Substituent-Modulated Excited-State Dynamics and Solvent-Sensitized Nanosecond Triplet Harvesting in Donor–Acceptor TADF Emitters

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Supplementary Information

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Section 1. Experimental Details

Steady State Spectroscopic Measurements

The absorption spectra were recorded using a Varian-Cary 50 UV–visible spectrophotometer in a 1 cm quartz cuvette, with solution concentrations ranging from 1×10^{-5} to 3×10^{-5} M. The solution emission spectra were obtained from 10^{-5} M solutions using a Shimadzu RF5301 PC spectrofluorophotometer. Solid-state emission spectra were recorded using a PerkinElmer LS 55 fluorescence spectrometer.

Time-Resolved Fluorescence Measurements

Lifetime measurements were conducted using time-correlated single photon counting (TCSPC) with a setup described elsewhere.[1] The TCSPC setup is a component of an ultrafast spectrometer (Halcyone, Ultrafast Systems, LLC) employed for measuring femtosecond fluorescence upconversion. In brief, an excitation source was achieved using a regenerative amplified Ti:sapphire laser (Libra, Coherent). This laser generated compressed pulses centered on 800 nm with a full width at half maximum (fwhm) of 70 fs, a power of 4.26 W, and a repetition rate of 5 kHz. Approximately 90% of the laser output was directed to a Coherent OPerA Solo optical parametric amplifier (Light Conversion Ltd.) to generate spectrally tunable light ranging from 240 to 2600 nm. For the current measurements, the OperA was set to 250 and 350 nm with an energy of approximately 50 nJ. The light passed through a depolarizer (DPU-25, Thorlabs) to eliminate contributions from rotational dynamics. A photomultiplier tube with an instrument response function (IRF) of approximately 250 ps, determined from scattered excitation light, was employed as the detector. The fluorescence signal was attenuated, directed to the detector, and the detection wavelength was adjusted using a monochromator. Decay curves were recorded with a peak channel count of approximately 10,000. The decay transients were fitted to multiexponential functions convoluted with the instrument response function (IRF).

Section 2. Effect of Oxygen Quenching: Comparison of TCSPC Decays in Air and Argon

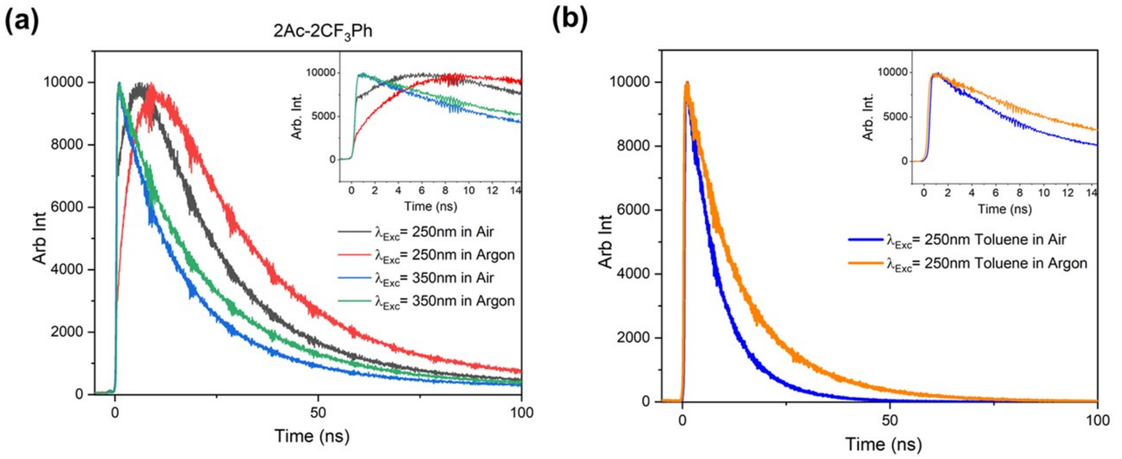


Figure S1. Time-correlated single-photon counting (TCSPC) measurements of 2Ac-2CF$_3$Ph and neat toluene under different atmospheric conditions. (a) Decays recorded in toluene at λ_{em} = 550 nm with λ_{exc} = 250 nm and 350 nm, comparing air (oxygen present) and argon (oxygen-free) environments. The rise component observed at 250 nm excitation is reduced in air due to oxygen quenching, compared to the same measurements under argon, confirming the involvement of triplet states. (b) Control experiment showing TCSPC traces of neat toluene at λ_{exc} = 250 nm in air and argon. The longer decay in argon indicates reduced quenching of toluene triplet states, supporting the Dexter energy transfer (DET) mechanism from solvent triplets to the emitter.

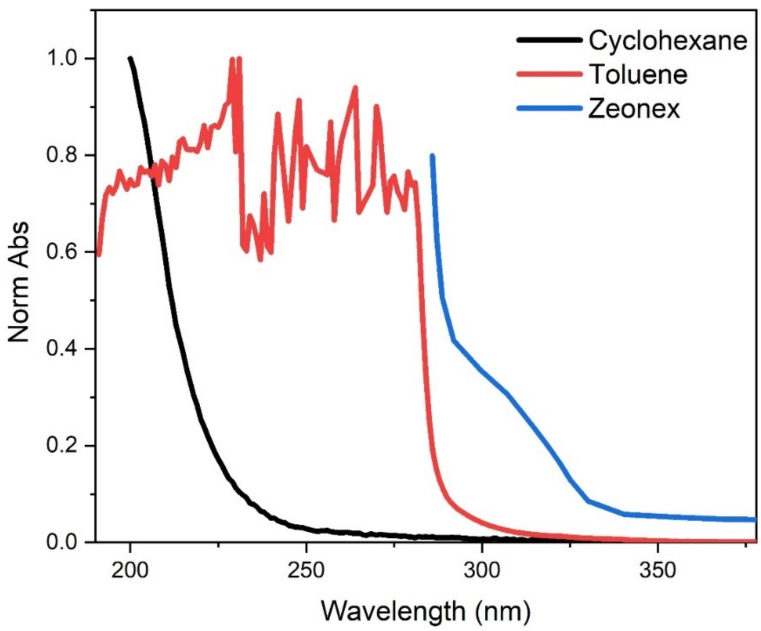


Figure S2. Normalized absorption spectra of cyclohexane, toluene, and zeonex.

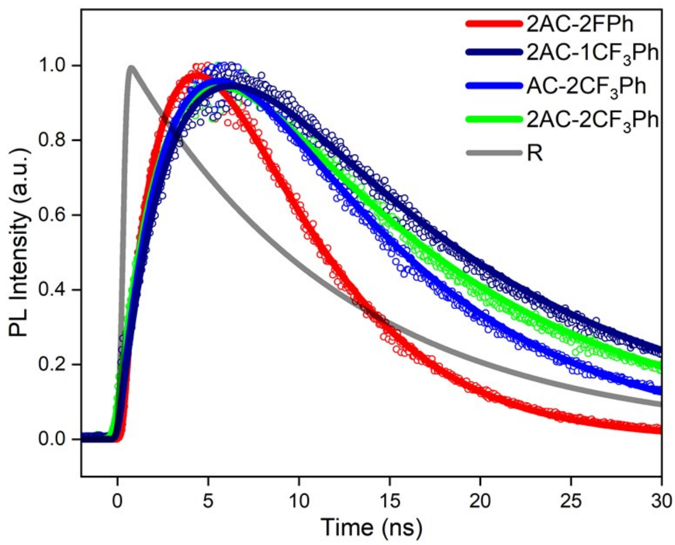


Figure S3: PL decay profiles of the TADF compounds in toluene at 250 nm excitation. The grey trace, R represents the decay of neat toluene measured under identical conditions.

Table S1. Fitted parameters obtained from the PL decay profiles of the TADF compounds in toluene at 250 nm excitation.

Compound	A_1	τ_1 (ns)	A_2	τ_2 (ns)
2Ac-2FPh	-0.50	**3.39 ± 0.27**	0.50	**5.37 ± 0.33**
2Ac-CF_3Ph	-0.50	**3.25 ± 0.10**	0.50	**14.44 ± 0.22**
Ac-2CF_3Ph	-0.50	**3.41 ± 0.19**	0.50	**9.98 ± 0.32**
2Ac-2CF_3Ph	-0.50	**3.00 ± 0.08**	0.50	**13.13 ± 0.17**

Section 3 : Ab Initio Molecular Dynamics

All molecular geometries are optimized using density functional calculations performed in Terachem 1.95[2] using the optimally tuned range-separated LC-ωPBEh functional at def2svp basis level under polarizable continuum model (PCM) with toluene as a solvent.[3] The calculations were performed using a GPU server that had 117 GB RAM installed to support three Tesla Titans graphic cards. The optimized geometries are then subjected to time-dependent ab initio molecular dynamics simulations using the same functional theory and basis set. The temperature is set at 300K using Langevin as a thermostat. Langevin is chosen to simulate the effect of jostling of solvents. The simulations are carried out with 1 femtosecond (fs) time step with 10000 steps. The solvent radius is set to be 3.48 Å and dielectric constant of 2.38, typical values for toluene.

Internal Conversion Calculation

The ESD module in ORCA 6.0 was employed to compute IC rates between minima on the respective triplet-state potential energy surfaces, using state specific Hessians for both the initial and final states. The calculations were performed at the full TDDFT/ω*PBEh/def2-SVP level. Vibronic effects were treated within the harmonic approximation, including Duschinsky rotation, while bulk solvent effects were described using the implicit CPCM model.

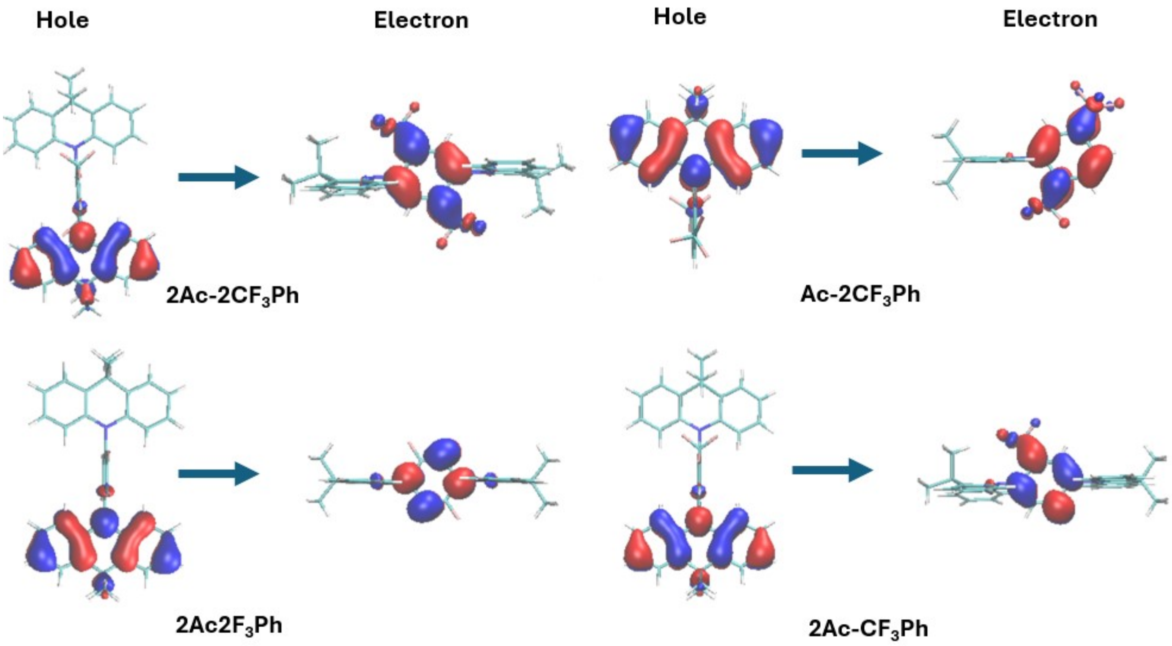


Figure S4 Hole and Electron NTOs of the S_1 state computed at the S_1 relaxed geometries for 2Ac-2CF_3Ph, Ac-2CF_3Ph, 2Ac_2F_3Ph, and 2Ac-CF_3Ph.

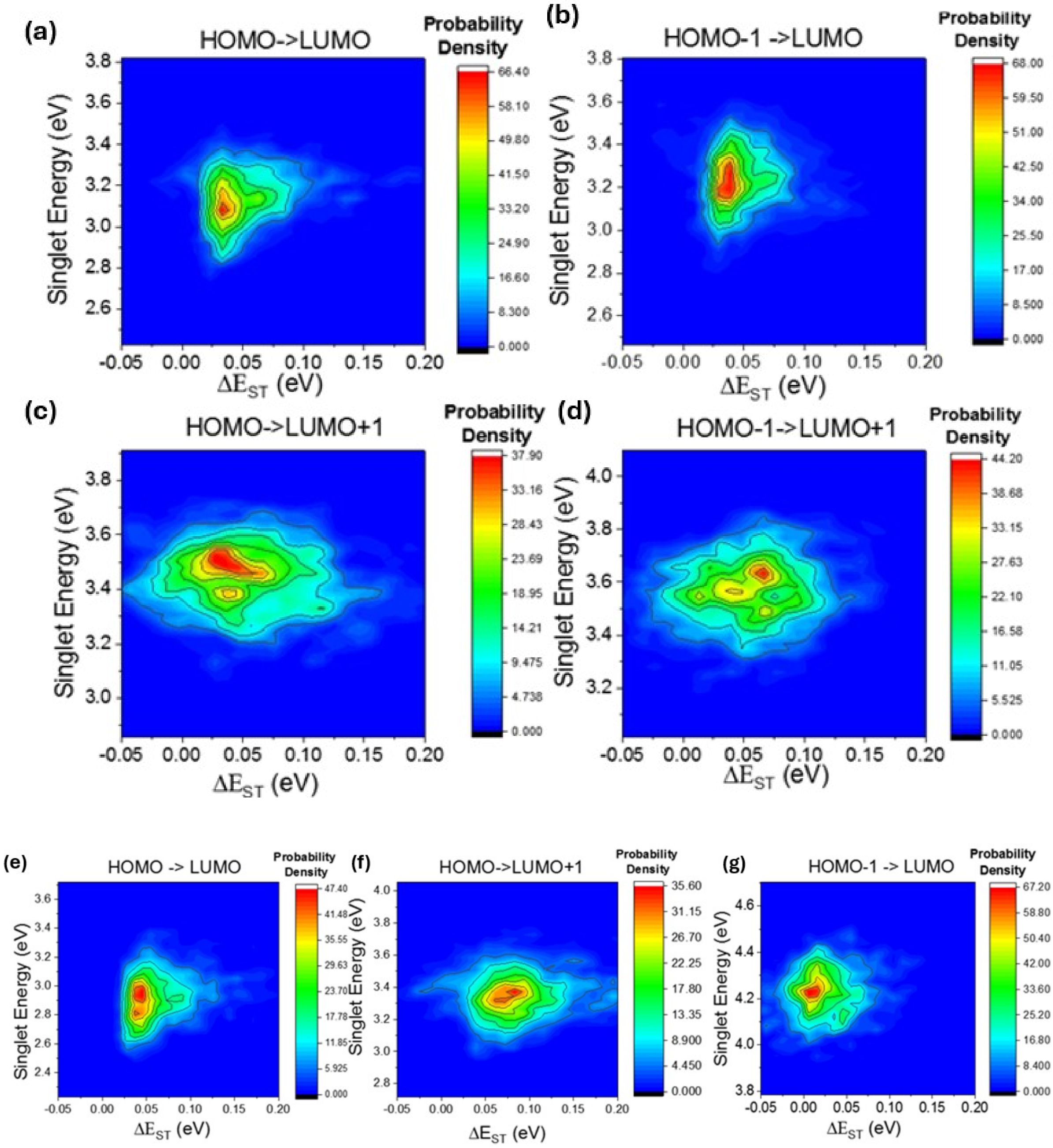
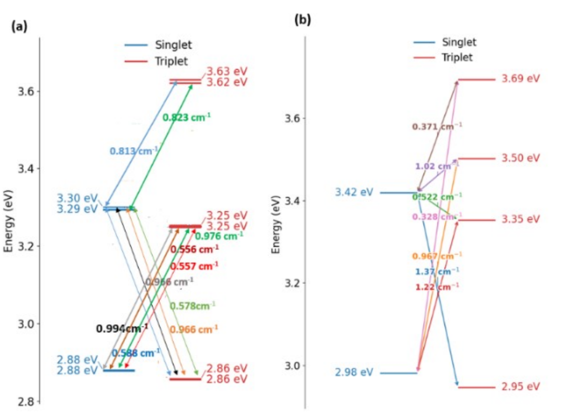


Figure S5 . Probability distribution density plot for ΔE_{ST} for (a-d) Ac-2CF$_3$Ph and (e-g) 2Ac-CF$_3$Ph.

Spin-Orbit Coupling

Spin–orbit coupling was calculated using the optimized geometries of the ground and excited states in ORCA 5.0.4,[4] employing the mean-field/effective potential approach with the optimally tuned *ωpbeh functional without Tamm–Dancoff Approximation (TDA). All calculations used the same functional and basis set in toluene. The calculations were carried out in Data-Intensive Computing Centre at University of Malaya.[4]



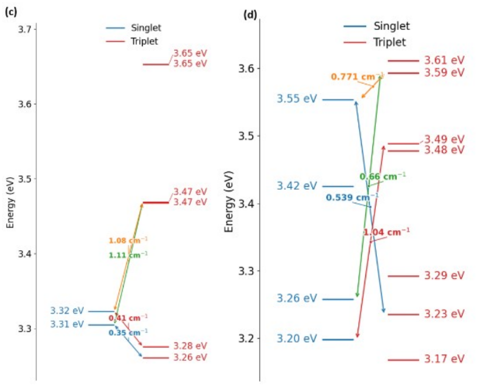


Figure S6 Spin-orbit coupling for SOC for (a) 2Ac-2CF_3Ph (only SOC >0.5 cm^{-1} is displayed) and (b) Ac-2CF_3Ph (only SOC >0.3 cm^{-1} is displayed). (c) 2Ac-2FPh (SOC>0.1 cm^{-1} is displayed) and (d) 2Ac-CF_3Ph (SOC > 0.5 cm^{-1} is displayed) Note the large energy gaps between the states which can slow down the internal conversion.

Table S2 SOC of 2Ac-2CF_3Ph, Ac-2CF_3Ph, 2Ac-2FPh, 2Ac-CF_3Ph

Ac-2CF$_3$Ph				
Triplet (T_m)	**T_m (eV)**	Singlet (S_n)	**S_n (eV)**	**SOC (cm^{-1})**
T1	2.947	S1	2.982	0.03
T1	2.947	S2	3.419	1.368832
T2	3.353	S1	2.982	1.215278
T2	3.353	S2	3.419	0.522494
T3	3.502	S1	2.982	0.967368
T3	3.502	S2	3.419	1.021959
T4	3.694	S1	2.982	0.327719
T4	3.694	S2	3.419	0.370675
T5	3.936	S1	2.982	1.440833
T5	3.936	S2	3.419	0.628331
2Ac-CF$_3$Ph				
Triplet (T_m)	**T_m (eV)**	Singlet (S_n)	**S_n (eV)**	**SOC (cm^{-1})**
T1	3.168	S1	3.198	0.109545
T1	3.168	S2	3.258	0.022361
T1	3.168	S3	3.425	0.399249
T1	3.168	S4	3.554	0.02
T2	3.235	S1	3.198	0.022361
T2	3.235	S2	3.258	0.051962
T2	3.235	S3	3.425	0
T2	3.235	S4	3.554	0.538609
T3	3.292	S1	3.198	0.2502
T3	3.292	S2	3.258	0.033166
T3	3.292	S3	3.425	0.494368
T3	3.292	S4	3.554	0.045826
T4	3.478	S1	3.198	0.152643
T4	3.478	S2	3.258	0.301164

T4	3.478	S3	3.425	0.051962
T4	3.478	S4	3.554	0.323728
T5	3.488	S1	3.198	1.037401
T5	3.488	S2	3.258	0.108167
T5	3.488	S3	3.425	0.491325
T5	3.488	S4	3.554	0.033166
T6	3.593	S1	3.198	0.044721
T6	3.593	S2	3.258	0.660454
T6	3.593	S3	3.425	0.053852
T6	3.593	S4	3.554	0.770584
T7	3.611	S1	3.198	0.267021
T7	3.611	S2	3.258	0.014142
T7	3.611	S3	3.425	0.376431
T7	3.611	S4	3.554	0.014142
2Ac2FPh				
Triplet (T_m)	**T_m (eV)**	Singlet (S_n)	**S_n (eV)**	**SOC (cm^{-1})**
T1	3.261	S1	3.305	0.35
T1	3.261	S2	3.323	0
T2	3.276	S1	3.305	0
T2	3.276	S2	3.323	0.41
T3	3.468	S1	3.305	1.11
T3	3.468	S2	3.323	0
T4	3.469	S1	3.305	0
T4	3.469	S2	3.323	1.08
T5	3.653	S1	3.305	0
T5	3.653	S2	3.323	0.067082
T6	3.653	S1	3.305	0.072111
T6	3.653	S2	3.323	0
2Ac-2CF$_3$Ph				
Triplet	**T_m (eV)**	Singlet (S_n)	**S_n (eV)**	**SOC (cm^{-1})**
T1	2.856	S1	2.878	0.014142
T1	2.856	S2	2.881	0.014142
T1	2.856	S3	3.294	0.588303
T1	2.856	S4	3.301	0.994485
T2	2.858	S1	2.878	0
T2	2.858	S2	2.881	0.014142
T2	2.858	S3	3.294	0.965867
T2	2.858	S4	3.301	0.577841
T3	3.25	S1	2.878	0.966851
T3	3.25	S2	2.881	0.556866
T3	3.25	S3	3.294	0.08544
T3	3.25	S4	3.301	0.094868
T4	3.254	S1	2.878	0.555878
T4	3.254	S2	2.881	0.976371

T4	3.254	S3	3.294	0.064031
T4	3.254	S4	3.301	0.094868
T5	3.621	S1	2.878	0.121244
T5	3.621	S2	2.881	0.369865
T5	3.621	S3	3.294	0.464435
T5	3.621	S4	3.301	0.812712
T6	3.629	S1	2.878	0.355949
T6	3.629	S2	2.881	0.117473
T6	3.629	S3	3.294	0.822982
T6	3.629	S4	3.301	0.464435

Table S3 hRISC for 2Ac-2CF$_3$Ph, Ac-2CF$_3$Ph, 2Ac-2FPh , 2Ac-CF$_3$Ph with triplet states are at least 0.1 eV higher than singlet states with reorganization energy set to be 0.1 eV.

2Ac-2CF$_3$Ph						
m	**n**	**SOC (cm^{-1})**	**S_n (eV)**	**T_m (eV)**	**T_m- S_n**	**k_{RISC} (s^{-1})**
3	1	0.966851	2.878	3.250	0.372	7.61E+08
3	2	0.556866	2.881	3.250	0.369	2.52E+08
4	1	0.555878	2.878	3.254	0.376	2.52E+08
4	2	0.976371	2.881	3.254	0.373	7.76E+08
5	1	0.121244	2.878	3.621	0.743	1.20E+07
5	2	0.369865	2.881	3.621	0.74	1.11E+08
5	3	0.464435	3.294	3.621	0.327	1.76E+08
5	4	0.812712	3.301	3.621	0.32	5.38E+08
6	1	0.355949	2.878	3.629	0.751	1.03E+08
6	2	0.117473	2.881	3.629	0.748	1.12E+07
6	3	0.822982	3.294	3.629	0.335	5.51E+08
6	4	0.464435	3.301	3.629	0.328	1.76E+08
					Sum	3.72E+09
Ac-2CF$_3$Ph						
2	1	1.215278	2.982	3.353	0.371	1.202E+09
3	1	0.967368	2.982	3.502	0.52	7.619E+08
4	1	0.327719	2.982	3.694	0.712	8.744E+07
4	2	0.370675	3.419	3.694	0.275	1.119E+08
					Sum	2.164E+09
2Ac-2FPh						
3	1	1.11	3.305	3.468	0.163	1.003E+09
3	2	0	3.323	3.468	0.145	0.000E+00
4	1	0	3.305	3.468	0.163	0.000E+00
4	2	1.08	3.323	3.468	0.145	9.496E+08
5	1	0	3.305	3.653	0.348	0.000E+00
5	2	0.067082	3.323	3.653	0.33	3.664E+06
6	1	0.072111	3.305	3.653	0.348	4.233E+06
6	2	0	3.323	3.653	0.33	0.000E+00

					Sum	1.961E+09
2Ac-CF_3Ph						
4	1	0.152643	3.198	3.478	0.28	1.897E+07
4	2	0.301164	3.258	3.478	0.22	7.384E+07
5	1	1.037401	3.198	3.488	0.29	8.762E+08
5	2	0.108167	3.258	3.488	0.23	9.525E+06
6	1	0.044721	3.198	3.593	0.395	1.628E+06
6	2	0.660454	3.258	3.593	0.335	3.551E+08
6	3	0.053852	3.425	3.593	0.168	2.361E+06
7	1	0.267021	3.198	3.611	0.413	5.805E+07
7	2	0.014142	3.258	3.611	0.353	1.628E+05
7	3	0.376431	3.425	3.611	0.186	1.154E+08
					Sum	1.511E+09

Excited Toluene density calculation

The data[5] at λ=250nm gives $\varepsilon = 1448$ m^{-1}cm^{-1}. The molar concentration of toluene is 9.41×10^{3} molm^{-3}. Using Beer–Lambert's law in decadic form, a 90% absorption of the incident light ($T = 0.1$, $A = 1$) corresponds to absorption length l, of 0.73 µm. The illuminated volume is approximated as a cylinder of radius $r = 50.0\ \mu\mathrm{m}$ with height l. The number of toluene molecules in this volume is 3.27 ×10^{13} molecules. A 50 nJ pulse of 250nm contains 6.29×10^{10} photons. If each absorbed photon generates one excited toluene molecule, assuming 90% of the pulse energy is absorbed in the volume defined above, the fraction of excited molecules is 0.173%. The corresponding excited-state number density is 9.83×10^{24} m^{-3} for singlet in which 45% is converted to triplet giving 4.42 ×10^{24} m^{-3}.

Numerical Extraction of the Effective Dexter Capture Radius a_{eff}

We model triplet–triplet Dexter transfer in a homogeneous medium using the 3D time-dependent Smoluchowski formulation. The relative motion of a donor–acceptor pair is treated as Brownian diffusion with relative diffusion coefficient D_{rel}, and reaction occurs upon encounter within a capture radius a_{eff}. For diffusion-controlled reaction in 3D, the time-dependent Smoluchowski second-order rate coefficient is taken as

$$k_2 = 4\pi D_{rel} a_{eff}\left[1 + \frac{a_{eff}}{\sqrt{\pi D_{rel} t}}\right] \quad \text{(S1)}$$

where t is time and D_{rel} is the relative diffusion constant. The instantaneous first-order Dexter rate for a single triplet is then

$$k_{Dex} = k_2 N_{T*} \quad \text{(S2)}$$

The total first-order decay rate of the triplet population includes the intrinsic monomolecular triplet decay of toluene, k_T, and the Dexter term:

$$k_{tot} = k_T + k_{Dex} \quad \text{(S3)}$$

The normalized triplet survival probability N_{T*} obeys a first-order kinetic equation with a time-dependent equation:

$$\frac{dN_{T*}}{dt} = -k_{tot}\, T(t), \; with \quad T(0) = 1 \qquad \text{(S4)}$$

The formal solution is

$$N_{T*} = \exp\left[-\int_0^t k_{tot} du \right] \qquad \text{(S5)}$$

Because $k_{Dex(t)}$ and $k_{tot(t)}$ varies significantly at short times ,we define a population-weighted effective Dexter rate. The full-time dependence of $k_{Dex(t)}$ into a single effective rate constant $k_{Dex\_eff,}$ the population-weighted average over the relevant time window can be given as follows:

$$< k_{Dex} >_{pop} A_{eff} = \frac{\int_0^{T_{max}} k_{Dex} N_{T*}\,(t) dt}{\int_0^{Tmax} N_{T*}\, dt} \qquad \text{(S6)}$$

$T_{max} = 3\,\tau_{rise}$ and τ_{rise} is the experimental rise time constant. This definition weights the instantaneous rate by how many excitons are available to react at time t.

Assuming that k_T is known independently (from the intrinsic triplet decay of toluene), the corresponding effective Dexter contribution is

$$k_{dex\_eff} = \frac{1}{\tau_{rise}} - k_T \qquad \text{(S7)}$$

Our goal is to determine a_{eff} such that

$$\langle k_{Dex} \rangle_{pop} a_{eff} = k_{dex\_eff} \quad \text{(S8)}$$

The integrals for T(t) and $\langle k_{Dex} \rangle_{pop}$ are evaluated numerically on a uniform time grid using the midpoint rule.

For a given τ_rise, we define

$$T_{max} = 3\,\tau_{rise} \quad \text{(S9)}$$

$$\Delta t = \frac{T_{max}}{N_{steps}} \quad \text{(S10)}$$

with N_{steps} = 8000. The midpoints are

$$t_i = \left(i + \frac{1}{2}\right)\Delta t, \quad for\; i = 0, 1, \ldots, N_{steps} - 1 \quad \text{(S11)}$$

At each t_i we compute k_2 k_{def_eff} and k_{tol}. The determination of a_{eff} is through bisection root finding.

Python code

```
import math

# Constants
D_rel = 3.79e-9              # m^2/s
k_T = 4.08e7                 # s^-1
N_ex = 0.45 * 9.83e24        # m^-3

def kDex_eff_population_weighted(a_eff, tau_rise, n_steps=8000):
   """
   Compute population-weighted effective Dexter rate for a given a_eff and tau_rise.
   k_Dex(t) = k2(t) * N_ex, where
   k2(t) = 4*pi*D_rel*a_eff * (1 + a_eff / sqrt(pi*D_rel*t))
   Total rate k_total(t) = k_T + k_Dex(t).
   We return <k_Dex>_pop = (∫ k_Dex(t) S(t) dt)/(∫ S(t) dt) over [0, 3*tau_rise].
   """
   T_max = 3.0 * tau_rise
   dt = T_max / n_steps
   t_values = [dt * (i + 0.5) for i in range(n_steps)]  # midpoints

   k_dex_vals = []
   k_total_vals = []
   for t in t_values:
      k2_t = 4.0 * math.pi * D_rel * a_eff * (1.0 + a_eff / math.sqrt(math.pi * D_rel * t))
      k_dex_t = k2_t * N_ex
      k_dex_vals.append(k_dex_t)
      k_total_vals.append(k_T + k_dex_t)

   # cumulative integral of k_total to get S(t)
   S_vals = []
   cumulative = 0.0
```

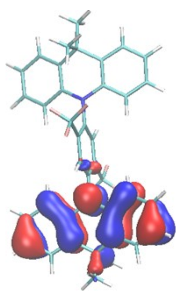
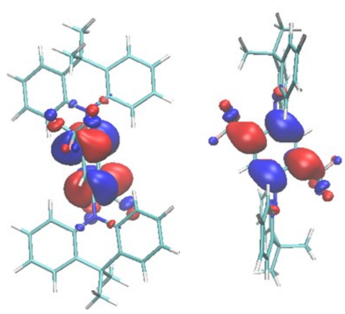
```
    for k_tot in k_total_vals:
        cumulative += k_tot * dt
        S_vals.append(math.exp(-cumulative))

    num = 0.0
    den = 0.0
    for k_dex_t, S_t in zip(k_dex_vals, S_vals):
        num += k_dex_t * S_t * dt
        den += S_t * dt

    return num / den

def solve_a_eff_for_tau(tau_rise_ns, a_min_nm=0.3, a_max_nm=1.5, tol_nm=1e-3, max_iter=50):
    tau_rise = tau_rise_ns * 1e-9  # s
    k_total_eff_target = 1.0 / tau_rise
    k_dex_eff_target = k_total_eff_target - k_T

    a_lo = a_min_nm * 1e-9
    a_hi = a_max_nm * 1e-9
    f_lo = kDex_eff_population_weighted(a_lo, tau_rise) - k_dex_eff_target
    f_hi = kDex_eff_population_weighted(a_hi, tau_rise) - k_dex_eff_target

    # Ensure we bracket a root
    if f_lo * f_hi > 0:
        return None, f_lo, f_hi, k_dex_eff_target

    for _ in range(max_iter):
        a_mid = 0.5 * (a_lo + a_hi)
        f_mid = kDex_eff_population_weighted(a_mid, tau_rise) - k_dex_eff_target
        if abs(a_hi - a_lo) < tol_nm * 1e-9:
            return a_mid, f_mid, k_dex_eff_target, None
        if f_lo * f_mid <= 0:
            a_hi, f_hi = a_mid, f_mid
        else:
            a_lo, f_lo = a_mid, f_mid
    return a_mid, f_mid, k_dex_eff_target, None

taus_ns = [3.00,3.25, 3.39, 3.41]
results = {}
for tau_ns in taus_ns:
    a_m, f_mid, k_target, _ = solve_a_eff_for_tau(tau_ns)
    if a_m is None:
        results[tau_ns] = ("no_root", f_mid, k_target)
    else:
        a_nm = a_m * 1e9
        results[tau_ns] = (a_nm, f_mid, k_target)

print(results)
```

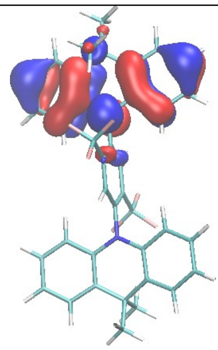
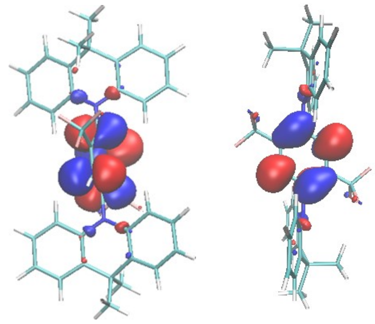
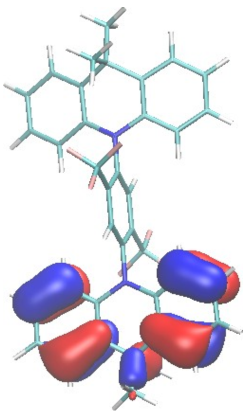
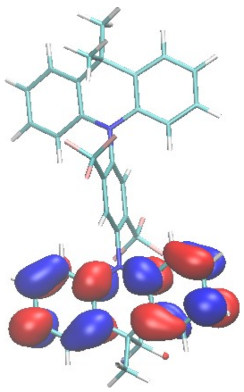
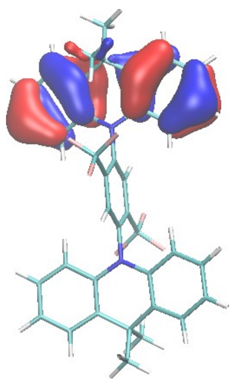
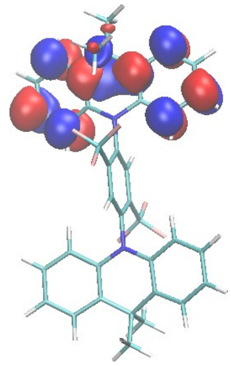
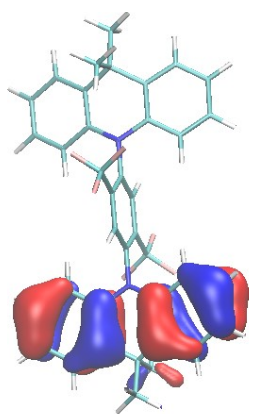
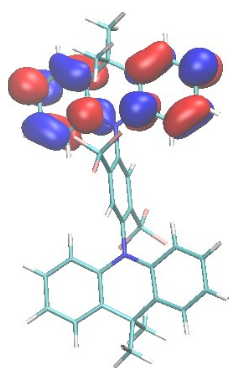
OUTPUT

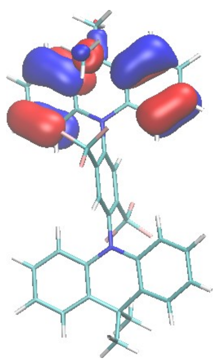
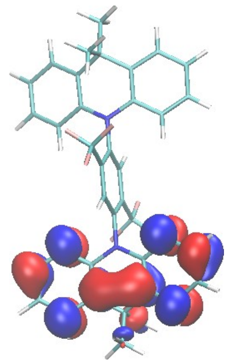
{3.0: (1.0543945312500003, -54877.29514122009, 292533333.3333333), 3.25: (0.98583984375, -26648.336749851704, 266892307.69230765), 3.39: (0.9506835937499999, 26011.405223160982, 254185250.73746306), 3.41: (0.9459960937499999, 91270.89239114523, 252455131.96480936)}

Table S4: List of contributions of orbital transitions and its corresponding orbital visualized for vertical absorption based on ground state geometry.

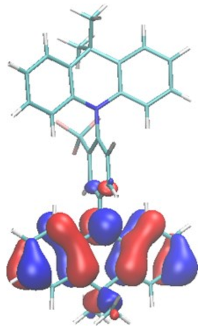
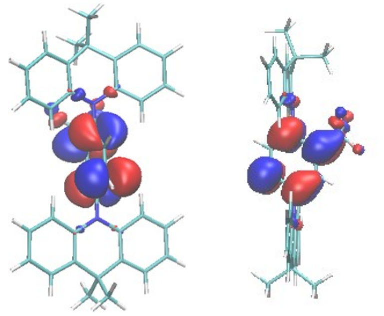
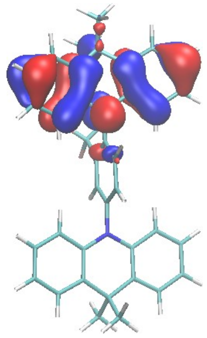
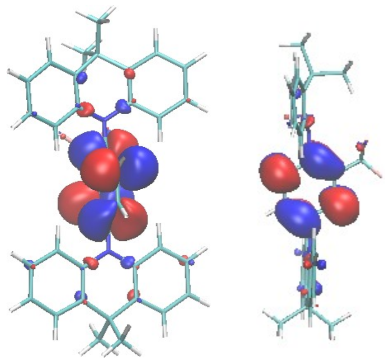
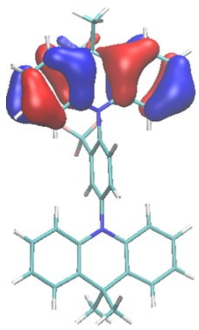
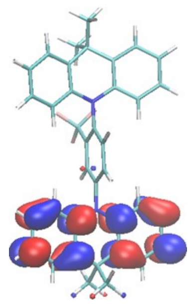
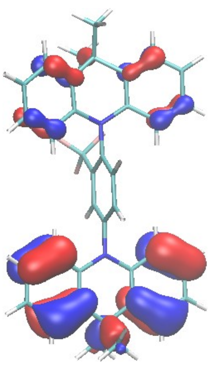
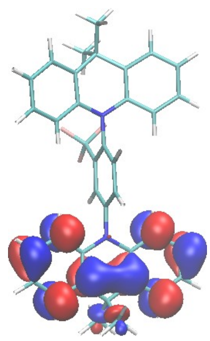
	Singlets (eV)	Transitions (2Ac-2CF$_3$Ph)		Triplets (eV)	Transitions (2Ac-2CF$_3$Ph)
S_1	2.878	HOMO -> LUMO : 0.962653	T_1	2.856	HOMO-1 -> LUMO : 0.664170; HOMO -> LUMO : 0.318128
S_2	2.881	HOMO-1 -> LUMO : 0.961228	T_2	2.858	HOMO-1 -> LUMO : 0.318361; HOMO -> LUMO : 0.664482
S_3	3.294	HOMO -> LUMO+1 : 0.973480	T_3	3.25	HOMO-1 -> LUMO+1 : 0.357148; HOMO -> LUMO+1 : 0.613875
S_4	3.301	HOMO-1 -> LUMO+1 : 0.971623	T_4	3.254	HOMO-1 -> LUMO+1 : 0.615176; HOMO -> LUMO+1 : 0.357538
S_5	2.878	HOMO -> LUMO : 0.962653	T_5	3.621	HOMO-1 -> LUMO+4 : 0.638178; HOMO -> LUMO+4 : 0.152446
			T_6	3.629	HOMO-1 -> LUMO+5 : 0.149566; HOMO -> LUMO+5 : 0.636954

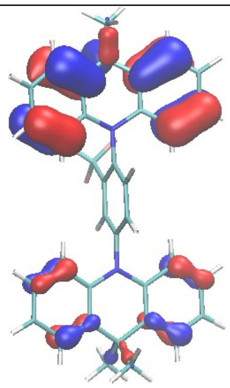
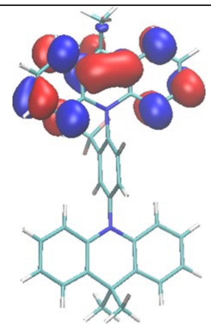
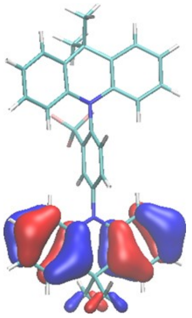
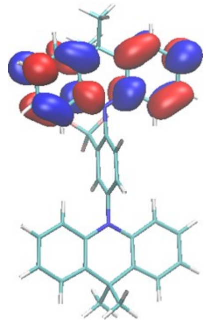
Occupied states (**2Ac-2CF$_3$Ph**)	Unoccupied states (**2Ac-2CF$_3$Ph**)
HOMO 	**LUMO** 
HOMO-1	**LUMO+1**

	
HOMO-2	**LUMO+2**
	
HOMO-3	**LUMO+3**
	
HOMO-4	**LUMO+4**
	

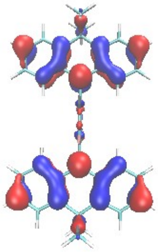
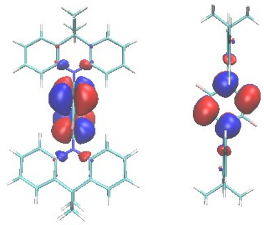
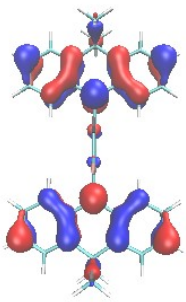
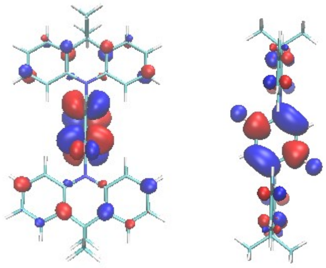
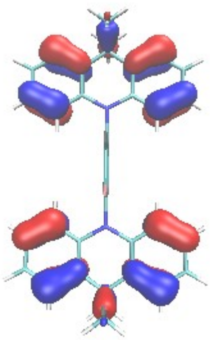
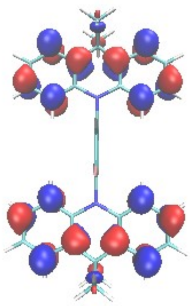
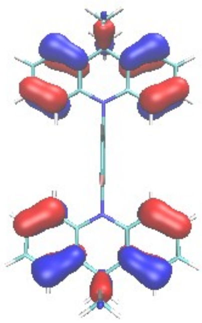
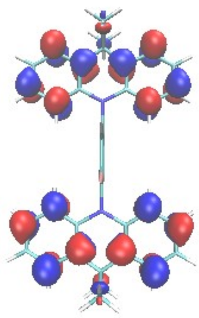
HOMO-5	**LUMO+5**
	

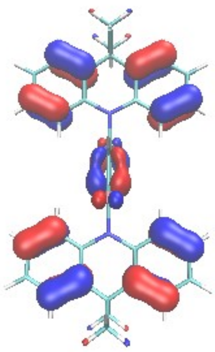
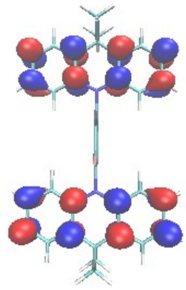
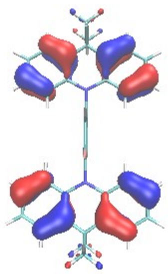
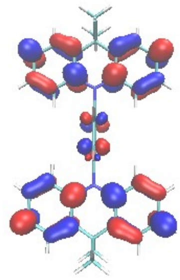
	Singlets (eV)	Transitions (2Ac-CF_3Ph)		Triplets (eV)	Transitions (2Ac-CF_3Ph)
S_1	3.198	HOMO -> LUMO : 0.952514	T_1	3.168	HOMO -> LUMO : 0.970074
S_2	3.258	HOMO-1 -> LUMO : 0.937363	T_2	3.235	HOMO-1 -> LUMO : 0.946814
S_3	3.425	HOMO -> LUMO+1 : 0.948412	T_3	3.292	HOMO -> LUMO+1 : 0.711472; HOMO -> LUMO+3 : 0.231574
S_4	3.554	HOMO-1 -> LUMO+1 : 0.931355	T_4	3.478	HOMO-1 -> LUMO+1 : 0.826551
			T_5	3.488	HOMO -> LUMO+1 : 0.238598; HOMO -> LUMO+3 : 0.581005
			T_6	3.593	HOMO-1 -> LUMO+5 : 0.743182
			T_7	3.611	HOMO -> LUMO+2 : 0.936403

Occupied states (2Ac-CF_3Ph)	Unoccupied states (2Ac-CF_3Ph)
HOMO 	**LUMO** 
HOMO-1 	**LUMO+1** 
HOMO-2 	**LUMO+2** 
HOMO-3 	**LUMO+3** 
HOMO-4	**LUMO+4**

	
HOMO-5 	**LUMO+5** 

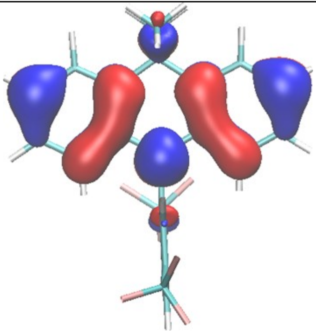
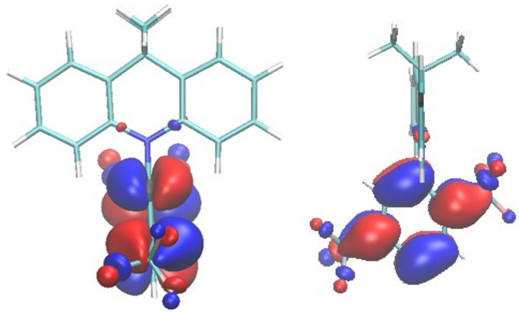
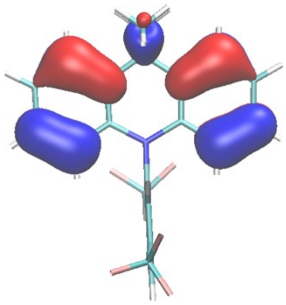
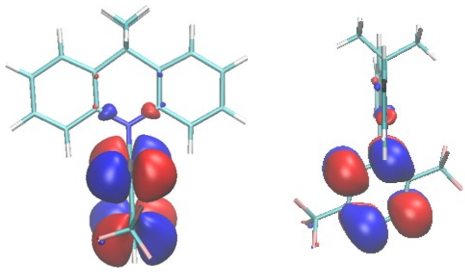
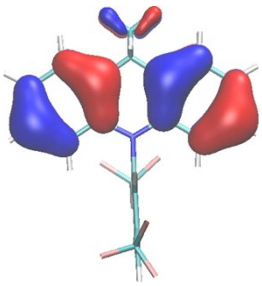
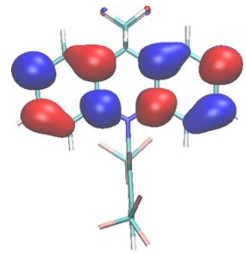
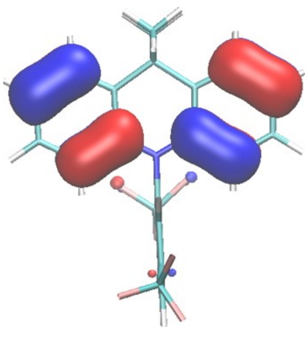
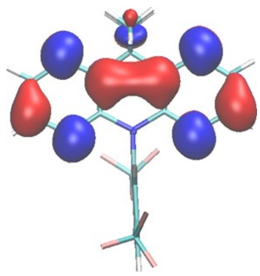
	Singlets (eV)	Transitions (2Ac2FPh)		Triplets (eV)	Transitions (2Ac2FPh)
S_1	3.305	HOMO -> LUMO : 0.982980	T_1	3.261	HOMO -> LUMO : 0.920935
S_2	3.323	HOMO-1 -> LUMO : 0.982323	T_2	3.276	HOMO-1 -> LUMO : 0.908714
			T_3	3.468	HOMO-1 -> LUMO+4 : 0.373752; HOMO -> LUMO+5 : 0.331640
			T_4	3.469	HOMO-1 -> LUMO+5 : 0.323668; HOMO -> LUMO+4 : 0.375167
			T_5	3.653	HOMO-1 -> LUMO+2 : 0.462518; HOMO -> LUMO+3 : 0.472314
			T_6	3.653	HOMO-1 -> LUMO+3 : 0.461405; HOMO -> LUMO+2 : 0.473618

Occupied states (2Ac2FPh)	Unoccupied states (2Ac2FPh)
HOMO 	**LUMO** 
HOMO-1 	**LUMO+1** 
HOMO-2 	**LUMO+2** 
HOMO-3 	**LUMO+3** 

HOMO-4	**LUMO+4**
	
HOMO-5	**LUMO+5**
	

	Singlets (eV)	Transitions (Ac-2CF_3Ph)		Triplets (eV)	Transitions (Ac-2CF_3Ph)
S_1	2.982	HOMO -> LUMO : 0.973383	T_1	2.947	HOMO -> LUMO : 0.975414
S_2	3.419	HOMO -> LUMO+1 : 0.971779	T_2	3.353	HOMO -> LUMO+1 : 0.878776
			T_3	3.502	HOMO -> LUMO+3 : 0.742126
			T_4	3.694	HOMO -> LUMO+2 : 0.927118

Occupied states (Ac-2CF_3Ph)	Unoccupied states (Ac-2CF_3Ph)
HOMO	**LUMO**

	
HOMO-1 	**LUMO+1** 
HOMO-2 	**LUMO+2** 
HOMO-3 	**LUMO+3** 

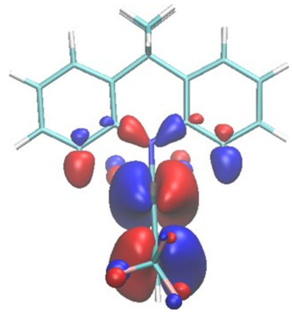
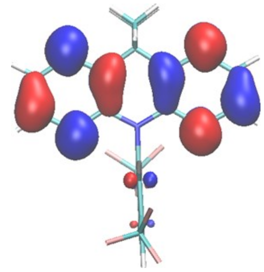
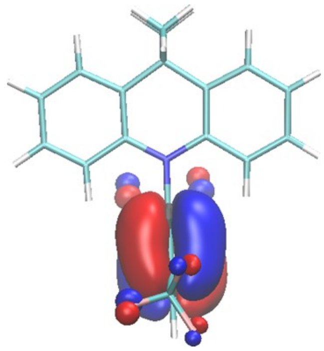
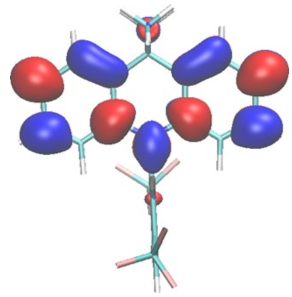
HOMO-4	**LUMO+4**
	
HOMO-5	**LUMO+5**
	

Table S5. Calculated IC rate constants for high-lying triplet to T_1 transitions in the studied molecules.

Molecule	Transition	Internal conversion rate, k_{IC} (s^{-1})	τ_{IC} ($1/k_{IC}$)
Ac-2CF_3Ph	T_4->T_1	7.37 x 10^{10}	13.6 ps
2Ac-2CF_3Ph	T_4->T_1	1.58 x10^{10}	63.3 ps
2Ac-CF_3Ph	T_6->T_1	1.18 x10^{10}	84.7 ps
2Ac-2F_3Ph	T_4->T_1	1.23 x10^{9}	813 ps

xyz coordinates of Ac-2CF_3Ph ω=0.0662 optimized at DFT/ω*pbeh/de2-svp PCM in Toluene

C 3.6793958171 0.6238095740 -0.0476641690

C 3.6704667204 -0.7705703551 -0.0693679654

C 2.4623336290 -1.4573867636 -0.1062711400

C 1.2342449181 -0.7674925534 -0.1240170062

C 1.2272062093 0.6414778383 -0.0913660687

C 2.4630471952 1.3020131583 -0.0577789126

N 0.0287846897 -1.4865358285 -0.1861946312

C -1.2164695856 -0.8423018738 -0.0965053771

C -1.2938906577 0.5645446212 -0.0608777403

C -0.0601464615 1.4636875128 -0.1119641927

C	-2.3999879760	-1.6052843714	-0.0535569011
C	-3.6463623479	-0.9931034499	0.0142682144
C	-3.7389236132	0.3980718047	0.0410363436
C	-2.5664104036	1.1486483534	0.0038316292
C	-0.1009276912	2.2964433545	-1.4114961127
C	-0.0728623756	2.4097078243	1.1072939346
C	0.0724121832	-2.9049331625	-0.0734758624
C	0.0940230237	-3.4789003169	1.2006134993
C	0.1386087417	-4.8636323634	1.3581373776
C	0.1682059725	-5.6926793006	0.2350684590
C	0.1457330777	-5.1280942163	-1.0380482713
C	0.0960256339	-3.7403161753	-1.2045381236
C	0.1105068665	-5.4657968145	2.7416878882
F	-1.1337209926	-5.8231779640	3.0941320589
F	0.8693459463	-6.5669559514	2.8163183091
F	0.5520930716	-4.6004730928	3.6627004621
C	0.0765004778	-3.1604260315	-2.6046977553
F	0.0760855150	-4.1318409285	-3.5315008485
F	-1.0128073922	-2.4146571363	-2.8196286534
F	1.1500641031	-2.3975658241	-2.8397223801
H	4.6217776712	1.1790941593	-0.0250972578
H	4.6087382077	-1.3342555117	-0.0622443935
H	2.4704586863	-2.5488697256	-0.1360575873
H	2.4709424873	2.3962217634	-0.0411195867
H	-2.3434121464	-2.6953731197	-0.0861377976
H	-4.5481588582	-1.6129231692	0.0415346090
H	-4.7122889557	0.8953320204	0.0878740871
H	-2.6416064501	2.2403955878	0.0229350919
H	-0.0949675699	1.6407778802	-2.2968153191
H	0.7719735095	2.9665559767	-1.4757519352
H	-1.0097490829	2.9192377016	-1.4524158881
H	-0.0367285797	1.8374647855	2.0482121633
H	-0.9816963534	3.0322869974	1.1210341908
H	0.7909779101	3.0932218174	1.0899377344
H	0.0809124459	-2.8186484526	2.0715449220
H	0.2146137624	-6.7785497520	0.3554977841
H	0.1691105372	-5.7706152540	-1.9213314717

Xyz coordinates of 2Ac-CF_3Ph ω= 0.0560 optimized at DFT/ω*pbeh/de2-svp PCM in Toluene

C	3.5910221366	0.7029705726	-0.4849303656
C	3.6041843333	-0.6828316642	-0.6283617626
C	2.4217669283	-1.4087346105	-0.5062186543
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H	0.0872647719	-11.6233826097	1.1849484320

Xyz coordinates of 2Ac-2F_3Ph ω= 0.0630 optimized at DFT/ω*pbeh/de2-svp PCM in Toluene

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Xyz coordinates of 2Ac-2CF_3Ph ω= 0.0425 optimized at DFT/ω*pbeh/de2-svp PCM in Toluene

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Section 4. Low Temperature Measurements

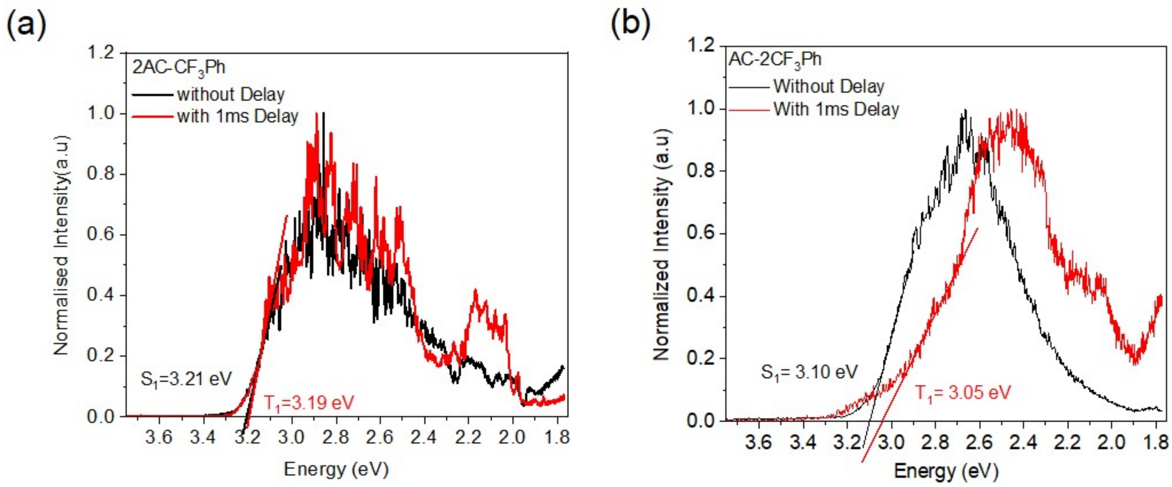


Figure S7 Fluorescence and phosphorescene emission at 77K in me-THF with and without gate delay for (a) 2Ac-CF_3Ph (b) AC-2CF_3Ph.

Section 5. Synthesis

10,10'-(2-(trifluoromethyl)-1,4-phenylene)bis(9,9-dimethyl-9,10-dihydroacridine), 2AC-CF_3Ph. A mixture of 1,4-Dibromo-2-(trifluoromethyl)benzene (1.0g, 3.29mmol), 9,10-Dihydro-9,9-dimethylacridine (1.515g, 7.238mmol), Tris(dibenzylideneacetone) dipalladium (0) (0,15g, 0.163mmol), X-phos (0.109g, 0.228mmol), Sodium tert-butoxide (0.695g, 7.231 mmol), dry toluene (5mL) were added in a flask under argon atmosphere. The reaction mixture was stirred at 110-120°C for 24 hours. When the reaction was completed, crude product was purified by column chromatography by using silica, Dcm/Hex=1/5 as an eluent. The target compound was obtained as white powder. Yield: 0.252g (13.46%),

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 2.4 Hz, 1H), 7.86 (dd, *J* = 8.3, 2.3 Hz, 1H), 7.69 (d, *J* = 8.3 Hz, 1H), 7.55 (dt, *J* = 7.6, 2.0 Hz, 4H), 7.17 – 7.01 (m, 8H), 6.42 (d, *J* = 8.1 Hz, 2H), 6.23 (d, *J* = 8.1 Hz, 2H), 1.97 (s, 3H), 1.75 (s, 6H), 1.48 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.98, 141.18, 140.50, 139.65, 137.73, 137.47, 131.88, 131.83, 130.96, 130.50, 126.81, 126.57, 125.68, 125.30, 121.64, 121.52, 114.12, 36.26, 36.21, 34.48, 31.13, 27.24.

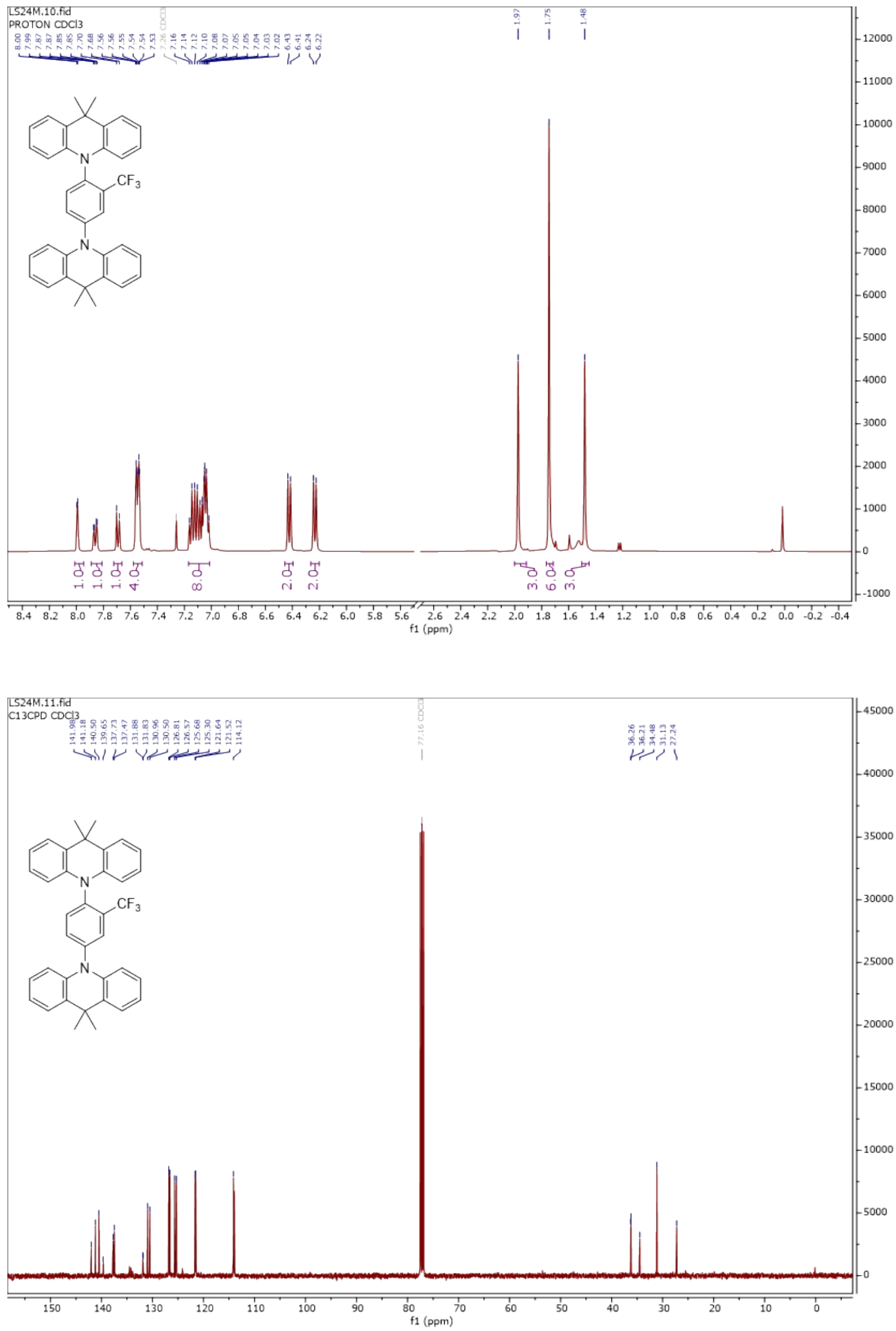
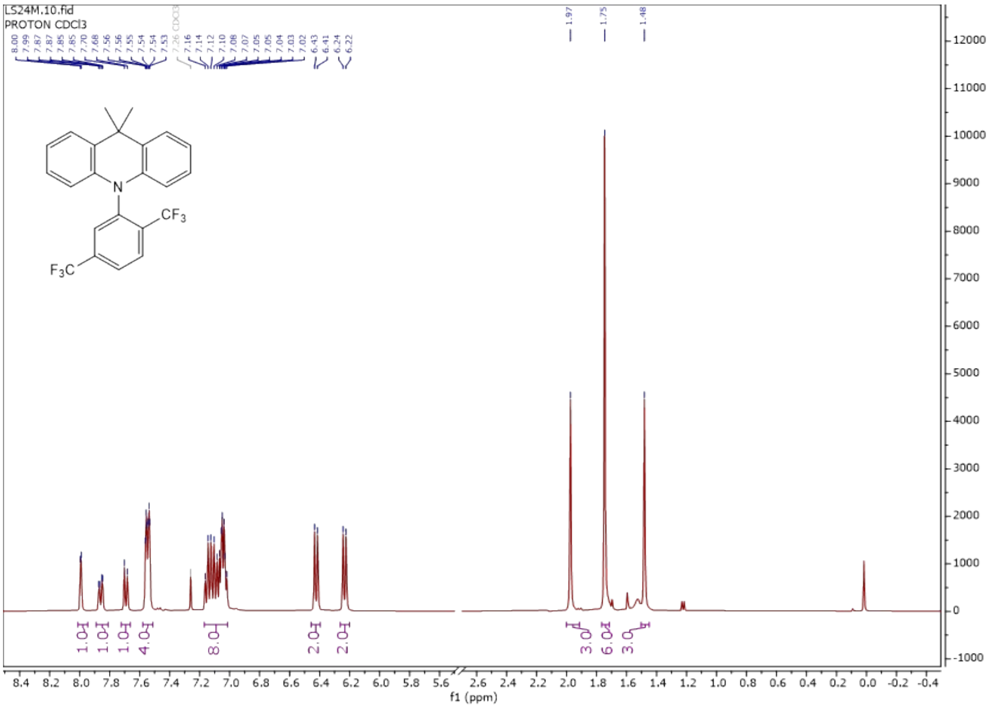


Figure S8 ^{1}H NMR spectrum (above) and ^{13}C NMR spectrum (below) of 2AC-CF_3Ph.

10-(2,5-bis(trifluoromethyl)phenyl)-9,9-dimethyl-9,10-dihydroacridine, AC-2CF$_3$Ph. A mixture of 2-Bromo-1,4-bis(trifluoromethyl)benzene (0.5g, 1.7mmol), 9,10-Dihydro-9,9-dimethylacridine (0.46g, 2.19mmol), Tris(dibenzylideneacetone) dipalladium (0) (0,07g, 0.35mmol), X-phos (0.05g, 0.1mmol), Sodium tert-butoxide (0.22g, 2.28mmol), dry toluene (5mL) were added in a flask under argon atmosphere. The reaction mixture was stirred at 110-120ºC for 24 hours. When the reaction was completed, crude product was purified by column chromatography by using silica, EA/Hex=1/9 as an eluent. The target compound was obtained as **white powder.** Yield: 0.67g (93.18%),

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.3 Hz, 1H), 7.94 (d, *J* = 8.3 Hz, 1H), 7.73 (s, 1H), 7.51 (dd, *J* = 5.9, 3.4 Hz, 2H), 7.00 (dd, *J* = 6.1, 3.4 Hz, 4H), 5.96 (dt, *J* = 7.5, 3.7 Hz, 2H), 1.93 (s, 3H), 1.45 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.16, 140.83, 132.11, 132.08, 130.43, 129.75, 129.70, 126.61, 125.94, 125.43, 121.66, 113.85, 36.15, 34.55, 29.86, 27.59.



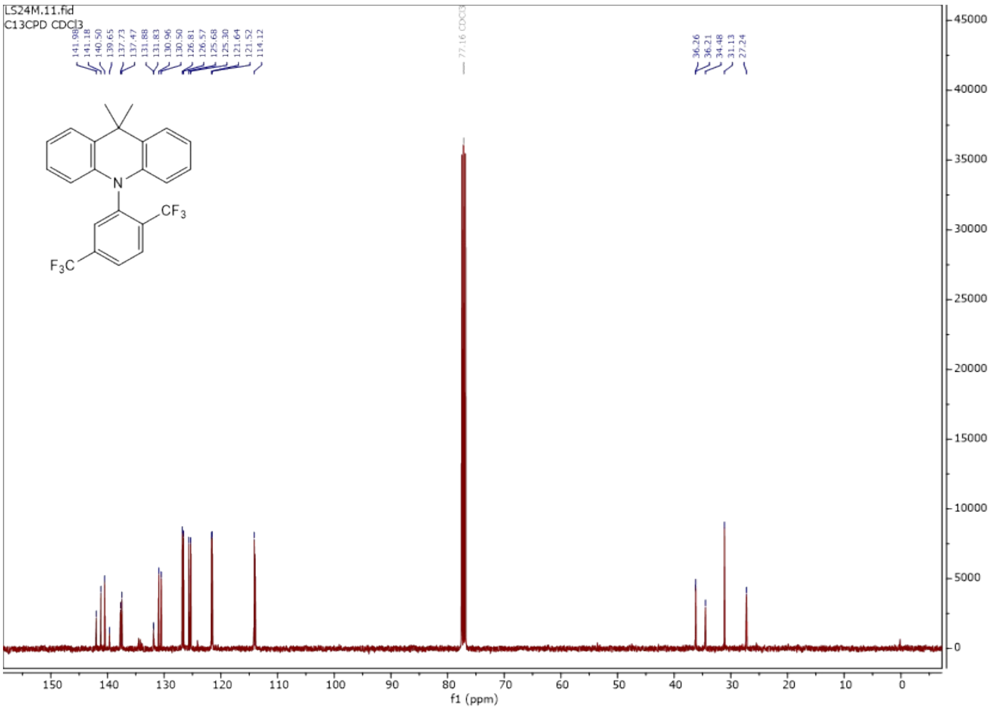


Figure S9 ^{1}H NMR spectrum (above) and ^{13}C NMR spectrum (below) of AC-2CF_3Ph.

The NMR data and synthetic procedures for structures 2Ac-2F_2Ph and 2Ac-2CF_3Ph are not included here, as both molecules have been previously reported in the literature.

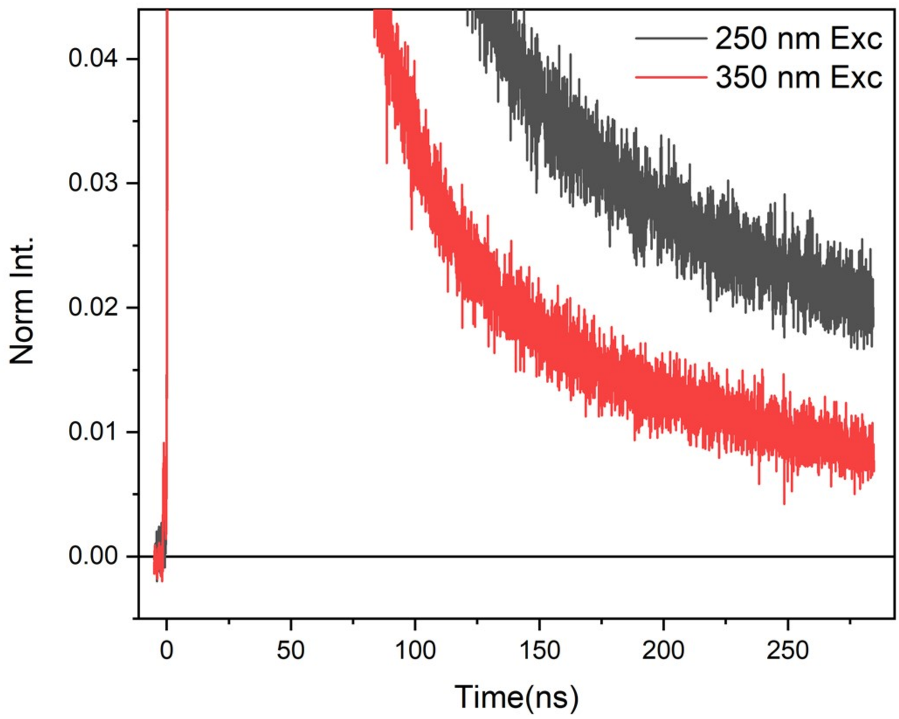


Figure S10. Rescaled time-resolved photoluminescence decay of 2Ac–2CF$_3$Ph measured at λ_{em} = 550 nm following excitation at λ_{exc} = 250 nm (black) and at λ_{exc} = 350 nm (red). The data are presented on an expanded intensity scale to highlight the long-time decay component. The delayed emission associated with thermally activated delayed fluorescence (TADF) becomes more apparent at longer times, confirming its presence despite being obscured by the dominant prompt emission in the main text.

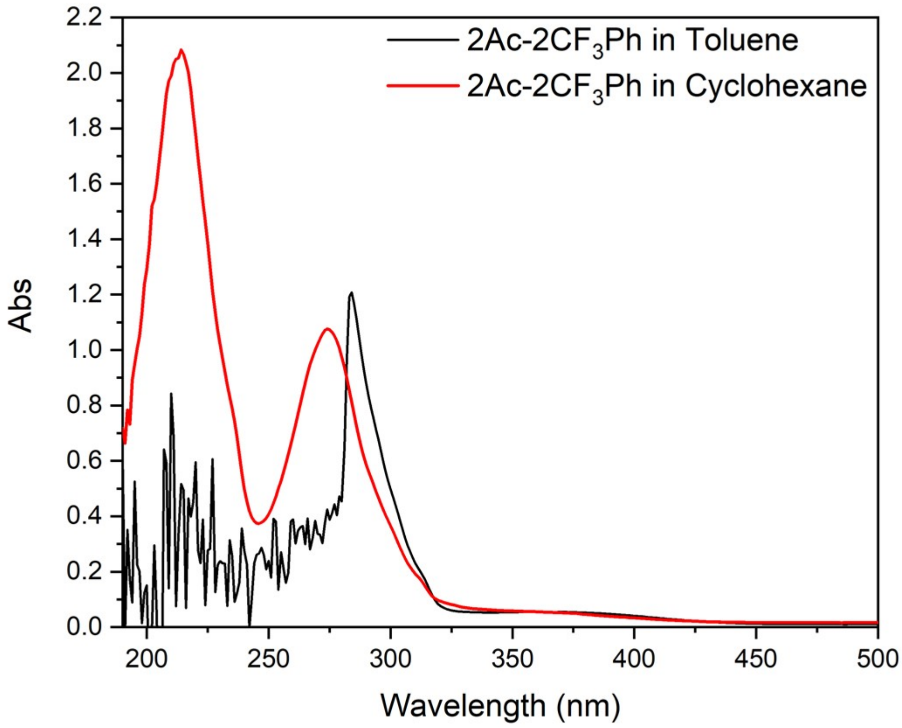


Figure S11. UV–vis absorption spectrum of 2Ac–2CF_3Ph in toluene and cyclohexane, measured using the respective solvent as a blank. The featureless absorbance observed between 200–300 nm in toluene arises from the strong intrinsic absorption of toluene in this region (see Figure S2 for the absorbance of the neat solvents).

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