Conjugation

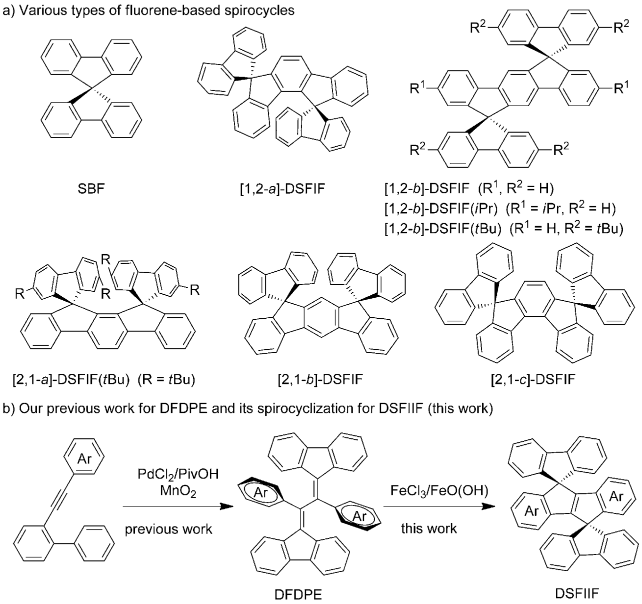
Deutsche Ausgabe: DOI: 10.1002/ange.201507794
Internationale Ausgabe: DOI: 10.1002/anie.201507794

$FeCl_3$-Mediated Oxidative Spirocyclization of Difluorenylidene Diarylethanes Leading to Dispiro[fluorene-9,5′-indeno[2,1-*a*]indene-10′,9′′-fluorene]s

*Jian Zhao, Zhanqiang Xu, Kazuaki Oniwa, Naoki Asao, Yoshinori Yamamoto, and Tienan Jin**

Abstract: *A novel $FeCl_3$-mediated oxidative spirocyclization for construction of a new class of di-spirolinked π-conjugated molecules, dispiro[fluorene-9,5′-indeno[2,1-a]indene-10′,9′′-fluorene]s (DSFIIFs), has been reported. The combination of $FeCl_3$ with FeO(OH) triggered an unprecedented double one-electron oxidation of difluorenylidene diarylethanes to afford the corresponding dispirocycles in high yields. The highest fluorescence quantum yield was up to 0.94 in solution. This protocol is also applicable to the synthesis of the non-spirolinked dihydroindenoindenes.*

Fluorene-based π-conjugated spirocycles have attracted attention as important optoelectronic materials in various fields of organic electronics because of their unique structural features.[1–14] As common features of π-conjugated spirocycles, the high rigidity of spiromolecules efficiently minimizes the electronic interactions between the π-systems and offers high solubility, high thermal and morphological stability, and intense fluorescence properties, without significantly changing their absorption and fluorescence spectra compared with the corresponding non-spirolinked parent compounds. In this context, many structural modifications have been made based on the spirobifluorene (SBF) unit in attempts to study the hole-transporting and light-emitting performances in various electronics (Scheme 1 a).[1–10] In addition, several positional isomers of di-spirofluorene indenofluorenes (DSFIFs), combining both di-hydroindenofluorene and fluorene units, have also been reported for high-performance organic light-emitting diodes (OLEDs).[11–16] For example, the [1,2-*a*], [1,2-*b*], and [2,1-*c*] isomers were used as hosts in blue and green phosphorescent OLEDs, the [2,1-*b*] and [1,2-*a*] isomers were used as efficient blue fluorophores, and the [2,1-*a*] isomer was used as an emitting layer for an excimer-based OLED (Scheme 1 a). Taking into consideration the prominent role of the spirolinked π-systems in organic electronics, the discovery of a novel class of spirocycles is highly challenging from the perspective of the structural diversity and the future of organic electronics.



Scheme 1. Reported fluorene-based spirocycles and our novel method for constructing a new class of dispirocycle DSFIIFs.

Very recently, we developed an interesting synthetic approach for constructing 9,9-bifluorenylidene (9,9′BF) and 1,2-di(9*H*-fluoren-9-ylidene)-1,2-diphenylethane (DFDPE; Scheme 1 b) units from the corresponding bis(biaryl) alkynes or biaryl alkynes through a novel palladium-catalyzed dual $C(sp^2)-H$ bond activation.[17] The facile synthetic method and the structurally intriguing DFDPE, having all sp^2-hybridized carbon atoms, led us to explore a new C–H oxidation reaction for constructing new π-conjugated fused systems. Recently, the 5,10-dihydro-[2,1,*a*]-indenoindene (DII) core, having aromatic 14π electrons, has been reported as a new class of chromophores in OLEDs to show high hole mobility and high sky-blue fluorescence.[18–21] However, to the best of our knowledge, the di-spirolinked indenoindenes, such as dispiro-[fluorene-9,5′-indeno[2,1-*a*]indene-10′,9′′-fluorene] (DSFIIF; Scheme 1 b), have not yet been reported, presumably owing to synthetic difficulties. Herein, we report a novel and highly efficient $FeCl_3$-mediated oxidative spirocyclization of DFDPEs towards the synthesis of a new class of di-spirolinked π-systems, that is, DSFIIFs (Scheme 1 b).

As stated in Scheme 1 b, DFDPEs were synthesized efficiently through our previously reported palladium-catalyzed C–H activation of biaryl alkynes.[17] In the presence of

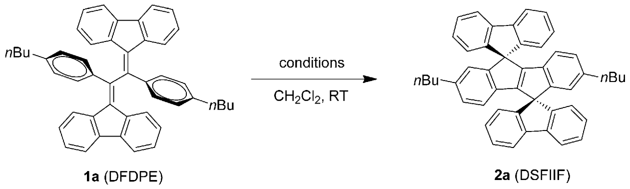
---

[*] Dr. J. Zhao, Z. Xu, Dr. K. Oniwa, Prof. N. Asao, Prof. Y. Yamamoto, Prof. T. Jin
WPI-Advanced Institute for Materials Research (WPI-AIMR)
Tohoku University
2-1-1, Aoba-ku Katahira, Sendai 980-8577 (Japan)
E-mail: tjin@m.tohoku.ac.jp
Prof. Y. Yamamoto
State Key Laboratory of Fine Chemicals and School of Chemistry, Dalian University of Technology
Dalian 116023 (China)

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201507794.

$PdCl_2$ (10 mol%), PivOH (10 mol%), and MnO_2 (3 equiv), various biaryl alkynes afforded the corresponding DFDPEs having a variety of functional groups on either the diphenyl or difluorenylidene moiety in good to high yields (see the Supporting Information). With these structurally intriguing molecules in hand, we examined many different oxidants and acids using the DFDPE **1a** as a substrate in dichloromethane at room temperature (Table 1). Interestingly, when the Lewis-acidic oxidant of anhydrous $FeCl_3$ (3 equiv) was used, a novel dispirocycle (**2a**) was formed in 58% yield along with decomposition of **1a** (entry 1). The structure of **2a** was confirmed unambiguously by X-ray crystallography analysis (Figure 1). In the crystal structure, the central indeno[2,1-*a*]-indene core is perfectly flat, and is nearly perpendicular to the two parallel two fluorene moieties having a dihedral angle of 89.98°. $FeCl_3{\cdot}6\,H_2O$ proved to be more effective for achieving a higher yield of **2a** (entry 2). The non-acidic $K_3[Fe(CN)_6]$ oxidant was ineffective (entry 3). The strong acidic oxidant of $MoCl_5$ resulted in complete decomposition of **1a** (entry 4). The reaction in the presence of other oxidants, such as $CuCl_2$ and I_2, afforded **2a** in very poor yields (entries 5 and 6). The classical oxidant systems of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) and CF_3CO_2H (TFA) produced **2a** in a reasonable yield of 75% with partial decomposition of **1a** (entry 7), and the use of either DDQ or TFA alone did not promote the present spirocyclization. It was worth noting that the reaction with the non-oxidizing Lewis acid $AlCl_3$ led to decomposition of **1a** (entry 8). The distinct reactivity difference between $FeCl_3$ and $AlCl_3$ implies that the present spirocyclization seems to undergo a well-known one-electron oxidation.[22] After screening various additives, **2a** was achieved in an excellent 99% yield when $FeCl_3{\cdot}6H_2O$ (1.5 equiv) was combined with either Fe_2O_3 (0.5 equiv) or FeO(OH) (1 equiv); the combination with FeO(OH) was more reactive (entries 9 and 10). In contrast, the use of bases, such as K_2CO_3 suppressed the effective spirocyclization (entry 11). We assumed that the effect of ferric oxide should be to regenerate the active $FeCl_3$ oxidant by the reaction with HCl generated in situ. It was noted that although $FeCl_3{\cdot}6\,H_2O$ could serve as the catalyst in this reaction, the catalytic reproducibility was not satisfactory. Consequently, the most effective oxidant systems of $FeCl_3{\cdot}6\,H_2O$ (1.5 equiv) and FeO(OH) (1 equiv) were chosen as optimal reaction conditions for investigating the substrate scope of various DFDPEs.

Table 1: Investigation of reaction conditions of spirocyclization of DFDPE **1a**.[a]



Entry	Oxidant or acid	Additive	*t* [h]	Yield [%][b]	
				2a	**1a**
1	$FeCl_3$	–	1	58	0
2	$FeCl_3{\cdot}6\,H_2O$	–	2	78	5
3	$K_3[Fe(CN)_6]$	–	12	0	99
4	$MoCl_5$	–	12	0	0
5	$CuCl_2$	–	20	14	60
6	I_2	–	12	12	36
7[c]	DDQ	CF_3CO_2H	12	75	0
8	$AlCl_3$	–	12	0	0
9	$FeCl_3{\cdot}6\,H_2O$	Fe_2O_3	24	99	0
10[d]	$FeCl_3{\cdot}6\,H_2O$	FeO(OH)	12	99[e]	0
11[d]	$FeCl_3{\cdot}6\,H_2O$	K_2CO_3[f]	24	26	73

[a] Reaction conditions: **1a** (0.1 mmol), acid or oxidant (3 equiv), additive, CH_2Cl_2 (0.05 M), under dark conditions at room temperature. [b] Both yields were determined by ^1H NMR spectroscopy using CH_2Br_2 as an internal standard. [c] DDQ (2 equiv) and CF_3CO_2H (5 equiv) were used. [d] $FeCl_3{\cdot}6H_2O$ (1.5 equiv) and Fe_2O_3 (0.5 equiv) or FeO(OH) (1 equiv) were used. [e] Yield of isolated product is shown after silica gel chromatography. [f] K_2CO_3 (4 equiv) was used.

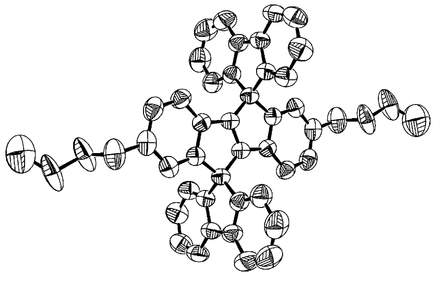
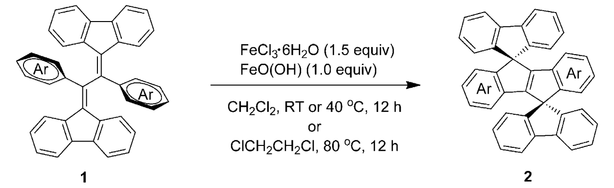
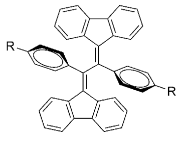
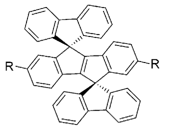
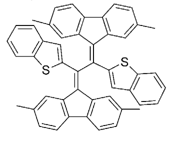
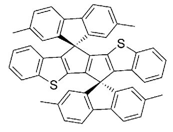
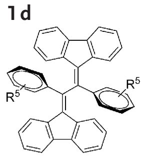
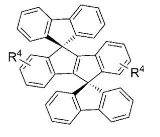
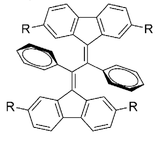
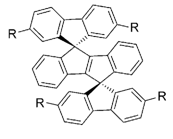
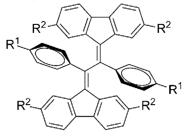
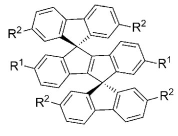


Figure 1. ORTEP drawing of the dispirocycle **2a**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at 50% probability.[25]

A variety of DFDPEs (**1**) having versatile functional groups were investigated under the optimized reaction conditions (Table 2). It was found that the electronic property of the phenyl ring significantly affected the reactivity of **1**. The reactions with **1a** and **1b**, having an electron-donating *n*-butyl and *tert*-butyl group, respectively, on the phenyl ring proceeded smoothly at room temperature to give the corresponding dispirocycles **2a** and **2b** in nearly quantitative yields. However, the reaction with **1c**, having a strong electron-donating methoxy group, required a higher temperature of 80°C, thus affording the corresponding product **2c** in 95% yield. Interestingly, **1d** with an electron-donating functional group, also underwent the present spirocyclization at room temperature to give the highly π-extended dispirocycle **2d** in 95% yield. Both the unsubstituted **1e** and **1f** were active at 40°C, thus affording the corresponding dispirocycles **2e** and **2f** in high yields within 12 hours, without being influenced by the protonated or deuterated phenyl group. The presence of the electron-donating groups on the fluorenyl moiety did not affect the reactivity of the DFDPEs. For example, **1g** and **1h**, having four methyl and four *tert*-butyl groups, respectively, on the fluorenyl moieties underwent the present spirocyclization at 40°C, thus leading to the formation of the dispirocycles **2g** and **2h**, respectively, in high yields. We found that the introduction of the electron-withdrawing groups, such as an ester (**1i**), CF_3 (**1j**), or Br (**1k** and **1l**), to the phenyl moiety of DFDPEs lowered the reaction efficiency at low temperatures, while the reaction at the elevated temperature of 80°C gave

Table 2: $FeCl_3$-mediated spirocyclization of various DFDPEs (**1**).[a]

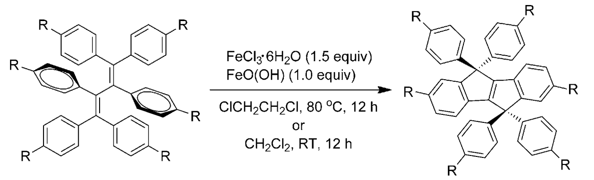


Entry	1	2
		
1	**1a**, R = *n*Bu	**2a**, 99 % (RT)
2	**1b**, R = *t*Bu	**2b**, 98 % (RT)
3	**1c**, R = OMe	**2c**, 95 % (80 °C)
		
4	**1d**	**2d**, 95 % (RT)
		
5	**1e**, R = H	**2e**, 95 % (40 °C)
6	**1f**, R = D	**2f**, 90 % (40 °C)
		
7	**1g**, R = Me	**2g**, 97 % (40 °C)
8	**1h**, R = *t*Bu	**2h**, 99 % (40 °C)
		
9	**1i**, $R^1 = CO_2Et$, $R^2 = H$	**2i**, 99 % (80 °C)
10	**1j**, $R^1 = CF_3$, $R^2 = H$	**2j**, 82 % (80 °C)
11	**1k**, $R^1 = Br$, $R^2 = H$	**2k**, 99 % (80 °C)
12	**1l**, $R^1 = Br$, $R^2 = Cl$	**2l**, 97 % (80 °C)

[a] Standard reaction conditions: **1** (0.1 mmol), $FeCl_3 \cdot 6H_2O$ (1.5 equiv), FeO(OH) (1.0 equiv), under dark conditions in CH_2Cl_2 at either RT or 40 °C, or in $ClCH_2CH_2Cl$ at 80 °C. Yields are those of the isolated products.

rise to the corresponding dispirocycles **2h–l** in good to excellent yields.

The present $FeCl_3$-mediated conditions have also proven effective for the non-fluorenyl-incorporated buta-1,3-dienes (Scheme 2). For example, the reaction of the multisubstituted diene **3a** led to the formation of the tetraphenyl-substituted 5,10-dihydroindeno[2,1-*a*]indene (DII) **4a** in 88 % yield at 80 °C, and was synthesized previously by multistep methods in low yields.[18,19] Similarly, the reaction of the multisubstituted diene **3b**, having electron-donating *p*-tolyl groups, reacted at room temperature to give the corresponding product **4b** in 99 % yield.



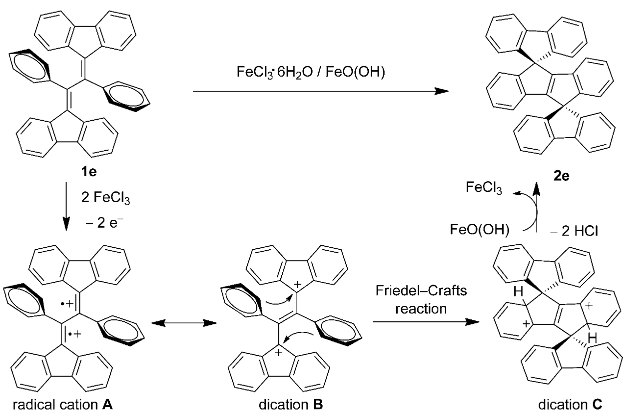
3a R = H
3b R = Me

4a, 88% (80 °C)
4b, 99% (RT)

Scheme 2. Synthesis of 5,10-dihydroindeno[2,1-*a*]indene.

Recently it has become clear that in the most oxidative aromatic couplings (Scholl type reaction) mediated by one-electron oxidants, such as $FeCl_3$ or DDQ, the oxidation could preferentially occur at the most electron-rich position to form radical cations.[22] Interestingly, the density functional theory (DFT) computational studies of the frontier molecular orbitals revealed that the highest occupied molecular orbitals (HOMOs) of the substrates **1a** and **3a** are more localized on the C=C bonds of the conjugated diene moiety rather than on the phenyl and fluorenyl moieties, thus indicating the highest electron density is on the diene moiety (see Figure S1 in the Supporting Information). These studies suggested that in the present spirocyclization, the C=C bond of the diene in DFDPEs should be oxidized preferably to form the radical cation species. In addition, the intermolecular competing reactions of the protonated **1e** and the deuterated **1f** under the standard reaction conditions for 2 hours, revealed that the kinetic isotope effect (KIE) was 1.14 (see Scheme S1), thus indicating that the C–H bond cleavage of the phenyl group was not the rate-determining step.

On the basis of the distinct activity of $FeCl_3$, electronic effects of substrates, and electron density distribution, we proposed a mechanism involving a one-electron oxidation reaction as shown in Scheme 3. $FeCl_3$ induces double one-electron oxidations of the two more-electron-rich C=C bonds of the diene moiety in **1e** to give the radical cation species **A**, which can exist as the dication intermediate **B**. It should be noted that the analogous dication having an I_3^- counteranion has been isolated and characterized by X-ray crystallography.[23] Subsequently, the double Friedel–Crafts reactions take place to form an arenium dication (**C**), which undergoes the rapid deprotonation by chloride anions to give the dispiro-



Scheme 3. Proposed reaction mechanism.

cycle **2e** and HCl. The DFT calculation shows that the HOMO of **B** is mainly localized in the central stilbene moiety, thus indicating the electron-donating nature of the phenyl rings, which are favorable for reacting with the cation electrophiles (see Figure S1). Either the FeO(OH) or Fe_2O_3 additive may react with HCl to supply the fresh $FeCl_3$ oxidant, thus suppressing the partial decomposition of **1e** by HCl, and it is crucial for achieving high yields of the dispirocycles.

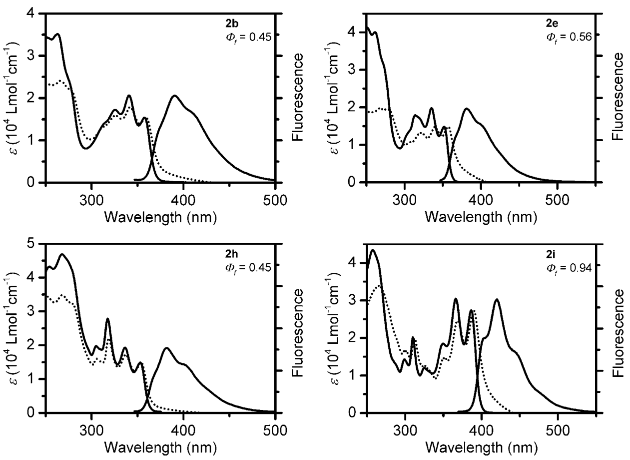


Figure 2. UV-vis spectra (left; solid line) and fluorescence spectra (right; solid line) of **2b**, **2e**, **2h**, and **2i** in chloroform solution. Normalized UV-vis absorption of spin-coated thin films on the quartz plates (dashed line) at room temperature. Φ_f = quantum yield.

The optical and electrochemical properties of the selected dispirocycles **2** are summarized in Table 3 and Figure 2 (see also Figures S2 and S3). The UV-vis absorption spectra of the nonsubstituted (**2e**) and *t*Bu-substituted (**2b** and **2h**) DSFIIFs exhibit bands of the central indeno[2,1-*a*]indene moiety in the range of $\lambda = 300$–360 nm in chloroform, and they are very similar to the [1,2-*b*]DSFIFs having similar substituents at the central dihydroindeno[1,2-*b*]fluorene moiety as reported by Poriel, Rault-Berthelot et al. (Scheme 1 a).[15,24] Thin-film absorption maxima of **2b**, **2e**, and **2h**, recorded on spin-coated films on the quartz plates, are slightly red-shifted compared to the corresponding solution absorption maxima, thus implying very weak intermolecular interactions in solid state. The photoluminescence spectra of the present DSFIIFs show Stock shifts of 15–17 nm, which are larger than that of [1,2-*b*]DSFIF analogues (2–3 nm),[15,24] thus indicating the reduced structural rigidity of the former. DSFIIFs exhibit the absolute fluorescence quantum yields of 0.45 for **2b**, 0.56 for **2e**, and 0.45 for **2h**, and are lower than the reported results of [1,2-*b*]DSFIFs (Scheme 1 a, 0.62–0.70). It is worth noting that the DSFIIF **2I**, having two electron-withdrawing ester groups at the central indeno[2,1-*a*]indene moiety, exhibits a red-shifted absorption and emission maxima compared to other DSFIIF derivatives. Interestingly, **2i** is highly fluorescent with the absolute quantum yield of 0.94 in $CHCl_3$, thus implying the distinct substituent effect of the ester group on the π-conjugated indeno[2,1-*a*]indene moiety. The HOMO energy levels of DSFIIFs were calculated from the oxidation potentials by cyclic voltammetry (CV) in CH_2Cl_2, and the lowest unoccupied molecular orbital (LUMO) energy levels were estimated from the optical bandgap and HOMOs. The HOMO energy levels of **2b**, having two electron-donating *tert*-butyl groups at the indeno[2,1-*a*]indene moiety is −5.49 eV, similar to the reported [2,1-*a*]DSFIF(*t*Bu) (−5.48 eV, Scheme 1a).[24] The nonsubstituted **2e** (−5.68 eV) and **2h** (5.62 eV), having four *tert*-butyl substituents at the fluorene moieties, exhibited slightly lower HOMOs than that of **2b**, and are similar to the reported values (−5.76 eV, −5.66 eV, 5.61 eV) of the three [1,2-*b*]DSFIF isomers (Scheme 1 a).[15,24] The LUMO energy levels of **2b**, **2e**, and **2h**, estimated to be in the range of −2.10 to −2.23 eV, are very near to the reported DSFIF series. **2i** shows both low HOMO and LUMO energy levels of −5.95 eV and −2.80 eV with a narrow energy bandgap of 3.15 eV resulting from the two electron-withdrawing ester groups at the indeno[2,1-*a*]indene moiety.

In conclusion, we have developed a novel and highly efficient $FeCl_3$-mediated oxidative spirocyclization of 1,2-di(9*H*-fluoren-9-ylidene)-1,2-diphenylethanes under mild reaction conditions. A new class of di-spirolinked indeno[2,1-*a*]indene π-conjugated systems having a wide range of functional groups have been synthesized in very high yields with the highest fluorescence quantum yield of 0.94 for the ester-substituted dispirocycle. The results led to the conclusion that the present mechanism involved two one-electron oxidations and a dication-induced Friedel–Crafts spirocyclization pathway. This protocol also can be applicable for the construction of non-spirolinked dihydroindenoindenes. The present method provides not only a novel and valuable spirocycle synthetic tool, but also a new type of spirolinked π-conjugated system which is expected to be highly applicable in the field of optoelectronics.

Table 3: Selected optical and electrochemical properties of DSFIIFs

DSFIIF	λ_{abs} [nm][a]	λ_{abs} [nm][b]	λ_{em} (λ_{exc}) [nm][c]	Φ_f[d]	E^{ox} [V][e]	ΔE^{opt} [eV][f]	HOMO [eV][g]	LUMO [eV][h]
2b	358, 341, 326, 263	359	390 (340)	0.45	0.91	−3.39	−5.49	−2.10
2e	352, 336, 315, 261	356	382 (320)	0.56	1.11	−3.45	−5.68	−2.23
2h	353, 336, 318, 305, 268, 254	353	382 (340)	0.45	1.04	−3.44	−5.62	−2.18
2i	386, 366, 350, 325, 310, 299	390	420 (340)	0.94	1.29	−3.15	−5.95	−2.80

[a] UV-vis absorptions were measured in chloroform. [b] UV-vis absorptions were measured using as-spun thin films on the quartz plates. [c] Fluorescence maxima were measured in chloroform. [d] Absolute fluorescence quantum yield (Φ_f) was measured by a photon-counting method using an integration sphere. [e] Oxidation potential (vs Ag/AgCl) was measured by cyclic voltammetry in CH_2Cl_2. [f] Optical bandgap (ΔE^{opt}) was estimated from the contact between the UV-vis absorption and the fluorescence spectra. [g] HOMO was calculated from the oxidation potential. [h] LUMO was calculated from the HOMO energy and the optical bandgap.

Experimental Section

General procedure of $FeCl_3$-mediated oxidative spirocyclization of **1a**. **1a** (0.1 mmol, 62 mg), $FeCl_3{\cdot}6\,H_2O$ (0.15 mmol, 40 mg), and FeO(OH) (0.1 mmol, 9 mg) were added to an anhydrous CH_2Cl_2 (2 mL, 0.05 M) solution. The reaction vial was capped. The reaction mixture was stirred vigorously at room temperature for 12 h. After monitoring by TLC, the reaction mixture was passed through a short silica (Merck) pad using CH_2Cl_2/hexanes as an eluent. After concentration, the residue was purified by silica gel (Merck) chromatography using a mixture of hexanes and CH_2Cl_2 [10:1 to 3:1 (v/v)] as the eluent to afford the product **2a** as a white solid (99 %, 61 mg).

Acknowledgements

This work was supported by Grants-in-Aid for Scientific Research (B) from Japan Society for Promotion of Science (JSPS) (No. 25288043), and World Premier International Research Center Initiative (WPI), MEXT, Japan.

Keywords: conjugation · fluorescence · materials science · oxidation · spirocompounds

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 259–263
Angew. Chem. **2016**, *128*, 267–271

---

[1] T. P. I. Saragi, T. Spehr, A. Siebert, T. F. Lieker, J. Salbeck, *Chem. Rev.* **2007**, *107*, 1011–1065.
[2] U. Bach, D. Lupo, P. Comte, J. E. Moser, F. Weissärtel, J. Salbeck, H. Spreitzer, M. Grätzel, *Nature* **1998**, *395*, 583–585.
[3] W. H. Nguyen, C. D. Bailie, E. L. Unger, M. D. McGehee, *J. Am. Chem. Soc.* **2014**, *136*, 10996–11001.
[4] C.-Y. Chan, Y.-C. Wong, M.-Y. Chan, S.-H. Cheung, S.-K. So, V. W.-W. Yam, *Chem. Mater.* **2014**, *26*, 6585–6594.
[5] Y. Li, Z. Wang, X. Li, G. Xie, D. Chen, Y.-F. Wang, C.-C. Lo, A. Lien, J. Peng, Y. Cao, S.-J. Su, *Chem. Mater.* **2015**, *27*, 1110–1119.
[6] J. Y. Kim, T. Yasuda, Y. S. Yang, N. Matsumoto, C. Adachi, *Chem. Commun.* **2014**, *50*, 1523–1526.
[7] Y.-L. Liao, W.-Y. Hung, T.-H. Hou, C.-Y. Lin, K.-T. Wong, *Chem. Mater.* **2007**, *19*, 6350–6357.
[8] A. Dualeh, T. Moehl, M. K. Nazeeruddin, M. Grätzel, *ACS Nano* **2013**, *7*, 2292–2301.
[9] H.-C. Ting, C.-H. Tsai, J.-H. Chen, L.-Y. Lin, S.-H. Chou, K.-T. Wong, T.-W. Huang, C.-C. Wu, *Org. Lett.* **2012**, *14*, 6338–6341.
[10] M. Kimura, S. Kuwano, Y. Sawaki, H. Fujikawa, K. Noda, Y. Taga, K. Takagi, *J. Mater. Chem.* **2005**, *15*, 2393–2398.
[11] M. Romain, S. Thiery, A. Shirinskaya, C. Declairieux, D. Tondelier, B. Geffroy, O. Jeannin, J. Rault-Berthelot, R. Métivier, C. Poriel, *Angew. Chem. Int. Ed.* **2015**, *54*, 1176–1180; *Angew. Chem.* **2015**, *127*, 1192–1196.
[12] M. Romain, D. Tondelier, J.-C. Vanel, B. Geffroy, O. Jeannin, J. Rault-Berthelot, R. Métivier, C. Poriel, *Angew. Chem. Int. Ed.* **2013**, *52*, 14147–14151; *Angew. Chem.* **2013**, *125*, 14397–14401.
[13] D. Thirion, M. Romain, J. Rault-Berthelot, C. Poriel, *J. Mater. Chem.* **2012**, *22*, 7149–7157.
[14] D. Thirion, C. Poriel, R. Métivier, J. Rault-Berthelot, F. Barrière, O. Jeannin, *Chem. Eur. J.* **2011**, *17*, 10272–10287.
[15] C. Poriel, J.-J. Liang, J. Rault-Berthelot, F. Barriére, N. Cocherel, A. M. Z. Slawin, D. Horhant, M. Virboul, G. Alcaraz, N. Audebrand, L. Vignau, N. Huby, G. Wantz, L. Hirsch, *Chem. Eur. J.* **2007**, *13*, 10055–10069.
[16] M. Romain, D. Tondelier, B. Geffroy, O. Jeannin, E. Jacques, J. Rault-Berthelot, C. Poriel, *Chem. Eur. J.* **2015**, *21*, 9426–9439.
[17] J. Zhao, N. Asao, Y. Yamamoto, T. Jin, *J. Am. Chem. Soc.* **2014**, *136*, 9540–9543.
[18] Y. Wei, W.-J. Wang, Y.-T. Huang, B.-C. Wang, W.-H. Chen, S.-H. Wu, C.-H. He, *J. Mater. Chem. C* **2014**, *2*, 1779–1782.
[19] Y. Wei, P.-J. Liu, R.-H. Lee, C.-P. Chen, *RSC Adv.* **2015**, *5*, 7897–7904.
[20] X. Zhu, C. Mitsui, H. Tsuji, E. Nakamura, *J. Am. Chem. Soc.* **2009**, *131*, 13596–13597.
[21] X. Zhu, H. Tsuji, J. L. N. Navarrete, J. Casado, E. Nakamura, *J. Am. Chem. Soc.* **2012**, *134*, 19254–19259.
[22] M. Grzybowski, K. Skonieczny, H. Butenschcön, D. T. Gryko, *Angew. Chem. Int. Ed.* **2013**, *52*, 9900–9930; *Angew. Chem.* **2013**, *125*, 10084–10115.
[23] T. Suzuki, H. Higuchi, M. Ohkita, T. Tsuji, *Chem. Commun.* **2001**, 1574–1575.
[24] C. Poriel, J. Rault-Berthelot, F. Barrière, A. M. Z. Slawin, *Org. Lett.* **2008**, *10*, 373–376.
[25] CCDC 1413747 (**2a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Received: August 20, 2015
Revised: September 21, 2015