
Formula weight	464.67	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	Orthorhombic, $Pn\bar{a}2_1$	
Unit cell dimensions	$a = 14.3381(8)$ Å	$\alpha = 90$ deg.
	$b = 25.3755(14)$ Å	$\beta = 90$ deg.
	$c = 6.1625(4)$ Å	$\gamma = 90$ deg.
Volume	2242.1(2) Å ³	
Z, Calculated density	4, 1.377 Mg/m ³	
Absorption coefficient	0.526 mm ⁻¹	
F(000)	960	
Crystal size	0.12 x 0.12 x 0.12 mm	
Theta range for data collection	2.953 to 24.997 deg.	
Limiting indices	$-17 \leq h \leq 17$, $-30 \leq k \leq 30$, $-7 \leq l \leq 6$	
Reflections collected / unique	48183 / 3918 [$R(\text{int}) = 0.0381$]	
Completeness to $\theta = 25.242$	97.5 %	
Max. and min. transmission	0.939 and 0.939	
Refinement method	Full-matrix least-squares on F^2	
Goodness-of-fit on F^2	1.244	
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0887$, $wR_2 = 0.2715$	
R indices (all data)	$R_1 = 0.1071$, $wR_2 = 0.2893$	

Table ST2. Crystal data and structure refinement for 1b CCDC 1882866.

Empirical formula	$C_{24}H_{16}S_5$	
Formula weight	464.67	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	Monoclinic, $P2_1/n$	
Unit cell dimensions	$a = 13.167(5)$ Å	$\alpha = 90$ deg.
	$b = 9.834(4)$ Å	$\beta = 104.538(12)$ deg.
	$c = 16.877(7)$ Å	$\gamma = 90$ deg.
Volume	2115.3(14) Å ³	
Z, Calculated density	4, 1.459 Mg/m ³	
Absorption coefficient	0.557 mm ⁻¹	
F(000)	960	
Theta range for data collection	3.066 to 27.585 deg.	
Limiting indices	$-17 \leq h \leq 17$, $-12 \leq k \leq 12$, $-21 \leq l \leq 21$	
Reflections collected / unique	83143 / 4883 [$R(\text{int}) = 0.0590$]	
Completeness to $\theta = 25.242$	99.8 %	
Refinement method	Full-matrix least-squares on F^2	
Goodness-of-fit on F^2	1.041	
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0578$, $wR_2 = 0.1533$	
R indices (all data)	$R_1 = 0.0774$, $wR_2 = 0.1709$	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.249 and -0.708 e.Å ⁻³

Figure S8. Intermolecular weak slipped $\pi\cdots\pi$ interactions in **1a**.

Figure S9. Intermolecular weak slipped $\pi\cdots\pi$ interactions in **1b**.

Figure S10. Luminescence spectra of polymorphs **1a** and **1b**

Figure S11. Excitation spectra of **1a** (green, $\lambda_{\text{exct}} = 500$ nm) and **1b** (red, $\lambda_{\text{exct}} = 600$ nm) crystals.

Figure S12. AFM (right) image of aggregates of **1** formed in 70% H₂O fraction in DMSO.

Figure S13. Prompt and delayed emission spectra of aggregates of **1** in 70% H₂O fraction in DMSO. A comparison of emission spectra of as prepared solid and aggregates of **1** in 70% H₂O fraction in DMSO. 1×10^{-5} M solutions of **1** was used for aggregation studies.

Figure S14. Prompt and delayed emission spectra of as prepared solids of **1** at ambient conditions (left) and 77 K (right).

Figure S15. Prompt and delayed emission spectra of polymorphs **1a** (left) and **1b** (right).

Figure S16. Photoluminescence Decay plots of **1a** (left) and **1b** (right) crystals.

Figure S17. Decay plot of aggregates (right) and solids (left) of **1** at 77K

Table ST3: Time resolved emission data 1

Medium	Lifetime (ns)
DMSO	$\tau_1= 0.33$ (16.60%) $\tau_2= 2.83$ (44.31%) $\tau_3= 9.44$ (39.09%)
Aggregates	$\tau_1=0.36$ (70.19%) $\tau_2=3.21$ (23.52 %) $\tau_3=21.47$ (6.28%)
As prepare solid	$\tau_1=0.4896$ (83.26%) $\tau_2=2.4909$ (14.81%) $\tau_3=17.5311$ (1.93%)
Crystal 1a	$\tau_1=0.5010$ (88.70%) $\tau_2=2.6556$ (9.22%) $\tau_3=34.996$ (2.08%)
Crystal 1b	$\tau_1=1.6738$ (51.08%) $\tau_2=3.4084$ (46.45%) $\tau_3=12.3210$ (1.84%)
77K	$\tau_1=0.89$ (68.60%) $\tau_2=2.20$ (29.40%) $\tau_3=7.29$ (2.0%)
300K	$\tau_1=0.5232$ (88.26%) $\tau_2=2.7582$ (10.40%) $\tau_3=22.3992$ (1.34%)

Table ST4. Photoluminescence lifetime of 1 in microsecond time-scale

Medium	Lifetime (μ s)
Aggregates	$\tau_1=4.2$ (67.93%) $\tau_2=8$ (32.07%)
As prepare solid	$\tau_1=1.2$ (33.91%) $\tau_2=10$ (66.09%)
Crystal 1a	$\tau_1=4.3$ (18.79%) $\tau_2=9.8$ (81.21%)
Crystal 1b	$\tau_1=2.7$ (33.91%) $\tau_2=7.2$ (66.09%)
77K	$\tau_1=5.7$ (81.35%) $\tau_2=53.3$ (18.65%)

Table ST5. Quantum yield of 1 in various states

State (%)	Φ
DMSO	4.6
Aggregates (fw = 90 % DMSO- Water fraction)	11.3
As prepared solid	17.3
Crystal 1a	40.6
Crystal 1b	63.1

Figure S18. DFT optimized ground state geometry of **1a** crystal (top). Calculated energy gap between optimized Ground state (S_0) and excited singlet (S_1) and Triplet (T_1) state [B3LYP functional 6-31G(d,p) basis set in Gaussian 09].

Figure S19. orbital coefficient distribution in **1a** crystal.

Figure S20. DFT optimized ground state geometry of **1b** crystal (top). Calculated energy gap between optimized Ground state (S_0) and excited singlet (S_1) and Triplet (T_1) state [B3LYP functional 6-31G(d,p) basis set in Gaussian 09].

Figure S21. orbital coefficient distribution in **1a** crystal.

Figure S22. DFT Optimized structure of **1** with thiophenes in trans configuration (**1c**) in ground state (S_0) (left) and singlet state (S_1) (right).

Figure S23: Frontier molecular orbitals of the free conformation of **1** in optimized ground state (S_0).

Table ST6: calculated singlet and triplet state energy of **1** in different molecular configurations **1a**, **1b** and **1c**.

Energy (eV)	1a	1b	1c
HOMO	-4.86	-4.86	-4.86
LUMO	-2.09	-2.09	-2.08
Singlet	S1 = 2.60	S1 = 2.60	S1 = 2.64
	S2 = 3.33	S2 = 3.33	S2 = 3.33
	S3 = 3.58	S3 = 3.55	S3 = 3.62
	S4 = 3.59	S4 = 3.62	S4 = 3.67
Triplet	T1 = 1.36	T1 = 1.36	T1 = 0.78
	T2 = 2.27	T2 = 2.27	T2 = 1.75
	T3 = 3.07	T3 = 3.06	T3 = 1.92
	T4 = 3.19	T4 = 3.17	T4 = 1.96

Donor (L)		Acceptor (NL)		E2 kcal/mol	(E _{NL} -E _L) a.u	F (L, NL) a.u
σ	C13-C26	σ^*	C5-S40	1.25	0.48	0.22
σ	C31-C33	σ^*	C4-S40	1.20	0.48	0.22

Figure S24. Preliminary data related to NBO analysis of **1** (rb3lyp/6-31g(d,p) basis set). E2 = Stabilization energy, E_{NL} and E_L are diagonal elements. F (L, NL) is the off diagonal NBO Fock matrix element.

Table ST7: Vertical transition contributions among the FMO.

Compound	Singlet Excited State (S _n)	Transition configuration (% contribution)	Triplet Excited State (T _n)	Transition configuration (% contribution)
Crystal 1a	S ₁	H→L (98.00%)	T ₁	H-1→L+1 (04.50%) H→L (95.22%) L→H (03.38%)
	S ₂	H-1→L (64.98%) H→L+1 (32.00%)	T ₂	H-1→L (48.02%) H→L+1 (42.32%)
	S ₃	H-3→L (56.18%) H-2→L (30.42%) H→L+1 (08.82%)	T ₃	H-2→L (08.00%) H-1→L+1 (19.22%) H-1→L+3 (03.38%)

				H→L+2 (11.52%) H→L+4 (18.00%)
	S ₄	H-3→L (27.38%) H-2→L (62.72%) H→L+1 (03.38%) H→L+2 (02.42%)	T ₄	H-3→L (24.50%) H-3→L+2 (12.50%) H-2→L+3 (11.52%) H-1→L (15.68%) H→L+1 (10.58%) H→L+3 (08.00%)
	S ₅	H-2→L (02.88%) H→L+2 (92.48%)	T ₅	H-2→L (12.50%) H-2→L+2 (18.00%) H-1→L (10.58%) H-1→L+1 (04.50%) H→L+1 (13.52%) H→L+2 (05.12%)
	S ₁	H→L (98.00%)	T ₁	H-1→L+1 (04.40%) H→L (96.09%) L→H (03.67%)
	S ₂	H-1→L (62.72%) H→L+1 (33.62%)	T ₂	H-1→L (48.61%) H→L+1 (43.00%)
	S ₃	H-3→L (13.52%) H-2→L (79.38%) H→L+1 (03.92%)	T ₃	H-3→L (11.52%) H-3→L+1 (04.50%) H-2→L (03.38%) H-1→L+1 (13.52%)

Crystal 1b				H→L+2 (15.68%) H→L+4 (12.50%)
	S ₄	H-3→L (69.62%) H-2→L (15.68%) H→L+1 (06.48%) H→L+2 (02.42%)	T ₄	H-3→L (16.82%) H-3→L+2 (15.68%) H-1→L (06.48%) H-1→L+1 (10.58%) H→L+1 (03.38%) H→L+4 (10.58%)
	S ₅	H-1→L (08.82%) H→L+1 (13.52%) H→L+2 (64.98%) H→L+3 (05.12%)	T ₅	H-4→L (02.42%) H-3→L+2 (02.88%) H-1→L (36.98%) H→L+1 (42.32%)

Figure S25.Time resolved fluorescence images of HeLa cells (control).

Figure S26. Time resolved fluorescence images of HeLa cells incubated with FNPs of 1 (imaging recorded after 0.52 μ s delay).

Figure S27. Time resolved fluorescence images of HeLa cells incubated with FNPs of 1 (imaging recorded after 0.76 μ s delay).

Figure S28. Time resolved fluorescence images of HeLa cells incubated with FNPs of **1** (imaging recorded after 4.12 μ s delay).

Figure S29. Time resolved fluorescence images of HeLa cells incubated with FNPs of **1** (imaging recorded after 20 μ s delay).

Figure S30. Comparison of PL intensity of **1** in HeLa cells in different time delay.

Figure S31. Cytotoxicity of FNPs of **1** in HeLa cells.

Excitation energies and oscillator strengths for **1a** crystal from ground state to singlet state:

Excited State 1:	Singlet-A	2.6015 eV	476.59 nm	f=1.1018	<S**2>=0.000
		120 ->121	0.70510		
This state for optimization and/or second-order correction.					
Total Energy, E(TD-HF/TD-KS) = -2914.98422921					
Copying the excited state density for this state as the 1-particle RhoCI density.					
Excited State 2:	Singlet-A	3.3301 eV	372.31 nm	f=0.0010	<S**2>=0.000
		119 ->121	0.57189		
		120 ->122	-0.40015		
Excited State 3:	Singlet-A	3.5884 eV	345.52 nm	f=0.0304	<S**2>=0.000
		117 ->121	0.53142		
		118 ->121	0.39178		
		120 ->122	-0.20940		
Excited State 4:	Singlet-A	3.5996 eV	344.43 nm	f=0.0600	<S**2>=0.000
		117 ->121	-0.36870		
		118 ->121	0.56604		
		120 ->122	0.13229		
		120 ->123	0.10765		
Excited State 5:	Singlet-A	3.7752 eV	328.41 nm	f=0.1045	<S**2>=0.000
		118 ->121	-0.11782		
		120 ->123	0.68278		
Excited State 6:	Singlet-A	3.8062 eV	325.74 nm	f=0.0210	<S**2>=0.000
		116 ->121	0.16488		
		117 ->121	-0.14080		
		119 ->121	-0.23061		
		120 ->122	-0.29107		
		120 ->124	0.54181		
Excited State 7:	Singlet-A	3.9393 eV	314.74 nm	f=0.0075	<S**2>=0.000
		116 ->121	-0.36061		
		117 ->121	0.18667		
		119 ->121	0.24959		
		120 ->122	0.28551		
		120 ->124	0.42479		
Excited State 8:	Singlet-A	4.0031 eV	309.72 nm	f=0.0017	<S**2>=0.000
		112 ->121	0.10068		
		115 ->121	0.68045		
Excited State 9:	Singlet-A	4.0242 eV	308.09 nm	f=0.0403	<S**2>=0.000

Excited State 1: Triplet-A 1.3574 eV 913.42 nm f=0.0000 <S**2>=2.000
 119 ->122 0.14717
 120 ->121 0.69329
 120 <-121 0.13553

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-KS) = -2915.02995003

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Triplet-A 2.2744 eV 545.12 nm f=0.0000 <S**2>=2.000
 119 ->121 0.49380
 120 ->122 0.46226

Excited State 3: Triplet-A 3.0739 eV 403.35 nm f=0.0000 <S**2>=2.000
 112 ->121 -0.26267
 113 ->121 0.10376
 115 ->121 0.21310
 117 ->122 0.12255
 118 ->121 0.20464
 119 ->122 0.30708
 119 ->124 0.12553
 120 ->123 -0.23977
 120 ->125 0.30356

Excited State 4: Triplet-A 3.1912 eV 388.52 nm f=0.0000 <S**2>=2.000
 117 ->121 0.35422
 117 ->123 0.24614
 118 ->122 0.11626
 118 ->124 -0.23771
 119 ->121 -0.28399
 119 ->123 -0.13490
 120 ->122 0.22906
 120 ->124 0.20088

Excited State 5: Triplet-A 3.2372 eV 383.00 nm f=0.0000 <S**2>=2.000
 112 ->121 0.14257
 117 ->124 -0.26592
 118 ->121 0.25150
 118 ->123 0.30283
 119 ->121 -0.23876
 119 ->122 -0.14890
 120 ->122 0.26013
 120 ->123 -0.15845
 120 ->125 -0.15418

Excited State 6: Triplet-A 3.2506 eV 381.42 nm f=0.0000 <S**2>=2.000

117 ->121	-0.16507
117 ->123	-0.17699
117 ->124	0.16059
118 ->121	-0.16950
118 ->123	-0.18802
118 ->124	0.21848
119 ->121	-0.29166
120 ->122	0.34372
120 ->124	-0.15966

Excited State 7: Triplet-A 3.4780 eV 356.48 nm f=0.0000 $\langle S^2 \rangle = 2.000$

111 ->121	0.22022
114 ->121	-0.18429
116 ->121	0.53813
117 ->121	0.21796
119 ->121	0.10991
120 ->122	-0.13734
120 ->124	-0.10894

Excited State 8: Triplet-A 3.6013 eV 344.27 nm f=0.0000 $\langle S^2 \rangle = 2.000$

117 ->124	0.12324
118 ->121	0.56188
118 ->123	-0.14747
120 ->123	0.33733

Excited State 9: Triplet-A 3.6382 eV 340.79 nm f=0.0000 $\langle S^2 \rangle = 2.000$

110 ->121	-0.11945
112 ->122	-0.10109
114 ->121	0.14985
116 ->121	-0.17332
117 ->121	0.45161
117 ->123	-0.23496
118 ->124	0.23662
119 ->125	0.12295
120 ->124	-0.12340
120 ->126	-0.12836

Excited State 10: Triplet-A 3.7067 eV 334.48 nm f=0.0000 $\langle S^2 \rangle = 2.000$

110 ->121	-0.20700
112 ->122	-0.14888
114 ->121	0.10537
116 ->121	0.19617
117 ->121	-0.21215
117 ->123	-0.14390
118 ->124	0.12152
119 ->125	0.17767

120 ->124	0.42423				
120 ->126	-0.18307				
120 ->130	-0.10325				
Excited State 11:	Triplet-A	3.7521 eV	330.44 nm	f=0.0000	<S**2>=2.000
113 ->121	-0.41075				
113 ->125	-0.10063				
114 ->122	0.20743				
115 ->121	0.45463				
120 ->123	0.14481				
Excited State 12:	Triplet-A	3.7747 eV	328.46 nm	f=0.0000	<S**2>=2.000
113 ->122	-0.23163				
114 ->121	0.57765				
116 ->121	0.17687				
120 ->124	-0.10492				
Excited State 13:	Triplet-A	3.8272 eV	323.96 nm	f=0.0000	<S**2>=2.000
113 ->121	0.35807				
115 ->121	0.18202				
117 ->124	-0.21886				
118 ->121	-0.13832				
118 ->123	0.21466				
120 ->123	0.41394				
Excited State 14:	Triplet-A	3.9784 eV	311.65 nm	f=0.0000	<S**2>=2.000
112 ->121	0.19880				
113 ->121	0.27676				
115 ->121	0.39310				
115 ->123	0.10038				
117 ->124	0.10951				
118 ->123	-0.16709				
119 ->122	-0.16993				
120 ->123	-0.25113				
120 ->124	0.11739				
120 ->125	-0.10890				
Excited State 15:	Triplet-A	4.0270 eV	307.88 nm	f=0.0000	<S**2>=2.000
110 ->121	0.20591				
111 ->121	0.17618				
116 ->121	-0.14631				
117 ->121	0.14467				
117 ->123	-0.16401				
118 ->124	0.12637				
119 ->125	-0.14753				
120 ->124	0.38842				

119 ->121	0.10749								
120 ->122	-0.13419								
120 ->123	-0.29435								
120 ->124	0.59879								
Excited State 7:	Singlet-A	3.9346 eV	315.12 nm	f=0.0213	<S**2>=0.000				
116 ->121	0.35013								
117 ->121	0.21274								
119 ->121	-0.26160								
120 ->122	0.29600								
120 ->123	0.25292								
120 ->124	0.31585								
Excited State 8:	Singlet-A	3.9996 eV	309.99 nm	f=0.0168	<S**2>=0.000				
112 ->121	0.12268								
115 ->121	0.52354								
116 ->121	-0.38297								
119 ->121	-0.10276								
120 ->122	0.16422								
Excited State 9:	Singlet-A	4.0273 eV	307.86 nm	f=0.0288	<S**2>=0.000				
111 ->121	0.13193								
115 ->121	0.44133								
116 ->121	0.42684								
119 ->121	0.15121								
120 ->122	-0.23358								
Excited State 10:	Singlet-A	4.2315 eV	293.00 nm	f=0.0087	<S**2>=0.000				
113 ->121	0.65735								
114 ->121	-0.10980								
120 ->125	-0.18503								
Excited State 11:	Singlet-A	4.2479 eV	291.87 nm	f=0.0036	<S**2>=0.000				
113 ->121	0.13403								
114 ->121	0.67833								
Excited State 12:	Singlet-A	4.3855 eV	282.71 nm	f=0.0015	<S**2>=0.000				
111 ->121	0.17193								
112 ->121	0.51942								
113 ->121	-0.13123								
120 ->125	-0.39642								
Excited State 13:	Singlet-A	4.4263 eV	280.11 nm	f=0.0208	<S**2>=0.000				
111 ->121	0.62727								
112 ->121	-0.23056								
120 ->122	0.11654								

Excited State 14: Singlet-A 4.5571 eV 272.07 nm f=0.0166 <S**2>=0.000
 112 ->121 0.15995
 119 ->122 0.58722
 120 ->125 0.31937

Excited State 15: Singlet-A 4.7708 eV 259.88 nm f=0.0183 <S**2>=0.000
 111 ->121 0.12411
 112 ->121 0.26672
 117 ->122 -0.24408
 118 ->122 0.31848
 119 ->122 -0.24979
 119 ->123 0.10328
 120 ->125 0.35183

Excited State 16: Singlet-A 4.8217 eV 257.14 nm f=0.0100 <S**2>=0.000
 112 ->121 -0.14588
 118 ->122 0.59585
 119 ->122 0.16004
 119 ->123 0.10287
 119 ->124 -0.12259
 120 ->125 -0.18218

SavETr: write IOETrn= 770 NScale= 10 NData= 16 NLR=1 NState= 16 LETran= 298.

Excitation energies and oscillator strengths for **1b** crystal from ground state to triplet state:

Excitation energies and oscillator strengths:

Excited State 1: Triplet-A 1.3573 eV 913.47 nm f=0.0000 <S**2>=2.000
 119 ->122 -0.14844
 120 ->121 0.69318
 120 <-121 0.13550

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-KS) = -2915.02996268

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Triplet-A 2.2668 eV 546.96 nm f=0.0000 <S**2>=2.000
 119 ->121 0.49304
 120 ->122 -0.46373

Excited State 3: Triplet-A 3.0595 eV 405.25 nm f=0.0000 <S**2>=2.000

112 ->121	0.19773						
115 ->121	-0.18868						
117 ->121	0.24268						
117 ->122	0.14543						
117 ->123	-0.11711						
118 ->121	0.13700						
119 ->122	-0.26012						
119 ->123	-0.12949						
120 ->123	0.27564						
120 ->125	0.25439						
Excited State	4:	Triplet-A	3.1736 eV	390.68 nm	f=0.0000	<S**2>=2.000	
112 ->121	-0.20536						
115 ->121	0.10367						
117 ->121	0.29368						
117 ->123	-0.27826						
117 ->124	-0.12515						
119 ->121	0.17990						
119 ->122	0.22874						
119 ->123	-0.10122						
120 ->122	0.12746						
120 ->123	0.10688						
120 ->124	0.12427						
120 ->125	-0.22761						
Excited State	5:	Triplet-A	3.2288 eV	383.99 nm	f=0.0000	<S**2>=2.000	
116 ->121	-0.11378						
117 ->123	0.12348						
119 ->121	0.43229						
120 ->122	0.46570						
Excited State	6:	Triplet-A	3.3143 eV	374.09 nm	f=0.0000	<S**2>=2.000	
117 ->121	-0.11299						
117 ->124	-0.18505						
118 ->121	0.29857						
118 ->123	-0.26865						
118 ->124	0.46146						
120 ->124	-0.14913						
Excited State	7:	Triplet-A	3.4708 eV	357.22 nm	f=0.0000	<S**2>=2.000	
111 ->121	-0.19719						
113 ->121	-0.10363						
114 ->121	-0.14406						
116 ->121	0.52191						
117 ->121	-0.24153						
119 ->121	0.11565						

	120 ->122	0.13745							
	120 ->123	0.11135							
Excited State	8:	Triplet-A	3.5633 eV	347.95 nm	f=0.0000	<S**2>=2.000			
	117 ->121	-0.16884							
	118 ->121	0.57892							
	118 ->123	0.11757							
	118 ->124	-0.25493							
	120 ->123	-0.11385							
Excited State	9:	Triplet-A	3.6556 eV	339.17 nm	f=0.0000	<S**2>=2.000			
	114 ->121	-0.12416							
	116 ->121	0.22989							
	117 ->121	0.42833							
	117 ->123	0.17367							
	118 ->121	0.14723							
	120 ->123	-0.33307							
Excited State	10:	Triplet-A	3.7070 eV	334.46 nm	f=0.0000	<S**2>=2.000			
	110 ->121	0.22137							
	112 ->122	0.14928							
	114 ->121	-0.14780							
	115 ->122	-0.10087							
	116 ->121	-0.17007							
	117 ->121	-0.11951							
	117 ->123	0.21116							
	119 ->125	-0.19234							
	120 ->123	0.14956							
	120 ->124	0.35021							
	120 ->126	0.19970							
	120 ->130	0.11365							
Excited State	11:	Triplet-A	3.7545 eV	330.23 nm	f=0.0000	<S**2>=2.000			
	113 ->121	0.34074							
	114 ->121	-0.28389							
	114 ->122	0.21677							
	115 ->121	0.41654							
	120 ->124	-0.12922							
Excited State	12:	Triplet-A	3.7750 eV	328.44 nm	f=0.0000	<S**2>=2.000			
	113 ->121	0.29195							
	113 ->122	0.21147							
	114 ->121	0.48647							
	115 ->121	0.14332							
	116 ->121	0.16725							

Excited State 13: Triplet-A 3.8213 eV 324.45 nm f=0.0000 <S**2>=2.000

113 ->121	0.25132
114 ->121	-0.10748
115 ->121	-0.13014
117 ->123	-0.12093
117 ->124	-0.14742
118 ->123	-0.13245
118 ->124	0.10370
120 ->123	-0.35881
120 ->124	0.39457

Excited State 14: Triplet-A 3.9360 eV 315.00 nm f=0.0000 <S**2>=2.000

110 ->121	-0.11703
111 ->121	0.16311
113 ->121	-0.31495
115 ->121	0.38125
115 ->123	-0.10220
119 ->122	-0.15270
120 ->124	0.25431
120 ->126	-0.11419

Excited State 15: Triplet-A 4.0735 eV 304.37 nm f=0.0000 <S**2>=2.000

110 ->121	-0.16725
112 ->121	-0.22500
115 ->121	-0.19547
116 ->121	0.15152
117 ->121	0.14192
117 ->123	0.22051
119 ->123	0.10217
119 ->125	0.11042
120 ->123	0.26614
120 ->124	0.20130
120 ->126	-0.14229

Excited State 16: Triplet-A 4.1181 eV 301.07 nm f=0.0000 <S**2>=2.000

111 ->121	0.53563
111 ->123	-0.10174
115 ->123	-0.10420
115 ->124	-0.10962
116 ->121	0.18865
116 ->123	-0.11626
119 ->122	0.24069

SavETr: write IOETrn= 770 NScale= 10 NData= 16 NLR=1 NState= 16 LETran= 298.

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