A luminescent organic radical with two pyridyl groups: high photostability and dual stimuli-responsive properties, with theoretical analyses of photophysical processes†

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Luminescent monoradicals are expected to show unique properties based on their doublet state, where establishing a method to improve their photostability is an important issue for expanding their photofunctionality. We synthesized a highly photostable luminescent organic radical, the bis(3,5-dichloro-4-pyridyl)(2,4,6-trichlorophenyl)methyl radical (bisPyTM), containing two pyridyl groups on a tris(2,4,6-trichlorophenyl)methyl radical (TTM) skeleton. bisPyTM in dichloromethane exhibited fluorescence with an emission peak wavelength, $\lambda_{em}$, of 650 nm. We visually detected an emission ($\lambda_{em} = 712$ nm) from crystalline bisPyTM at 77 K, which is the first example of definite solid-state emission in a radical. Introducing the two nitrogen atoms into the TTM skeleton was shown to lower the energies of the frontier orbitals. The oscillator strength, $f$, of the electronic transition between the lowest excited state and the ground state, and the off-diagonal vibronic coupling constants (VCCs) were calculated theoretically for bisPyTM and the (3,5-dichloro-4-pyridyl)(bis(2,4,6-trichlorophenyl)methyl radical (PyBTM). The calculated PyBTM to bisPyTM ratios for $f$ or VCC agreed well with experimental radiative and non-radiative rate constants ($k_r$ and $k_{nr}$) ratios, respectively. This study shows that scaled $k_r$ and $k_{nr}$ can be estimated and compared in this class of radicals using theoretical calculations, greatly advancing the prediction and design of their photofunctionality. The half-life of bisPyTM upon continuous UV light irradiation in dichloromethane was 47 or 3000 times longer those that of PyBTM (which contains one pyridyl group) and TTM (which has no pyridyl rings), respectively. The electrochemical and luminescent properties of bisPyTM were modulated in two stages using protons or B(C$_6$F$_5$)$_3$. 

Introduction

Luminescent molecules are attracting increasing attention because of their suitability for a wide variety of scientific and engineering applications, such as organic light-emitting diodes and chemosensors. Several emission mechanisms, such as fluorescence via the singlet excited state, phosphorescence from the triplet excited state, and thermally activated delayed fluorescence, have been used to obtain the desired device properties. In contrast with conventional luminescent molecules, which are closed-shell with singlet ground states, radicals with an unpaired electron have been the focus of research into next-generation luminophores. Radicals, in which fluorescence occurs from the lowest doublet excited state ($D_1$) to the doublet ground state ($D_0$), can exhibit unique characteristics, such as having long emission wavelengths without extended π-conjugation. Of particular importance in electroluminescent devices is the high efficiency of the internal electron (hole) → photon conversion ratio, up to 100%, which has been experimentally suggested recently. Although closed-shell fluorescent emitters suffer from quenching via the lowest triplet excited state ($T_1$), which is statistically formed together with the lowest singlet excited state ($S_1$) in a ratio of 3 : 1, particular monoradicals do not suffer from this quenching problem because of the absence of excited states between $D_1$ and $D_0$ and the spin-allowed $D_1 → D_0$ transition.

The doublet luminescence of radicals has been investigated much less than that of closed-shell luminescent molecules, because of its rarity and low chemical stability under ambient conditions.
conditions or in photostimulated states.\textsuperscript{17,18} Following studies on the emission properties of \textit{in situ}-generated unstable diarylmethyl or triarylmethyl radicals,\textsuperscript{19–22} polychlorinated triarylmethyl (PTM) and tris[2,4,6-trichlorophenyl)methyl (TTM) radicals (Fig. 1) have been developed as luminescent radicals.\textsuperscript{23,24} They show excellent chemical stability under ambient conditions, although they decompose upon photolysis.\textsuperscript{17–18} Improving the photostability of radicals is an important step toward developing unique doublet-based photofunctionality or novel phenomena arising from the interplay between luminescent and magnetic (spin) properties.

A drastic increase in the photostability of luminescent radicals has been achieved in the \{3,5-dichloro-4-pyridyl\}bis\{2,4,6-trichlorophenyl\}methyl radical (PyBTM; Fig. 1), prepared by our group.\textsuperscript{14} PyBTM has a pyridyl ring in the TTM skeleton and showed fluorescence with an absolute quantum yield ($\phi_{em}$) of 0.01–0.03 in solution and a $\phi_{em}$ value of 0.26 in a rigid matrix at room temperature. Importantly, its stability upon UV irradiation was up to 115 times higher than that of TTM. The excellent photostability has expanded the scope of doublet-based photofunctionality in radicals. We have reported on stimuli responsiveness,\textsuperscript{25} the halogen atom substitution effect,\textsuperscript{26} and increased $\phi_{em}$ and photostability upon coordination to metal ions in PyBTM.\textsuperscript{27–29} Studies on PyBTM have suggested that introducing a pyridyl group may lead to radicals with improved photostability, owing to the lowering of energy levels around the frontier orbitals. However, the utility of this method is not well established.

In this study, we developed a new bis\{3,5-dichloro-4-pyridyl\}\{2,4,6-trichlorophenyl\}methyl radical (bisPyTM; Fig. 1), which has two pyridyl groups, and is stable and luminescent. We aimed to resolve two issues in understanding the fundamental properties of luminescent triarylmethyl radicals. The first is the effects of introducing an additional pyridyl ring into the PyBTM skeleton on the energies of the frontier orbitals, luminescent properties, and photostability. The increase in the number of pyridyl rings is expected to increase the photostability and to expand the variation of the coordination structure in relation to multistage chemical responses or high-dimensional assemblies.\textsuperscript{30,31}

The second challenge is interpreting the luminescence characteristics and photophysical parameters, including the radiative and non-radiative rate constants ($k_r$ and $k_{nr}$), through theoretical calculations using density functional theory (DFT) and time-dependent (TD)-DFT. The technical challenges and limited number of compounds mean that joint theoretical and experimental studies on the relaxation processes of luminescent radicals in their excited state are still rare. However, conical intersection\textsuperscript{32} and back-electron transfer\textsuperscript{8} have been investigated theoretically as non-radiative relaxation processes of radicals in the excited state. We calculated the excited states and molecular and electronic structures of PyBTM and bisPyTM, and investigated non-radiative relaxation processes via vibronic coupling density (VCD) analysis\textsuperscript{33} to evaluate the rate of internal conversion. The differences in $k_r$ and $k_{nr}$ between the two radicals can be explained through the difference in oscillator strengths and off-diagonal vibronic coupling constants (VCCs).

**Results and discussion**

**Theoretical methods for estimating photophysical parameters**

The relaxation process from the $D_1$ state to the $D_0$ state consists of radiative and non-radiative transitions (Scheme 1). Luminescence corresponds to the radiative $D_1 \rightarrow D_0$ transition; thus, $k_r$ is proportional to the oscillator strength, $f$, of the transition for the $D_1$ nuclear coordinates. The $f$ value is calculated using TD-DFT in this study. In contrast, the non-radiative transition is expected to consist of internal conversion followed by vibrational relaxation in the radicals studied here (Scheme 1). Intersystem crossing from $S_1$ to $T_n$ states can also provide a non-radiative relaxation pathway in conventional closed-shell luminescent molecules. However, intersystem crossing from $D_1$ to other excited states with different multiplicities, such as a quartet state ($Q_1$), is negligible, because the $Q_1$ state is energetically much higher than the $D_1$ state.\textsuperscript{14} Thus, $k_{nr}$ is determined mainly by the rate of internal conversion. Internal conversion has been suggested as a major pathway in the non-radiative decay of some radicals,\textsuperscript{11,28,34} however, no theoretical calculations have been performed to clarify the deactivation mechanism. In this study, VCD analysis of the luminescent radicals elucidated the mechanism of their non-radiative decay. This was suitable for our radicals, because it allowed us to evaluate the rate of internal conversion and to determine the vibrational modes that contribute to internal conversion. Internal conversion is caused by off-diagonal vibronic coupling. The rate of internal conversion is proportional to the square of

![Scheme 1 Monoradical deactivation processes from the lowest excited ($D_1$) state.](image-url)
the off-diagonal VCCs.\textsuperscript{33} The off-diagonal VCC of mode \(z\) between electronic states \(m\) and \(n\) is defined by

\[
V_{mn,z} = \left\langle \Psi_m(r, R_0) \left( \frac{\partial H(r, R)}{\partial Q_{z}} \right)_{R_0} \Psi_n(r, R_0) \rightangle,
\]

where \(H(r, R)\) is the molecular Hamiltonian for a set of electronic coordinates \(r = \{r_1, \ldots, r_n, \ldots, r_N\}\) and a set of nuclear coordinates \(R = \{R_1, \ldots, R_{N_b}, \ldots, R_M\}\). \(\Psi_m\) and \(\Psi_n\) are the electronic wavefunctions of states \(m\) and \(n\), respectively. \(Q_{z}\) is the normal coordinate of mode \(z\), and \(R_0\) denotes a reference nuclear configuration. We took the geometries after the vibrational relaxations as reference nuclear configurations.

The origin of a vibronic coupling in terms of the electronic and vibrational states can be visualized using VCD analysis,\textsuperscript{34} which provides insight into the vibronic coupling in a molecule. Furthermore, we can control vibronic couplings to suppress relaxations as reference nuclear configurations.

The synthetic route for bisPyTM is shown in Scheme 2. The next highest occupied molecular orbital (NHOMO; \(14N\) (0.108 mT)) was comparable to that of PyBTM (0.115 mT). This result indicates that the spin density on the N atom was delocalized over the molecule, including the central C1 atom and two pyridyl nitrogen atoms (Fig. 3b). The simulated hcc of \(14N\) (0.108 mT) was comparable to that of PyBTM (0.115 mT). This result indicates that the spin density on the N atom was similar in bisPyTM and PyBTM;\textsuperscript{44} the densities estimated from the simulated hcc and DFT were 0.06 and 0.069, respectively.

### ESR spectroscopy at 177 K

An ESR spectrum of bisPyTM in dichloromethane was measured at 177 K to estimate the spin density distribution over the bisPyTM skeleton (Fig. 3a). The spectrum showed a characteristic hyperfine structure with a \(g\) value of 2.004, similar to that of PyBTM. The spectrum was reproduced \(via\) computational simulation, considering hyperfine coupling with six \(^1\)H and two \(^1\)N atoms. The obtained hyperfine coupling constants (hccs) were qualitatively similar to those calculated \(via\) DFT (Table S2†). The results indicate that the spin density was delocalized over the molecule, including the central C1 atom and two pyridyl nitrogen atoms (Fig. 3b). The simulated hcc of \(^1\)N (0.108 mT) was comparable to that of PyBTM (0.115 mT). This result indicates that the spin density on the N atom was similar in bisPyTM and PyBTM;\textsuperscript{44} the densities estimated from the simulated hcc and DFT were 0.06 and 0.069, respectively.

### Electronic structure in the ground state (\(D_0\) state)

The electronic properties of bisPyTM were calculated \(via\) DFT, to reveal the effects of introducing two pyridyl rings to the TTm framework on the distribution and energies around the frontier orbitals. The unrestricted B3LYP level of theory with 6-31G(d,p) basis sets was used, and the solvent effect (dichloromethane) was treated using the polarizable continuum model. The calculated molecular orbitals (MOs) of bisPyTM are shown in Fig. 4. The next highest occupied molecular orbital (NHOMO; 120z and \(\beta\)) and NHOMO−1 (119z and \(\beta\)) were assumed to be the bonding and antibonding combination of wavefunctions at

Scheme 2 The synthetic route for bisPyTM.

![Image](image-url)
the two pyridyl rings, which were distributed mainly on the two pyridyl rings. These two MOs were almost degenerate. The next lowest unoccupied molecular orbital (NLUMO; 122\(\alpha\) and \(\beta\)) of bisPyTM was delocalized on the two pyridyl rings, whereas the singly occupied molecular orbital (SOMO; 121\(\alpha\) and \(\beta\)) was located mainly on the central carbon atom with non-negligible delocalization on the three aromatic rings. The distribution of the MOs was similar to that in PyBTM, where the NHOMO and NLUMO were distributed mainly on the pyridyl ring, and the SOMO was located on the central carbon atom and extended to the aromatic rings.

The energy diagram shows that the energies of the frontier orbitals (119\(\alpha\)–122\(\alpha\) and 119\(\beta\)–122\(\beta\)) of the radicals all decreased as the number of pyridyl rings increased; bisPyTM had energies 0.10–0.20 eV lower than PyBTM. This decrease is expected to change the optical and redox properties and stabilities of the compounds, because the frontier orbital energies directly or indirectly determine the optical and redox properties. The lowering of the energy of the \(\beta\)-SOMO (121\(\beta\)) for bisPyTM and 121\(\beta\) for PyBTM was confirmed via cyclic voltammetry.

### Cyclic voltammetry

The redox properties of the radicals were investigated via cyclic voltammetry. The cyclic voltammogram of bisPyTM in 0.1 M \(Bu4N\text{ClO}_4/\text{CH}_2\text{Cl}_2\) (Fig. 5a and S1†) showed a reversible reduction wave at \(E^{\text{red}} = -0.57\) V vs. the ferrocenium/ferrocene (Fc/Fc) redox couple, corresponding to the reduction of bisPyTM (Scheme 3a). This process was explained through the injection of an electron into the \(\beta\)-SOMO. The \(E^{\text{red}}\) value of bisPyTM was more positive than that of PyBTM (–0.74 V) and TTM (–0.99 V) under identical conditions, suggesting that increasing the number of pyridyl rings increases the electron-accepting ability of the radical and decreases the energy level of the \(\beta\)-SOMO. This observation can be explained by the higher electronegativity of nitrogen compared to carbon.\(^{14}\)

### Optical properties

The UV/vis absorption spectrum of bisPyTM in dichloromethane displayed a strong near-UV band (\(\lambda_{\text{abs}} = 355\) nm, transition from 121\(\alpha\) to 122\(\alpha\) and 123\(\alpha\)) and a low-lying band (Fig. 6a). The lowest-energy transition band (transition from 120\(\beta\) to 121\(\beta\)) that formed the lowest excited state (D\(_1\) state) was observed at a peak wavelength of 356 nm. These transitions were assigned based on TD-DFT calculations (ESI†). The relative wavelengths and oscillator strengths for the calculated transition bands agreed with the absorption spectrum obtained experimentally, supporting the orbital assignments and the validity of the calculations. A \(\beta\)-electron-centered 120\(\beta\) \(\rightarrow\) 121\(\beta\) electronic transition induced the D\(_1\) state, as in TTM, PyBTM, and PyBTM derivatives.\(^{14,32-39}\)

bisPyTM in dichloromethane displayed fluorescence, with an emission maximum wavelength, \(\lambda_{\text{em}}\), of 650 nm upon excitation at \(\lambda_{\text{ex}} = 355\) nm (Fig. 6a and c). \(\phi_{\text{em}}\) and the lifetime (\(\tau\)) were measured as being 0.009 and 3.6 ns, respectively. This emission wavelength was strongly red-shifted compared with PyBTM and TTM, indicating the large structural change in bisPyTM in the excited state.

We estimated \(k_r\) and \(k_{\text{nr}}\) of bisPyTM and PyBTM using eqn (6) and (7) (Table 1). \(k_r\) of bisPyTM was smaller than that of PyBTM, whereas \(k_{\text{nr}}\) was considerably larger. The observed PyBTM to bisPyTM ratio of the \(k_r\) values was consistent with results from the theoretical calculation described in the next section. The greater \(k_{\text{nr}}\) of bisPyTM was explained by accelerated internal conversion, which is also described in the next section.

\[
\phi_{\text{em}} = k_r/(k_r + k_{\text{nr}})
\]

\[
\tau = 1/(k_r + k_{\text{nr}})
\]

Surprisingly, bisPyTM exhibited luminescence both in solution and in the solid state. Deep red luminescence with \(\lambda_{\text{em}} = 712\) nm was observed in the crystalline state (Fig. 6a and d) at 77 K. To the best of our knowledge, this is the first reported organic radical showing distinct luminescence in its crystalline state.\(^{37}\)

We propose that quenching via intermolecular interactions in the crystalline state is weaker for bisPyTM than for the other radicals, explaining the luminescence in the crystalline state. Solid-state luminescence was also observed when we doped bisPyTM into the \(\pi\)-H-bisPyTM crystal, the precursor for bisPyTM (Scheme 2). The emission wavelength of the 3 wt%-doped sample was shorter than that of bisPyTM in dichloromethane, which would be caused by reduced reorientation energy due to rigid packing. The emission wavelength was red-shifted, and the intensity decreased with increasing bisPyTM concentration (Fig. 6b and e), implying that an excimer was formed under highly doped conditions.\(^{38}\)

### Molecular and electronic structures in the lowest excited state (D\(_1\) state)

The molecular and electronic structures of bisPyTM in the D\(_1\) state were calculated via TD-DFT (UB3LYP/6-31G(d,p)) to clarify the characteristics of the radiative and non-radiative processes that occurred from the D\(_1\) state.

In the optimized molecular structure of bisPyTM in its D\(_1\) state, the bond lengths between the central carbon atom and the aryl moieties (C1–C4, C1–C9, C1–C15) and between carbon atoms at the ortho and meta positions (C5–C6, C2–C3, C7–C8,
C10–C11, C16–C17, C13–C14) were shorter than those in the D₀ state, whereas the other C–C and C–N bonds were longer (Fig. 7a). The N1–C4–C1 and N2–C9–C1 bond angles in the two pyridyl rings decreased (Fig. 7b). These results indicate the increased quinoid character of the aryl groups as the aromaticity of the pyridyl rings decreased in the D₁ state.

The MOs of bisPyTM in the D₁ state in dichloromethane are shown in Fig. 4. The distribution of each MO is similar to that in the D₀ state, except the σ(β)-NHOMO (120α(β)). The distribution of the σ(β)-NHOMO was similar to that of the σ(β)-NHOMO–3 in the D₀ state. The structural change between the D₁ and the D₀ states induced the energy level reordering of the energetically closed MOs.
The MOs of the reference compound, PyBTM, in the D1 state in dichloromethane were calculated (Fig. 4). The MO distributions were similar to those in the D0 state in the unoccupied orbitals, whereas modulation of the distribution was detected in the a\(\beta\)(b\(\beta\))-NHOMO level. The a\(\beta\)(b\(\beta\))-NHOMO was delocalized on the pyridyl group and two trichlorophenyl groups in the D0 state, whereas it was delocalized on the two trichlorophenyl groups in the D1 state. Introducing the solvent effect using the polarizable continuum model caused the reordering of energy levels and altered the distribution of MOs, including the a\(\beta\)(b\(\beta\))-NHOMO. The a\(\beta\)(b\(\beta\))-NHOMO was located at the pyridyl ring in the D1 state without the solvent effect, whereas it was distributed on the trichlorophenyl moieties with negligible extension to the pyridyl ring with the solvent effect (Fig. 4 and S2†). Because the \(\beta\)-NHOMO was directly involved in forming the D1 state, the change in the distribution on the \(\beta\)-NHOMO should affect the photophysical properties. These results demonstrate the importance of considering the solvent effect in these calculations. Therefore, we performed theoretical analysis considering the effects of dichloromethane.

**Fig. 5** Cyclic voltammograms of bisPyTM (0.5 mM) in 0.1 M \(\text{Bu}_4\text{NClO}_4/\text{CH}_2\text{Cl}_2\) at a scan rate of 0.1 V s\(^{-1}\) (a) with no additives and (b) with 2.0 eq. and (c) 5.0 eq. of TfOH.

**Scheme 3** Redox behaviors of (a)bisPyTM, (b)[HN-bisPyTM]\(^+\) and (c) [HN\(_2\)-bisPyTM]\(^2+\).

The MOs of the reference compound, PyBTM, in the D1 state in dichloromethane were calculated (Fig. 4). The MO distributions were similar to those in the D0 state in the unoccupied orbitals, whereas modulation of the distribution was detected in the a\(\beta\)-NHOMO level. The a\(\beta\)-NHOMO was delocalized on the pyridyl group and two trichlorophenyl groups in the D0 state, whereas it was delocalized on the two trichlorophenyl groups in the D1 state. Introducing the solvent effect using the polarizable continuum model caused the reordering of energy levels and altered the distribution of MOs, including the a\(\beta\)-NHOMO. The a\(\beta\)-NHOMO was located at the pyridyl ring in the D1 state without the solvent effect, whereas it was distributed on the trichlorophenyl moieties with negligible extension to the pyridyl ring with the solvent effect (Fig. 4 and S2†). Because the \(\beta\)-NHOMO was directly involved in forming the D1 state, the change in the distribution on the \(\beta\)-NHOMO should affect the photophysical properties. These results demonstrate the importance of considering the solvent effect in these calculations. Therefore, we performed theoretical analysis considering the effects of dichloromethane.

**Theoretical analyses of photophysical parameters**

We estimated the rates of photophysical processes, \(k_r\) and \(k_{nr}\), for PyBTM and bisPyTM to explain the experimentally observed difference in \(\phi_{em}\). \(k_r\) and \(k_{nr}\) can be evaluated by calculating the \(f\) values and off-diagonal VCCs between the D1 and the D0 states, as mentioned in the section ‘Theoretical methods for estimating photophysical parameters’. Off-diagonal VCDs...
indicate the vibrational modes that contribute to internal conversion.

The $f$ values for the $D_1$ nuclear coordinates calculated using TD-DFT, considering the effects of the solvent (dichloromethane), were 0.0290 and 0.0457 for bisPyTM and PyBTM, respectively. The PyBTM to bisPyTM ratio of $f$ calculated was 1.58. Neglecting the effects of Franck–Condon factors on the radiative rate constants, we compared this ratio with the observed ratio of the radiative rate constants. The observed ratio of PyBTM to bisPyTM was 1.6. The calculated $f$ values reproduced the ratio of the observed $k_r$ values for the two radicals well.

Fig. 8 shows the off-diagonal VCCs and VCDs of bisPyTM and PyBTM. The VCCs of bisPyTM were smaller than those of common organic compounds. For instance, the maximum VCC in a triphenylamine derivative that is known as a non-fluorescent molecule is ca. $8 \times 10^{-4}$ a.u., while that in bisPyTM is less than $7 \times 10^{-4}$ a.u. The square sum of the VCCs of bisPyTM was $1.9 \times 10^{-6}$ a.u., which is larger than that of PyBTM ($1.4 \times 10^{-6}$ a.u.), reproducing the greater $k_{nr}$ value of bisPyTM. The observed ratio of $k_{nr}$, $k_{nr}$ (bisPyTM)/$k_{nr}$ (PyBTM), was 1.9 (Table 1). Neglecting the effects of Franck–Condon factors on $k_{nr}$, we calculated the ratio of $k_{nr}$ values from the square sums of the off-diagonal VCCs. The ratio of the square sum for bisPyTM to that for PyBTM is 1.36, which is reasonably consistent with the observed ratio. This difference in off-

Table 1 The photophysical parameters of the radicals

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<tr>
<th></th>
<th>$\lambda_{\text{abs}}^\text{exp}$/nm</th>
<th>$\lambda_{\text{abs}}^\text{calc}$/nm ($f$)</th>
<th>$\lambda_{\text{em}}^\text{calc}$/nm ($f$)</th>
<th>$\phi_{\text{em}}$</th>
<th>$\tau$/ns</th>
<th>$k_r/10^6$ s$^{-1}$</th>
<th>$k_{nr}/10^8$ s$^{-1}$</th>
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<tbody>
<tr>
<td>bisPyTM</td>
<td>355</td>
<td>643 (0.0290)</td>
<td>572 (0.0457)</td>
<td>0.009(0)</td>
<td>3.6</td>
<td>2.5</td>
<td>2.8</td>
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<td>572 (0.0457)</td>
<td>0.025(0)</td>
<td>6.4</td>
<td>3.9</td>
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<td>572 (0.0457)</td>
<td>0.02</td>
<td>7.0</td>
<td>3</td>
<td>1.4</td>
</tr>
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Fig. 7 A schematic diagram of the structural changes from the $D_0$ to $D_1$ states of bisPyTM and PyBTM: (a) changes in the bond lengths, in units of Å, and angles; and (b) changes in the N1–C4–C1 and N2–C9–C1 angles of bisPyTM.

Fig. 8 Off-diagonal VCCs between the adiabatic $D_1$ and $D_0$ states for the normal mode of (a) bisPyTM and (d) PyBTM in dichloromethane. The overlap density (isovalue of $\rho = 0.01$) of (b) bisPyTM and (e) PyBTM, and the off-diagonal VCD between the adiabatic $D_1$ and $D_0$ states for selected vibrational modes of (c) bisPyTM and (f) PyBTM (isovalue of $4 \times 10^{-6}$ a.u.).
The low photostability of luminescent radicals is an important problem that must be overcome. The decay of bisPy and PyBTM upon continuous irradiation with light at each maximum absorption wavelength. Fig. 9 shows the decay of luminescence intensity for each compound, and the degree of decay represents the decomposition rate upon exposure to light. The estimated half-life (t1/2) in dichloromethane was 6.7 x 10^3 s; this value was 43 times larger than that of PyBTM (1.6 x 10^2 s). Considering our previous results, the photostability of bisPyTM was 30 times higher than PyBTM. In other aprotic solvents such as acetone, the photostability is defined as a product of the absorption coefficients (ε) at the frontier orbitals and the overlap density (ff) for the radicals. This trend suggests that there is a specific interaction between the radical and solvent molecules that modulates the photostability. For example, exceptionally low t1/2 values in dichloromethane, hexane, and chloroform; and the overlap density, which arises from the distribution of the HOMOs and LUMOs of the radicals, greatly advances the prediction and design of their photofunctionality.

Photostability

Table 2 The half-lives (t1/2) of compounds upon light irradiation

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<th>Compound</th>
<th>t1/2/s</th>
<th>ε/M⁻¹ cm⁻¹</th>
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<th>t1/2/s</th>
<th>ε/M⁻¹ cm⁻¹</th>
<th>t1/2 × ε</th>
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<td>PyBTM</td>
<td></td>
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<td></td>
<td></td>
<td></td>
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<td></td>
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<td>Acetonitrile</td>
<td>1.4(1)</td>
<td>2.19 x 10⁴</td>
<td>3.2 x 10⁸</td>
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<td>2.47 x 10⁴</td>
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<td>2.30 x 10⁵</td>
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<td>1.4 x 10⁹</td>
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<td>1.85 x 10⁵</td>
<td>1.4 x 10⁹</td>
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<td>3.90 x 10⁵</td>
<td>4.3 x 10⁹</td>
<td>1.9(0)</td>
<td>1.25 x 10⁶</td>
<td>2.4 x 10⁸</td>
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<td>Chloroform</td>
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<td>1.65 x 10⁵</td>
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<td>2.25 x 10⁵</td>
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<td>1.78 x 10⁵</td>
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<td>3.1 x 10⁹</td>
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<td>1.23 x 10⁵</td>
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<td>2.25 x 10⁵</td>
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a) λex = 355 nm, b) λex = 370 nm, c) λex = 310 nm in dichloromethane, hexane, and chloroform; d) λex = 300 nm in acetonitrile; and e) λex = 330 nm in acetone. A comparison of t1/2 and t1/2 × ε for the compounds. Molar absorption coefficients at the irradiation wavelengths.

Fig. 9 Plots showing the emission decay of bisPyTM, PyBTM, and TIPS pentacene in dichloromethane under continuous excitation with light at λex = 355 nm (bisPyTM), 370 nm (PyBTM), and 310 nm (TIPS pentacene). The emission intensities are normalized.
may result from hydrogen bonds formed between nitrogen atoms on the radicals and hydrogen atoms in the EtOH or MeOH molecules, which accelerate decomposition in the photoexcited state.

For industrial applications, the photostabilities of bisPyTM and 6,13-bis(triisopropylsilyl)pentacene (TIPS pentacene) were compared. TIPS pentacene is a closed-shell molecule commonly used in organic semiconductors as a benchmark material due to its high photostability and solubility. Its fluorescence peak maximum (λ_{ex} = 650 nm upon excitation at λ_{em} = 360 nm) was similar to those of PyBTM and bisPyTM. Table 2 and Fig. 9 provide clear evidence for the superior photostability of bisPyTM; the photostability of the radical was 0.6 to 61 times higher (4 to 660 times larger τ_{1/2} values) than TIPS pentacene. This result demonstrates the potential of the compound for practical applications.

**Dual responsive properties**

We aimed to control the optical and electrochemical properties of bisPyTM by using the two pyridyl nitrogen atoms in the molecular structure as chemical stimulus-responsive sites. First, we investigated the effects of adding a Bronsted–Lowry acid. The reversible response of the radical to protonation and deprotonation was confirmed via UV/vis absorption spectroscopy during an acid–base titration (Fig. 10a and c). A new transition band at λ = 409 nm appeared as the intensity of the absorption at λ = 355 nm decreased upon the addition of trifluoromethanesulfonic acid (TFOH). The initial spectral shape was almost recovered by adding triethylamine (NEt3). Protonation affected the luminescence properties; the fluorescence intensity decreased substantially upon addition of TFOH (Fig. 10b and d). PyBTM showed similar absorption and emission spectra upon protonation and deprotonation.

The redox properties, examined via cyclic voltammetry, also changed drastically upon protonation. Upon the successive addition of TFOH, two new redox waves at E^0 = −0.05 and 0.55 V appeared, and only one redox wave at E^0 = 0.55 V was observed after the addition of excess TFOH (Fig. 5c). This result suggests a two-stage increase in the electron-accepting ability of the molecule resulting from single-to-double protonation of the two pyridyl rings. Accordingly, the redox waves at E^0 = −0.05 and 0.55 V were ascribed to the [HN-bisPyTM]^+ and [HN-bisPyTM]^{2+} redox couples, respectively, where [HN-bisPyTM]^+ and [HN-bisPyTM]^{2+} are monoprotonated and diprotonated bisPyTM, respectively (Scheme 3). Monoprotonation or diprotonation shifted the reduction potential of bisPyTM by 0.52 or 1.12 V in the positive direction, respectively. Similar positive shifts were observed in the protonation or methylation of PyBTM, and were explained by a decrease in electron density upon protonation, which increased the electron-accepting ability.

The reduction potential of [HN]^{2+}-bisPyTM was higher than that of F_{4}TCNQ (2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane, E^0 = 0.16 V), which is commonly used as an electron acceptor or hole dopant in molecule-based devices and materials, showing that [HN]^{2+}-bisPyTM functions as a superior electron acceptor (i.e., oxidizing agent).

Next, we used B(C_{6}F_{5})_{3}, which is a Lewis acid capable of binding to nitrogen atoms, as an external stimulus. Upon the addition of B(C_{6}F_{5})_{3}, two isosbestic points (λ = 371 and 378 nm for 0–1 and 1–3 eq., respectively) were obtained in the UV/vis spectra. These two points can be assigned as the equilibrium of bisPyTM and one B(C_{6}F_{5})_{3} adduct, and that of one and two adducts, indicating the stepwise response of the two nitrogen atoms to B(C_{6}F_{5})_{3} (Fig. 10e). The emission characteristics of bisPyTM also showed a two-stage response to B(C_{6}F_{5})_{3}. The

![Fig. 10](image-url)

(a) UV/vis absorption spectra of bisPyTM in CH_{2}Cl_{2} following addition of TFOH: bisPyTM (red) + 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 (blue) eq. of TFOH. (b) Emission spectra of bisPyTM in CH_{2}Cl_{2} following addition of TFOH (λ_{ex} = 380 nm, isosbestic point wavelength): bisPyTM (red) + 0.5, 1.0, 2.0, and 3.0 (blue) eq. of TFOH. (c) UV/vis absorption spectra and (d) emission spectra of bisPyTM in CH_{2}Cl_{2} following addition of NEt_{3} (λ_{ex} = 380 nm): bisPyTM + 3.0 eq. of TFOH (blue) + 1.0, 2.0, and 3.0 (green) eq. of NEt_{3}. (e) UV/vis absorption spectra and (f) emission spectra of bisPyTM in CH_{2}Cl_{2} with addition of B(C_{6}F_{5})_{3} (λ_{ex} = 375 nm): bisPyTM + 3.5 eq. of B(C_{6}F_{5})_{3} (red) + 0, 0.5, 1.0, 2.0, 2.5, 3.0, and 3.5 (green) eq. of NEt_{3}. Fresh solutions were prepared for each measurement. (g) UV/vis absorption spectra and (h) emission spectra of bisPyTM in CH_{2}Cl_{2} with addition of 3.5 eq. of NEt_{3} (λ_{ex} = 375 nm): bisPyTM + 3.5 eq. of B(C_{6}F_{5})_{3} (red) + 0, 0.5, 1.0, 2.0, 2.5, 3.0, and 3.5 (green) eq. of NEt_{3}. Fresh solutions were prepared for each measurement.
emission maximum wavelengths were gradually red-shifted upon the addition of B(C₆F₅)₃, and the resulting emission band at λ = 756 nm extended over 850 nm [Fig. 10f], suggesting the near-IR emission of [(C₆F₅)₂BN]_2-bisPyTM. The mechanism of the red shift is similar to that for (C₆F₅)₂BN-PyBTM.²⁸ Upon the addition of NEt₃, the emission and UV/vis absorption spectra did not return to the initial states, indicating the incomplete recovery and partial decomposition of bisPyTM (Fig. 10g and h). These results show the partly reversible response of the radical to B(C₆F₅)₃ and NEt₃.

Conclusions

We prepared bisPyTM, a luminescent stable organic radical that has two pyridyl moieties. Upon continuous UV light irradiation, it exhibited a half-life in dichloromethane that was 43 and 200 times longer than those of PyBTM and TIPS pentacene, respectively. The photostabilities of the radicals were greatly improved as the number of pyridyl groups in the TTM skeleton increased. We confirmed the luminescence of crystalline bisPyTM at 77 K, which would be the first example of visible solid-state emission from a radical. The two nitrogen atoms of bisPyTM can act as chemical stimulus-responsive sites and react with TIOH and B(C₆F₅)₃ to modulate the optical and electrochemical characteristics. The differences in the kᵣ and kᵣ values of bisPyTM and PyBTM were reproduced through theoretical calculations based on DFT, TD-DFT, and VCD analyses. The VCDs indicated that the difference in the off-diagonal VCCs in the two radicals comes from the difference in the overlap density, which originates from the distribution of the NHOMOs.

Our results showed that introducing a pyridyl ring increases the photostability by lowering the energy levels of frontier orbitals. We also demonstrated that the scaled kᵣ and kᵣ values, important parameters that determine the photophysical properties, can be estimated and compared in this class of radicals via theoretical calculations. These findings contribute greatly to predicting the photophysical properties of luminescent radicals, thereby achieving high emission efficiency and controlled photofunctionality.

Experimental

Materials

All chemicals were reagent grade and purchased commercially. Water was purified using an AUTOPURE WD500 system (Yamato Scientific Co., Ltd). The acetonitrile (MeCN), dichloromethane (CH₂Cl₂), diethyl ether (Et₂O), hexane, tetrahydrofuran (THF) and toluene used for syntheses were purified through an organic solvent purifier (Nikko Hansen Co., Ltd).

Equipment

NMR spectra were recorded with a Bruker US500 spectrometer at room temperature. Chemical shifts in ppm were referenced using tetramethylsilane (0.00 ppm) as an internal standard. Microwave assisted synthesis was performed using a Biotage Initiator+. UV-vis-NIR absorption spectra were recorded with a JASCO V570 spectrophotometer. Steady-state emission spectra were recorded with HITACHI F-4500 and JASCO FP8600 spectrometers. Absolute photoluminescence quantum yields were measured using a Hamamatsu Photonics C9920-02G system. Fluorescence lifetime measurements were measured using a Hamamatsu Photonics Quantaurus-Tau C11367-02 system. ESR spectra were recorded with a JEOI JES-F1A00 spectrometer. 4-Hydroxy-TEMPO was used as a standard for estimating the spin concentration. Observed g-values were calibrated with an Mn²⁺/MgO marker. Cyclic voltammetry was carried out under an argon atmosphere with a GC working electrode, a platinum wire counter electrode and an Ag⁺/Ag reference electrode (10 mM AgClO₄ and 0.1 mM Bu₄NClO₄ in MeCN solution), with an ALS-650DT voltammetric analyzer. The platinum working electrode was polished with an alumina abrasive and washed with water and acetone with ultrasonication. The counter electrode was heated with an oxygen flame to remove organic compounds on the surface and washed with acetone. The reference electrode was washed with acetone. A Fc⁺/Fc redox couple was observed at 0.188 V under these experimental conditions. The potential of the voltammograms is shown relative to the Fc⁺/Fc redox couple.

Single crystal X-ray crystallography

The data for single crystal X-ray diffraction analysis were collected at 113 K on a Rigaku AFC10 diffractometer, with a Rigaku Saturn CCD system equipped with a rotating-anode X-ray generator that emitted graphite-monochromated Mo Kα radiation (0.7107 Å). A suitable single crystal was mounted on a looped film (micromount) with liquid paraffin. An empirical absorption correction, using equivalent reflections and Lorentzian polarization correction, was performed with the program CrystalClear 1.3.6. The structure was solved using SIR-92²⁹ and the whole structure was refined against F² with SHELXL-97.³⁰ All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located in idealized positions and were refined using a riding model with fixed thermal parameters.

Computational details

DFT calculations were executed using the Gaussian 09 program package.³¹ The geometries of the compounds were optimized with the grid = ultrasfine option without symmetry constraints, using the crystal structure coordinates as the starting structure. Calculations were performed using the unrestricted Becke three-parameter hybrid functional with the Lee-Yang-Parr correlation functional (B3LYP)⁴⁸ with the 6-31G(d,p) basis set.⁴⁹ Frequency calculations were carried out to ensure that the optimized geometries were minima on the potential energy surface, in which no imaginary frequencies were observed in any of the compounds. TD-DFT calculations were performed using UB3LYP to calculate the first 15 doublet transitions. The solvent effect was considered using the PCM model.⁵⁰ VCCs and VCDs were calculated using our in-house codes.
Evaluation of the stabilities of bisPyTM, PyBTM and TIPS pentacene under UV light

A solution (ca. 5 × 10⁻⁶ M, 1.0 mL) in a 1 cm optical path length quartz cell was bubbled with argon, sealed, and set in a JASCO FP8600 spectrometer. The intensity of luminescence at 650 and 585 nm was monitored, exciting with 355 and 370 nm light (the excitation slit was 20 nm, and the shutter control was off), for bisPyTM and PyBTM, respectively. For TIPS pentacene, the intensity of luminescence at 650 nm was monitored, exciting with 310 (in dichloromethane), 300 (in acetonitrile) and 330 (in acetone) nm light. The logarithm of fluorescence intensity versus time was plotted and the slope of an approximate line was estimated to be the rate of photolysis.

Synthesis

Synthesis of bis(3,5-dichloro-4-pyridyl)(1,3,5-trichlorophenyl) methane (zH-bisPyTM): under an argon atmosphere, a mixture of bis(3,5-dichloro-4-pyridyl)methanol ¹ (7.78 g, 24.0 mmol), 1,3,5-trichlorobenzene (96.4 g, 382 mmol) and aluminum chloride (31.98 g, 240 mmol) was heated to 300 °C for 10 min via microwave irradiation. The resulting dark-brown mixture was cooled to room temperature, dissolved in CH₂Cl₂ and added to ice water. The mixture was neutralized using aqueous NaHCO₃ and the organic layer was separated. The water layer was extracted with CH₂Cl₂ (3 times). The organic layers were combined, dried with Na₂SO₄, and evaporated. The crude product was purified via silica gel column chromatography (eluent: ethyl acetate/hexane = 1/4, v/v) and recrystallization from CH₂Cl₂/hexane. Preparative GPC yielded the pure product as a pale yellow solid (96 mg, 1%). The steric hindrance of methylene carbon atoms, instability of the reaction intermediate (methyl cation) and lowered electron densities of pyridine rings upon coordination to aluminum chloride can cause this low yield. The major product is bis(3,5-dichloro-4-pyridyl)methane, which would be produced by the decomposition of the starting material due to the severe reaction temperature, whereas the target compound was not formed at lower reaction temperatures. ³¹H NMR (CDCl₃, 300 MHz): δ = 6.70 (s, 1H), 7.28 (d, 1H, J = 2.5 Hz), 7.41 (d, 1H, J = 2.5 Hz), 8.37 (s, 1H), 8.40 (s, 1H), 8.51 (s, 1H), 8.52 (s, 1H). GC-MS: m/z = 486 ([C₁₇H₁₁Cl₇N₂⁺]). Elem. anal. calcld for C₁₇H₆Cl₇N₂: C 41.89, H 1.80, N 5.75; found: C 41.67, H 1.80, N 5.67.

Synthesis of the bis(3,5-dichloro-4-pyridyl)(1,3,5-trichlorophenyl)methyl radical (bisPyTM): under a nitrogen atmosphere, zH-bisPyTM (31.0 mg, 63.8 μmol) was dissolved in dry THF (3.0 mL). A 1 M solution of tBuOK in THF (130 μL) was added dropwise, and the color of the solution changed to red. The reaction mixture was stirred overnight in the dark. I₂ (121 mg, 476 μmol) in dry diethyl ether (10.8 mL) was added dropwise and stirred for 2.25 h. The remaining I₂ was reduced by washing withaq. 10% Na₂S₂O₅ 3 times. The water layer was extracted with diethyl ether once, and the combined organic layer was dried with Na₂SO₄. The red solution was filtered, evaporated, purified via Al₂O₃ column chromatography (eluent: diethyl ether/hexane = 1/4, v/v) and dried in vacuo to afford bisPyTM (28.1 mg, 91%) as a red solid. HRMS (negative ion mode ESI-TOF) m/z: [M]⁻. Caled for C₁₇H₁₁Cl₇N₂: 484.8322; found 484.8303. Elem. anal. calcld for C₁₇H₁₁Cl₇N₂: C 41.98, H 1.24, N 5.76; found: C 41.73, H 1.83, N 5.31. ESR: the spin concentration of bisPyTM in toluene (1.2 × 10⁻⁵ M) was estimated by comparing the value of the twice-integration of the signal intensity with that of a reference sample (4-hydroxy-TEMPO in toluene; 1.5 × 10⁻⁵ M). The existence of S = 1/2 spin on one bisPyTM molecule was confirmed.

Conflicts of interest

There are no conflicts to declare.

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Notes and references


