Thiele’s Fluorocarbons: Stable Diradicaloids with Efficient Vis-NIR Fluorescence from a Zwitterionic Excited State

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Abstract
Thiele’s hydrocarbon was the first synthesized diradicaloid in the search for stable open-shell structures but itself remains sensitive to oxygen and light. We here report the synthesis of Thiele’s fluorocarbon (TFC) and its derivatives exhibiting exceptional thermal, oxidative, and photostability. TFCs have remarkable luminescent properties with yellow to NIR fluorescence and up to 100% quantum yields. X-ray crystallography and ESR spectroscopy confirm their closed-shell quinoidal ground state. As expected from their uniform HOMO/LUMO distributions, TFCs’ absorption spectra show no solvent effect, but their emission reveals an extraordinarily large Stokes shift which increases with solvent polarity (from 0.9 eV in cyclohexane to 1.5 eV in acetonitrile). We show that this behavior is a result of sudden polarization leading to a zwitterionic excited state.

In 1904, Thiele reported the first isolable diradicaloid, tetraphenyl-p-quinodimethane, an oxygen and light-sensitive compound, now referred to as Thiele’s hydrocarbon (TC, Figure 1a).1 Numerous diradicaloids have since been developed, especially in the recent decades.2,3 This includes several substituted (including perchlorinated4),5 ring-fused,6,7,8 macrocyclic,9,10,11 and oligomeric5,12 derivatives of TC (Figure 1b). Diradicaloids are commonly described by a superposition of two resonant structures: a closed-shell (Kekulé) quinoid, and an open-shell (non-Kekulé) diradical which is stabilized by an aromatic resonance energy (Figure 1a).2,13 The properties of diradicaloids are defined by the weak interaction between the two frontier π-electrons, manifested in their small triplet-singlet gaps (ΔE(T1-S0)) and radical-like reactivity.14 The ground state of TC and most other p-quinodimethanes are closed-shell,13,15 but their diradical character
can be enhanced by increasing the aromatic stabilization energy\textsuperscript{2,16} or suppressed by planarization in ring-fused derivatives.\textsuperscript{6}

The distinct electronic structure of diradicaloids have attracted enduring attention both in terms of their fundamental understanding\textsuperscript{17} as well as their potential as functional materials.\textsuperscript{18,19} π-Extended diradicaloids have been applied as organic conductors,\textsuperscript{20,21,22} near-IR chromophores,\textsuperscript{23} electrochromics,\textsuperscript{6,8} singlet fission materials,\textsuperscript{24,25} non-linear optical materials,\textsuperscript{26,27} and magnetic materials such as spin-switches.\textsuperscript{28,29,30} Most applications require considerable chemical and photostability, which remains a challenge despite significant synthetic efforts to design thermodynamic and kinetic stabilization in such molecules.\textsuperscript{31}

Out of all properties, luminescence in diradicaloids is scarcely reported, despite the recent traction in luminescent radicals which allow circumventing non-emissive (triplet) states in organic light-emitting diodes.\textsuperscript{32,33} Most diradicaloids are non-emissive. The few known exceptions – mostly rigid planar molecules – show a low-to-moderate photoluminescence quantum yield (PLQY).\textsuperscript{6,25,30,34,35,36,37} In his original paper, Thiele noted “magnificent golden yellow fluorescence of the solutions” of TC, but the compound was “extremely reactive”.\textsuperscript{1}

Figure 1. a) Resonant structures of Thiele’s hydrocarbon (TC). b) Examples of reported derivatives of TC. (c) Structures of Thiele’s fluorocarbons, TFCs (ellipsoid drawn to 50% probability), CCDC number 2262129, 2262130, 2262131.
In this paper, we introduce fluorinated derivatives of Thiele’s hydrocarbon (TFC\textsuperscript{F}, TFC\textsuperscript{H}, TFC\textsuperscript{I}, Figure 1a) as exceptionally stable diradicaloids with highly efficient fluorescence in the visible to NIR region. Despite the non-polar ground states, TFCs exhibit an unexpectedly strong emission-only solvatochromism with large Stokes shifts (0.9–1.5 eV). We demonstrate that the first excited state undergoes a sudden polarization (SP\textsuperscript{38}) to form a zwitterionic excited state. The high quantum yield and wide tunability of their emission open new opportunities for applications of diradicaloid compounds.

Thiele’s fluorocarbons were synthesized from tetra-/pentafluorobenzene in three steps with an overall 30-52% yield (see Supporting Information, Scheme S1). As with other fluorocarbons, e.g. Teflon (polytetrafluoroethylene), TFCs exhibit extraordinary oxidative, photo, and thermal stability in solution and solid state. Notably, TFC\textsuperscript{F} shows no decomposition after 100 h of stirring in hot (100°C) piranha solution (Figure S3). Accelerated photobleaching studies with a 370 nm LED light (near $\lambda_{\text{max}}, \sim$100 mW cm\textsuperscript{-2}) in aerated benzene showed very slow degradation of TFCs ($\tau_{1/2} = 60$-170 h), in contrast to common stable dyes (including coumarin-153, N,N’-bis(ethylhexyl)naphthalenediimide (NDI-EH), alkylated BODIPY (PM567), and perylene) which degrade with $\tau_{1/2} \sim 1.5$-10 h under these conditions (Figure 2d, Figure S2). Thermogravimetric analysis (TGA) shows clean sublimations ($T_{\text{onset}} \sim$200-300 °C) in air (Figure S1), and spectroscopically pure crystals of TFC\textsuperscript{F} have been grown by sublimation at ambient pressure in air (Figure 2b).

X-ray crystallography reveals similar geometries for all three TFCs with alternating single/double bonds along the quinodimethane moiety, indicative of a quinoidal ground state, consistent with DFT results (Figure S33, Table S5). Accordingly, no signal was observed in Electron Spin Resonance (ESR) spectroscopy at room temperature (Figure S6). The central quinoid moiety is approximately planar ($\Theta_1 = 13$-20°, comparable to 14° for TC\textsuperscript{15}), while the peripheral phenyl rings are rotated by $\Theta_2 = 60$-68°, substantially more than in TC (52°) – an expected steric effect of the fluorine atoms (Figure 1c). These angles correlate well with DFT predictions (Table S5). Spin-flip TD-DFT shows a moderate increase in the diradical character upon fluorination: the $\Delta E(T_1$-$S_0$) decreases from 0.39 eV in TC to 0.28-0.31 eV in TFCs (Table S7).
Cyclic voltammetry indicates two reversible reduction peaks that positively shift from TFC^H to TFC^F to TFC^I (Figure S4, Table S1, S6). The corresponding LUMO levels are at -3.9 to -4.0 eV from which the HOMO levels of -6.75 to -6.6 eV could be deduced using the optical bandgaps. Such low-lying frontier orbitals of TFCs explain their high oxidative stability as well as the thermodynamic stability of the corresponding radical-anions. The electrochemically formed TFC^{F^-} shows a broad singlet in the ESR spectrum (g-value 2.0057, Figure S5) and a characteristic NIR absorption at $\lambda_{max} = 950$ nm.

Figure 2. a) The absorption (solid line), excitation (dotted line), and emission (solid line) of TFC^I in different solvents (see Fig. S9-10 for TFC^F and TFC^H). b) TFC^F crystals from flash-sublimation in air, and TFC^I emission in different solvents. c) Lifetime of TFC^I emission maximum in different solvents. d) Photobleaching studies of the TFCs in comparison with common stable closed-shell dyes in air-saturated benzene (370 nm LED, ~100 mW cm^{-2}).

UV-vis absorption of TFCs in solution reveals a dominant peak at $\lambda_{max} = 385-416$ nm ($\varepsilon \sim 10^4$ M^{-1}·cm^{-1}) with negligible solvent dependence (<10 nm shift, Figures 2a, S9-11). The emission spectra, however, bear an unexpectedly strong solvent dependence and reveal large Stokes shifts.
(Table S3), extending deep into NIR region. The solution PLQY of TFCs approaches 100% in cyclohexane (Table 1) but drops significantly as the emission redshifts in polar solvents (Table S3). Solid-state fluorescence is also observed with up to 23% PLQY (Figures S23-24, Table S4). The emission lifetime measurements showed monoexponential decays (Figures 2c, S16-18) with lifetimes decreasing from 25 ns in cyclohexane to <1.3 ns in acetonitrile (for TFC₉), primarily due to faster non-radiative deactivation. A quantitative PLQY observed for TFC¹ indicates inefficient inter-system crossing ($k_{ISC} < 10^6 \text{s}^{-1}$) despite the expected heavy atom effect of iodine. We attribute this slow singlet-triplet transition to the large energy gap $\Delta E(S_1-T_1)$ (~1.8 eV in TFC¹ in cyclohexane) that is characteristic of diradicaloids.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda_{abs}$ (nm)</th>
<th>$\lambda_{fl}$ (nm)</th>
<th>$\Delta h\nu$ (eV)</th>
<th>PLQY (% ± 10%)</th>
<th>$\tau$ (ns ± 0.1)</th>
<th>$k_r$ (s$^{-1}$)</th>
</tr>
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<tr>
<td>TFC₉</td>
<td>387</td>
<td>611</td>
<td>1.17</td>
<td>100</td>
<td>29.8</td>
<td>3.4×10⁷</td>
</tr>
<tr>
<td>TFC₉</td>
<td>394</td>
<td>610</td>
<td>1.11</td>
<td>100</td>
<td>25.2</td>
<td>4.0×10⁷</td>
</tr>
<tr>
<td>TFC¹</td>
<td>415</td>
<td>601</td>
<td>0.92</td>
<td>100</td>
<td>10.5</td>
<td>9.5×10⁷</td>
</tr>
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TFCs’ luminescent behavior implies substantial structural reorganization of the excited state. The pronounced solvatochromism in the emission but not in absorption suggests that TFCs are non-polar in the ground state (as expected from the symmetry and shown by DFT, Table S6) but develop large dipole moments in their excited state during the relaxation from the Franck-Condon region. Lippert-Mataga plots indicate a moderate correlation ($R^2$~0.7) between fluorescence Stokes shift ($\nu_a - \nu_f$) and orientation polarizability of the solvent ($\Delta f_{LM}$). The slopes of these plots suggest excited state dipole moments of 8 – 11 Debye (Figures S14-15, Table S2).
Figure 3. a) Femtosecond transient absorption of TFC\(^1\) in cyclohexane at room temperature. b) Time-resolved emission spectra (TRES) of TFC\(^F\) in cyclohexane at 195 K (integration time 0.3 ns) compared with steady-state spectra at different temperatures. c) Jablonski diagram of TFCs showing sudden polarization to Z\(_1^*\) state. d) Schematics of excited state rearrangement leading to Z\(_1^*\) state.

This high polarity of the excited state of a non-polar symmetric molecule is rather counter-intuitive, but it was previously invoked to explain the photochemistry of olefins\(^38,41\) More recently, sudden polarization has been observed via time-resolved optical and microwave spectroscopy in tetraphenylethylene,\(^42\) biphenanthrenylidene,\(^43\) and fluorinated stilbenes.\(^44\) Under photoexcitation, some of these non-polar molecules relax to a non-polar metastable minimum near the Frank-Condon region (S\(_1^*\)) before twisting and forming a zwitterionic state (Z\(_1^*\)) state with a planar sp\(^2\) carbocation and a pyramidalized sp\(^3\) carbanion (Figure S25). Slow \(k_r\), resulting from the near-zero transition oscillator strength at the 90° twisted geometry (cf. 0.008 for tetraphenylethylene, Table S10), and rapid \(k_{nr}\) enabled by a conical intersection\(^45,46\) (Figure S25) result in negligible fluorescence from the Z\(_1^*\) state of these olefins (e.g., PLQY <0.01% in tetraphenylethylene\(^42\)). For TFCs (and potentially other quinodimethanes), Z\(_1^*\) can remain highly emissive because of the maintained \(\pi\)-bonding through the central aromatic ring (\(f_{osc} \sim 0.3\), Table S10).
The formation of the $Z_1^*$ state can be facilitated by fluorines in TFCs as they provide resonance stabilization to the carbocation and inductive stabilization to the carbanion centers. Indeed, Thiele’s chlorocarbon (TCC), with a less efficient resonance stabilization of carbocation by chlorines, displays a significantly smaller polarization in its excited state (dipole moment of $\sim$6 D calculated from solvatochromism, Table S2) and lower Stokes shift ($\leq$0.68 eV, Figures S12, S14-15).

To observe the relaxation to $Z_1^*$, solution photoemission was measured at 77 K. The fluorescence of TFCs is substantially blue-shifted (787 nm at 298 K to 488 nm at 77 K in TFC$^l$ in ethyl acetate) with smaller Stokes shifts (0.30–0.44 eV for TFC$^l$) (Figures S19-20). No delayed luminescence was observed, and the emission decay at 77 K is much faster than that at room temperature (e.g. for TFC$^l$ in cyclohexane, $\tau = 1.6$ ns vs 10.5 ns, Figures S17, S21). The implied faster $k_r$ and much lower Stokes shift at 77 K suggest this emission originates from a less twisted conformation $S_1^*$, as its relaxation to $Z_1^*$ is slowed down in frozen matrices. This suppression is a joint effect of temperature and matrix rigidification: a similar but smaller blue shift was observed in polystyrene solid solution vs toluene at 298 K (Figure S22).

Femtosecond transient absorption (fs-TA) allows a direct observation of the SP kinetics. In cyclohexane solution, TFC$^l$ shows the rapid formation of an excited state absorption (ESA) at $\sim$700 nm (secondary feature at 567 nm), which progressively redshifts and decays monoexponentially with $\tau \sim 0.5$ ps (Figures 3a, S31). We attribute this to the formation and rapid relaxation of $S_1^*$. This decay coincides with the formation ($\tau \sim 0.4$ ps, Figure S31) of a second, long-lived ESA band at 558 nm (secondary features at 510 nm and 740 nm) with a lifetime of $\sim$7 ns, which matches the fluorescence lifetime ($\sim$10 ns) and is attributed to $Z_1^*$ state. The two ESA features are also observed in ethyl acetate, with a more rapid decay ($\tau \sim 0.1$ ns) of the long-lived ESA (Figures S30, S32). There were no signatures of triplet states in either solvent. The ultrafast transition between these distinct excited states is consistent with the solution-stabilized SP model.$^{47}$

To show the evolution of the emission from $S_1^*$ to $Z_1^*$ state, we performed nanosecond time-resolved emission spectroscopy (ns-TRES) of TFC$^f$ at 195 K in frozen cyclohexane (to slow down the excited state reorganization, Figure S26). The results show the expected progressive emission redshift over the course of $\sim$20 ns (Figure 3c, Figure S27), indicating a restriction of the structural reorganization.
In conclusion, we demonstrated that fluorine substitution of Thiele’s hydrocarbon results in diradicaloids with exceptionally high thermal, oxidative, and photostability. Upon photoexcitation at room temperature, these symmetric non-polar diradicaloids undergo SP to form highly polar zwitterionic excited states. Although SP has been observed in olefins, the resulting $Z_1^*$ states were essentially non-emissive (‘phantom states’$^{42}$). We show that properly designed diradicaloids can have quantitative fluorescence from $Z_1^*$ state. The polar nature of this excited state leads to large environmental dependence of emission energies. The NIR emission attained in polar media is especially remarkable considering these molecules’ large HOMO-LUMO gaps (2.6-2.8 eV). The photophysical behavior of TFCs can also be compared to that of twisted intramolecular charge-transfer (TICT) excited state of sterically congested D-π-A fluorophores,$^{48}$ but it results from the diradical character of the molecule, in lieu of donor/acceptor fragments. Overall, our work establishes a new design principle towards emissive diradicaloids for fundamental photophysics investigations (e.g. SP and $Z_1^*$ to $S_0$ emission) and functional materials (e.g. large Stokes shift NIR emitter has potential for biomedical imaging).

Acknowledgement

This work was supported by NSERC of Canada. High-performance computing resources were provided by Digital Alliance Canada. We thank Dr. H. M. Titi (McGill University) for X-ray crystallography, Dr. J. S. R. V. Winfred and Prof. K. Hanson (Florida State University) for femtosecond transient absorption studies. C.-H. Liu acknowledges support by the Vanier scholarship, Z. He, C. Ruchlin, Y. Che acknowledge support by FRQNT scholarships.
Reference


