Volume 57 Number 14 18 February 2021 Pages 1683-1828

ChemComm

Chemical Communications



ISSN 1359-7345



COMMUNICATION Shuzo Hirata *et al.* Chiral approach to investigate mechanism of highly efficient thermally activated delayed fluorescence

ChemComm

COMMUNICATION

Check for updates

Cite this: Chem. Commun., 2021, 57, 1738

Received 11th December 2020, Accepted 18th January 2021

DOI: 10.1039/d0cc08064k

rsc.li/chemcomm

Chiral approach to investigate mechanism of highly efficient thermally activated delayed fluorescence[†]

Kikuya Hayashi,^a Arimasa Matsumoto^b and Shuzo Hirata 吵 *^a

Published on 21 January 2021. Downloaded by RUTGERS STATE UNIVERSITY on 5/15/2021 7:19:49 AM.

A chiral chromophore with thermally activated delayed fluorescence characteristics is designed. A model describing vibrations of the dihedral angle between donor and acceptor units allowed at room temperature explains the enhanced fluorescence rate of the molecule, including a nearly 100% photoluminescence quantum yield and the absence of circularly polarized emission characteristics from enantiomers of the chromophore.

Chromophores that undergo thermally activated delayed fluorescence (TADF) can harvest electronically generated triplet energy as delayed fluorescence *via* reverse intersystem crossing (RISC) from the lowest triplet excited state (T₁) to the lowest singlet excited state (S₁).^{1,2} Because this mechanism allows for 100% conversion of electrons to photons, chromophores with efficient TADF characteristics are candidate emitters for display and lighting applications. To obtain efficient and rapid RISC processes, the energy difference between S₁ and T₁ (ΔE_{ST}) should be minimized by ensuring separation of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO).

Density functional theory (DFT) is often used to predict and screen for molecules that have a small $\Delta E_{\rm ST}$ suitable for TADF processes. Recently reported TADF emitters have a fast delayed fluorescence lifetime that suppresses roll-off problems and gives a high electron-photon conversion efficiency.³⁻¹¹ Among some of these molecules, several have dihedral angles between the donating unit and acceptor unit (θ) of approximately 90 degrees according to DFT calculations.^{3-9,12} Because $\theta \approx$ 90 degree, the oscillator strength for fluorescence ($f_{\rm f}$) is expected to be zero. However, the optically observed $f_{\rm f}$ is often much larger than that calculated for chromophores. Artificial intelligence (AI) methods have been used to rapidly predict $f_{\rm f}$ and $\Delta E_{\rm ST}$ in screening for suitable TADF molecules.¹³ However, molecules that have $f_{\rm f} = 0$ are not typically considered to have potential as state-of-the-art TADF emitters. Therefore, there is a need to clarify the mechanism by which $f_{\rm f}$ is enhanced to improve AI screening methods. To date, chromophores with a variety of fixed θ values in solid semiconductor hosts have been identified as potential candidates to offer insights into this phenomenon.¹² However, analysis based on a combination of theoretical and experimental approaches may better highlight the mechanism of enhancement and guide the optimization of AI methods used to screen for TADF emitters.

Herein, we report a chemical approach to explain the difference in between calculated and optically measured oscillator strengths in a fluorescence based on a chiral charge transfer (CT) chromophore. We designed a chiral chromophore with θ of 90° based on time-dependent DFT (TD-DFT). The chromophore had an emission yield of nearly 100% in an appropriate semiconductor host. The $f_{\rm f}$ value of the chromophore observed for optical measurements was 0.018. However, $f_{\rm f}$ of the chromophore was <0.0001 based on a structure optimized at S1. Enantiomers of the chromophore did not have circularly polarized luminescence (CPL) in the optical measurement. A theoretical analysis based on varying θ of the chiral chromophore from the central value of 90° suggested that the CPL of the enantiomers of the chromophore was cancelled out by vibrations of θ . The vibrations of θ also explained the much larger optically observed $f_{\rm f}$ value than that calculated based on the optimized S₁ geometry.

Enantiomers of 10,10'-bis[4-(4,6-diphenyl-1,3,5-triazin-2-yl) phenyl]-2,2'-dimethyl-10*H*,10'*H*-9,9'-spirobi[acridine] (1) (Fig. 1a) consisting of a 2,2'-dimethyl-10*H*,10'*H*-9,9'-spirobi[acridine] (1d) moiety with chiral carbon as a donating unit and a 2-(4-bromophenyl)-4,6-diphenyl-1,3,5-triazine as an acceptor unit were synthesized (see Fig. S1–S15, ESI†).¹⁴ DFT calculations suggested that 1 has $\theta \approx 90^{\circ}$ in the optimized ground state (S₀) (Fig. 1b) and electron transfer between HOMO and LUMO is related to an S₀–S₁ transition of the S₀ geometry. Because the HOMO and



View Article Online View Journal | View Issue

^a Department of Engineering Science, The University of Electro-Communications,

¹⁻⁵⁻¹ Chofugaoka, Chofu, Tokyo 182-8585, Japan. E-mail: shuzohirata@uec.ac.jp ^b Department of Chemistry, Biology, and Environmental Science, Nara Women's

University, Kita-Uoya, Nishi-machi, Nara 630-8506, Japan † Electronic supplementary information (ESI) available. See DOI: 10.1039/

docc08064k



Fig. 1 (a) Chemical structure of **1** and **1d**. * indicates a chiral carbon. (b) Illustration indicating θ in (S)-**1** (left) and view form right side of the illustration (right). (c) Absorption (blue) and fluorescence (green) spectra of **1** (1.0×10^{-4} M) in toluene. Inset A represents the HOMO and LUMO at the S₀ geometry. Inset B shows the HOMO and LUMO at the optimized S₁ geometry. (d) Transient photoluminescence decay characteristics of **1** (10 wt%) doped in 1,3-bis(carbazol-9-yl)benzene (mCP) and **1** (1.0×10^{-4} M) in toluene (inset). Inset represents a photograph showing emission of **1** (10 wt%) doped in mCP under 365 nm ultraviolet irradiation.

LUMO are localized at the donor and the acceptor units (Fig. 1c, inset A), respectively, the absorption and emission characteristics of **1** should have CT characteristics.

Indeed, **1** had broad and weak absorption at the first absorption band and a broad fluorescence spectrum in toluene. The absorption spectrum of the first absorption band of **1** is located in the range of 360–480 nm and the molar absorption coefficient (ε) at the peak of the first absorption band was 4.8 × 10³ M⁻¹ cm⁻¹ (Fig. 1c), indicating the strong CT nature. Additionally, **1** had a broad fluorescence spectrum. The separation of the HOMO and LUMO in the optimized S₁ structure (Fig. 1c, inset B) also explains the broad spectrum. TD-DFT calculations estimated $\Delta E_{\rm ST}$ of **1** to be 6.1 meV owing to the large separation between the HOMO and LUMO. Because of the small $\Delta E_{\rm ST}$ value, we expected **1** to show TADF.

Chromophore 1 had highly efficient TADF in mCP as an amorphous semiconductor host with a large T_1 - S_0 energy. The prompt fluorescence lifetime (τ_f) of **1** was 14 ns in toluene (Fig. 1d, top), and the fluorescence quantum yield (Φ_f) was 24%. The rate constant of fluorescence ($k_{\rm f}$) of **1** was 1.6 \times 10⁷ s⁻¹ based on $k_f = \Phi_f \tau_f^{-1.3}$ The value of f_f was determined to be 0.018 by substituting the $k_{\rm f}$ value into $k_{\rm f} = 2.88 \times 10^{-9} n^2 \nu_{\rm max}^2 \left[\varepsilon'(\nu) d\nu \right]$ and $f = 4.32 \times 10^{-9} n^{-1} \left[\varepsilon'(\nu) d\nu \right]$ in toluene solution, where *n* is the refractive index of toluene, ν_{max} is the wavenumber at the fluorescence peak, and $\varepsilon'(\nu)$ is the molar absorption coefficient of the S₁ geometry at ν .¹⁵ In mCP, however, chromophore **1** not only showed prompt fluorescence but also delayed fluorescence. The lifetimes of prompt fluorescence (τ_{pf}) and delayed fluorescence (τ_{df}) were 39 ns and 5.5 µs, respectively (Fig. 1d, bottom). The photoluminescence quantum yield ($\Phi_{\rm PL}$) of 1 doped in mCP was 94% at room temperature (RT) (Fig. 1d, insert photo). The yield of the prompt fluorescence (Φ_{pf}) and the yields of the delayed fluorescence ($\Phi_{\rm df}$) were 48 and 46% at RT, respectively, indicating that most of the emission is associated with delayed fluorescence. Comparable shapes of the fluorescence spectrum at RT and the phosphorescence spectrum at 77 K were observed for 1 doped in mCP, suggesting that $\Delta E_{\rm ST}$ was approximately 0.01 eV from the difference of the onset energy between the fluorescence and phosphorescence spectra (Fig. S16, ESI[†]). The small value of ΔE_{ST} suggests that the delayed fluorescence component is caused by TADF. In mCP, the $k_{\rm f}$ value of 1 was determined to be $1.2 \times 10^7 {\rm s}^{-1}$ by substituting the values of $\Phi_{\rm pf}$ and $\tau_{\rm pf}$ into $k_{\rm f} = \varphi_{\rm pf} \tau_{\rm pf}^{-1.3}$ The value of $f_{\rm f}$ was estimated as 0.0080–0.0095 by substituting the value of $k_{\rm f}$ into $k_{\rm f} = 2.88 \times 10^{-9} n^2 \nu_{\rm max}^2 \int \varepsilon'(\nu) d\nu$ and $f = 4.32 \times 10^{-9} n^{-1} \left[\varepsilon'(\nu) d\nu \right]$ in toluene solution (Table 1),¹⁵ where n of mCP is assumed to be 1.7–1.8, which is a typical range for carbazole derivatives.¹⁶ The value of **1** in mCP was slightly smaller than that in toluene but both values were the same order of magnitude. However, $f_{\rm f}$ calculated by TD-DFT at the S₁ geometry was 0.0000. Thus, the optically determined value of $f_{\rm f}$ for 1 was at least >100 times greater than that calculated by TD-DFT.

Table 1Summary of optical and theoretical properties of 1. Concentration of 1 in toluene is 1.0×10^{-4} M. Concentration of 1 in mCP is 10 wt%.Theoretical values are calculated at S1 geometry

Matrices	Experimental					Calculation	
	$arPhi_{ m pf}$ (%)	$arPhi_{ m df}$ (%)	$\tau_{\rm pf}$ (ns)	$\Delta E_{ m ST}$ (eV)	f_{f}	$\Delta E_{\rm ST}$ (eV)	$f_{ m f}$
Toluene mCP	24 48	46	14 39	 0.010	0.018 0.0095	0.0061	0.0000

To investigate this large difference, we estimated the dependence of $f_{\rm f}$ on θ . The S₁ geometry of **1** was the most stable at θ = 89.9°. The energy change from the optimized S₁ state *versus* $\theta(E)$ was calculated [Fig. 2a, blue plots in (i)]. The values of E were used to estimate the probability of the chromophore depending on θ at the potential curve of S₁ (P) based on the Boltzmann distribution [Fig. 2a, green plots in (i)]. The dependence of f_f on θ was also calculated [Fig. 2a, orange plots in (ii)]. Finally, a multiple of *P* and f_f depending on θ was determined to estimate the average value of $f_{\rm f}$ based on vibrations of θ that are allowed at RT [Fig. 2a, red plots in (ii)]. As θ deviated from 90°, P decreased because of the increase of E. The value of $f_{\rm f}$ increased as θ deviated from 90°. At θ = 90°, the electron density at the donor cannot interact with that at the acceptor because of the two orthogonal electronic structures, resulting in no coupling between the HOMO and LUMO [Fig. 2b, (ii)]. However, for $\theta = 70^{\circ}$ and $\theta = 110^{\circ}$, the electron density at the donor can interact with that at the acceptor, forming overlap between the HOMO and LUMO [Fig. 2b, (i) and (iii)]. The overlap increases when θ deviates from 90°, resulting in an increase of f_f [Fig. 2a, orange plots in (ii)].

We assume that θ vibrates around the center of 90° according to a Boltzmann distribution (Fig. 3a, model 1). The average value of $f_f(\langle f_f \rangle)$ was determined by integrating $f_f P$ over θ . Thus, the determined $\langle f_f \rangle = 0.0182$ was comparable to the optically



Fig. 2 Calculated photophysical parameters and molecular orbitals dependence on θ for **1**. θ was varied without changing other bond lengths and angles between atoms in the S₁ geometry. (a) (i) *E vs.* θ plots (blue) and *P vs.* θ plots (green). (ii) f_f vs. θ plots (orange) and $f_f P$ vs. θ plots (red). (b) HOMO and LUMO for **1** at different θ . (i) $\theta = 70^\circ$, (ii) $\theta = 90^\circ$, (iii) $\theta = 110^\circ$. Inset illustrates views from left side of the chromophore.



Fig. 3 (a) Comparison of calculated and optically measured values of $f_{\rm f}$ and $|g_{\rm lum}|$ for models 1–3 of **1** are summarized in the calculation. (b) CD (top) and absorption (bottom) spectra of the enantiomers of **1** and the enantiomers of **1d** in toluene. Concentration of **1** and **1d** is 3.0×10^{-5} M and 1.0×10^{-4} M, respectively. (c) CPL (top) and fluorescence (bottom) spectra of the enantiomers of 2.0 × 10 M⁻⁴ M **1** in toluene. (d) $g_{\rm lum}$ vs. θ plots (top) and $g_{\rm lum}P$ vs. θ plots (bottom). In (a and d), θ was changed as explained in the caption of Fig. 2.

measured $f_{\rm f}$. However, the optically measured $f_{\rm f}$ with a magnitude of 10^{-2} might also be explained by the following two models (Fig. 3a, models 2 and 3). Molecules of chromophore 1 have a distribution of fixed θ values based on the Boltzmann distribution (Fig. 2a). When dispersed in mCP without vibration (Fig. 3a, model 2), a value of $\langle f_f \rangle = 0.0182$ would also result. Chromophores with θ values approaching 90° are not expected to emit because of their negligibly small $f_{\rm f}$, however, the optically observed large Φ_{PL} (94%) precludes this possibility. In addition, the existence of a variety of $f_{\rm f}$ values should lead to a wide distribution of decay characteristics for the prompt and delayed fluorescence features; however, no such features were observed. Alternatively, the large $f_{\rm f}$ value might be explained by chromophores with a specific θ allowing for a large $f_{\rm f}$ value when dispersed in mCP without any vibrations (Fig. 3c, model 3). The feasibility of this model may be confirmed by analysis of the CPL characteristics, as follows.

Indeed, analyses of the circular dichroism (CD) and CPL characteristics from experimental and theoretical viewpoints supports the existence of such vibrations. The predicated CD characteristics of enantiomers of 1 and racemic 1d are represented in Fig. 3b. However, no distinct CD characteristics of enantiomers of 1 were observed in the range of 370-450 nm as the first absorption band but were observed in the range of 300-350 nm. In addition, a comparable Cotton effect of the CD characteristics in the range of 300-350 nm was observed in enantiomers of 1d. Therefore, the CD characteristics of the enantiomers of 1 are attributed to electronic transitions of the donating unit of the compound. Thus, the CT transition characteristics of 1 induced a negligible Cotton effect on the CD characteristics of the first absorption band. A distinct Cotton effect was also absent from the CPL characteristics (Fig. 3c) because the CPL is also caused by a CT transition. The absolute value of the dissymmetry factor of CPL $(|g_{lum}|)$,¹⁷ was at least less than 1.2 \times $10^{-4}.$ Despite the minimal CPL characteristics, the theoretical value of $|g_{lum}|$ when θ was fixed at 80° and 100° was estimated to be 3.2 \times 10 $^{-3}$ (Fig. 3a, model 3), which is much larger than the optically observed result. Therefore, the large different $|g_{lum}|$ between the optical measurement and the calculation confirms that model 3 does not describe the phenomenon. To investigate the possibility of model 1 in Fig. 3a, the relationship between g_{lum} and θ (Fig. 3d, top) was calculated based on TD-DFT (Section S2, ESI⁺). Chromophore **1** has negative and positive values for θ when θ is less than or greater than 90° , respectively. The average value of g_{lum} ($\langle g_{\text{lum}} \rangle$) was calculated as -6.5×10^{-6} from the integrated value of $g_{lum}P$ as a function of θ (Fig. 3d, bottom). This result explains the very small value of the optically measured $|g_{\text{lum}}|$ of **1**. The very small dissymmetry factor for S₀-S₁ transition was also calculated using S₀ geometry of 1 (Fig. S17, ESI[†]), which could be also explained by the no CD signal at first absorption band of enantiomers of 1 (Fig. 3b, top). Therefore, only model of symmetrically vibration at the center of $\theta = 90^{\circ}$ (Fig. 3a, model 1) well expresses the comparable values regarding $f_{\rm f}$ and $g_{\rm lum}$ between optically and calculated results. The large value of $f_{\rm f}$ and no detectable small value of g_{lum} have been observed from 1 doped into mCP (Fig. S18, ESI^{\dagger}). Therefore, the vibrations of θ for orthogonal donor-acceptor structure trigger the increase of the oscillator strength for fluorescence which is a driving force of highly efficient delayed fluorescence.

To date, research on TADF with chiral structures has focused on generation of CPL characteristics.¹⁸ In this report, by considering chiral structures we examined the reason for the highly efficient TADF. Chromophore 1 doped into mCP had a nearly 100% photoluminescence yield and efficient TADF. The $f_{\rm f}$ value of the chromophore doped into mCP was 0.0080-0.0095. However, $f_{\rm f}$ calculated based on the optimized S₁ geometry was less than 0.0001. A comparison of g_{lum} between the optically observed and calculated results indicates that θ of **1** vibrates around its central value of 90° in solution and doped films. The vibrations also explained the large $f_{\rm f}$ enhancement of 1 in solution and doped film conditions. High-throughput virtual

screening based on a consideration of $f_{\rm f}$ and the lifetime of the delayed fluorescence has been started. It is likely that potentially effective orthogonal donor-acceptor structures have been disregarded as state-of-the-art chromophores because their $f_{\rm f}$ values have been determined from optimized structures that considerably underestimate f_f . Therefore, although it is computationally intensive, estimations of $f_{\rm f}$ should incorporate the vibrational point clearly induces a large change of the overlap between the HOMO and LUMO. Algorithms to reduce the cost of these vibrational calculations will be important in the prediction of state-of-the-art chromophores for highly efficient TADF materials, suitable for display and lighting technologies.

We acknowledge support through a Grant-in-aid from the Leading Initiative for Excellent Young Researchers (LEADER) program from the Japan Society for the Promotion of Science (JSPS) and JSPS KAKENHI (Grant Numbers JP18H02046, JP18H04507, and JP20H04664).

Conflicts of interest

There are no conflicts to declare.

Notes and references

- 1 H. Uoyama, K. Goushi, K. Shizu, H. Nomura and C. Adachi, Nature, 2012, 492, 234-238.
- 2 A. Endo, K. Sato, K. Yoshimura, T. Kai, A. Kawada, H. Miyazaki and C. Adachi, Appl. Phys. Lett., 2011, 98, 083302.
- 3 Q. Zhang, B. Li, S. Huang, H. Nomura, H. Tanaka and C. Adachi, Nat. Photonics, 2014, 8, 326-332.
- 4 W. Tsai, M. Huang, W. Lee, Y. Hsu, K. Pan, Y. Huang, H. Ting, M. Sarma, Y. Ho, H. Hu, C. Chen, M. Lee, K. Wong and C. Wu, Chem. Commun., 2015, 51, 13662-13665.
- 5 M. Liu, R. Komatsu, X. Cai, K. Hotta, S. Sato, K. Liu, D. Chen, Y. Kato, H. Sasabe, S. Ohisa, Y. Suzuri, D. Yokoyama, S. Su and J. Kido, Chem. Mater., 2017, 29, 8630-8636.
- 6 W. Zeng, H. Lai, W. Lee, M. Jiao, Y. Shiu, C. Zhong, S. Gong, T. Zhou, G. Xie, M. Sarma, K. Wong, C. Wu and C. Yang, Adv. Mater., 2018, 30. 201704961.
- 7 I. S. Park, K. Matsuo, N. Aizawa and T. Yasuda, Adv. Funct. Mater., 2018, 28, 1802031.
- 8 Z. Chen, F. Ni, Z. Wu, Y. Hou, C. Zhong, M. Huang, G. Xie, D. Ma and C. Yang, J. Phys. Chem. Lett., 2019, 10, 2669-2675.
- 9 S. Kothavale, W. J. Chung and J. Y. Lee, ACS Appl. Mater. Interfaces, 2020, 12, 18730-18738.
- 10 J. U. Kim, I. S. Park, C.-Y. Chan, M. Tanaka, Y. Tsuchiya, H. Nakanotani and C. Adachi, Nat. Commun., 2020, 11, 1765.
- 11 Y. Wada, H. Nakagawa, S. Matsumoto, Y. Wakisaka and H. Kaji, Nat. Photonics, 2020, 14, 643-649.
- 12 S. Weissenseel, N. A. Drigo, L. G. Kudriashova, M. Schmid, T. Morgenstern, K.-H. Lin, A. Prlj, C. Corminboeuf, A. Sperlich, W. Brutting, M. K. Nazeeruddin and V. Dyakonov, J. Phys. Chem. C, 2019, 123, 27778-27784.
- 13 R. Gomez-Bombarelli, J. Aguilera-Iparraguirre, T. D. Hirzel, D. Duvenaud, D. Maclaurin, M. A. Blood-Forsythe, H. S. Chae, M. Einzinger, D. Ha, T. Wu, G. Markopoulos, S. Jeon, H. kang, H. Miyazaki, M. Numata, S. Kim, W. Huang, S. I. Hong, M. Baldo, R. P. Adams and A. Aspuru-Guzik, Nat. Mater., 2016, 15, 1120-1127.
- 14 M. Ooishi, M. Seino, R. Imachi, T. Ishida and T. Nogami, Tetrahedron Lett., 2002, 43, 5521-5524.
- 15 S. J. Strickler and R. A. Berg, J. Chem. Phys., 1962, 37, 814-822. 16 A. Salehi, Y. Chen, X. Fu, C. Peng and F. So, ACS Appl. Mater. Interfaces, 2018, 10, 9595-9601.
- 17 F. S. Richardson, Inorg. Chem., 1980, 19, 2806-2812.
- 18 Z. Wu, H. Han, Z. Yan, X. Luo, Y. Wang, Y. Zheng, J. Zuo and Y. Pan, Adv. Mater., 2019, 31, 1900524.