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# Iridium-Catalyzed Direct C−H Amidation Producing Multicolor Fluorescent Molecules Emitting Blue-to-Red Light and White Light

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Cite This: https://dx.doi.org/10.1021/acs.orglett.0c00618 Read Online

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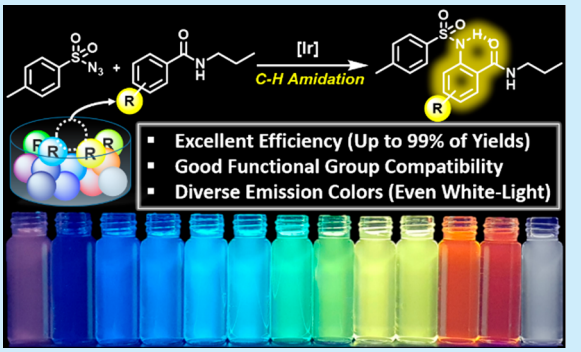
**ABSTRACT:** We report a powerful strategy, iridium-catalyzed direct C−H amidation (DCA) for synthesizing various fluorescent sulfonamides that emit light over the entire visible spectrum with excellent efficiency (up to 99% yields). By controlling electronic characters of the resulting sulfonamides, a wide range of blue-to-red emissions was predictably obtained via an excited-state intramolecular proton-transfer process. Furthermore, we even succeeded in a white-light generation, highlighting that this DCA is an excellent synthetic method to prepare a library of fluorophores.

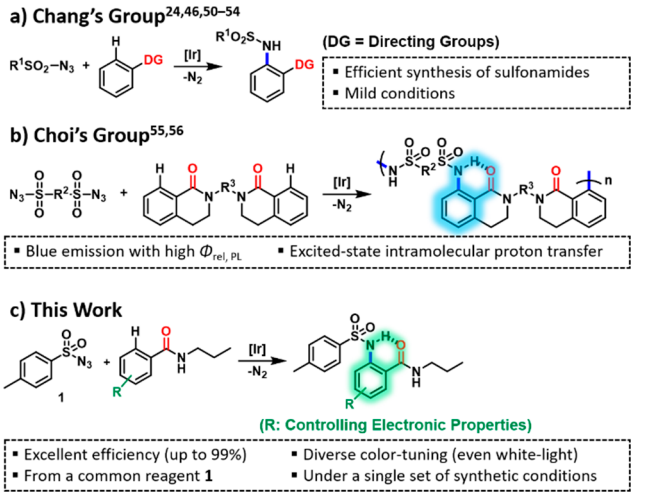





Over the past decades, multicolor fluorescent materials have received extensive attention, because of their potential applications in the next-generation lighting sources and displays,[1−8] as well as in optical imaging agents to decipher biological events.[9−17] To prepare multicolor fluorescent molecules, chemists have generally synthesized fluorophores from various precursors, or frequently, under different reaction conditions. Sometimes one must use even totally different synthetic pathways, because of a lack of versatility of synthetic scheme. Therefore, it is crucial to develop a versatile and efficient synthetic method capable of predictably preparing multicolor fluorophores under a single set of synthetic conditions, or more desirably, from a common reagent.

During the last two decades, C−H activation chemistry has gained widespread attention, because it provides an atom- and step-economical route for preparing not only complex molecules, such as natural products and pharmaceuticals,[18−32] but also fluorophores that can be applied in organic light-emitting diodes (OLEDs).[33−42] In the field of C−H activation chemistry, C−C bond formation has been mainly studied so far, but recently, direct C−H amination/amidation strategies resulting in C−N bond formation have also been actively investigated.[43−49] Among them, Chang's group developed iridium-catalyzed direct C−H amidation (DCA) reactions between sulfonyl azides and arenes containing carbonyl (or imine) directing groups, thus enabling efficient synthesis of various sulfonamides under mild conditions (Scheme 1a).[24,46,50−54] Inspired by the highly efficient DCA, we recently reported direct C−H amidation polymerization (DCAP) of bis-sulfonyl azides and bis-benzamides to produce polysulfonamides by an atom-economical and green method (Scheme 1b).[55,56] Interestingly, unique intramolecular hydrogen-bonds are formed between the proton on the sulfonamide group and adjacent carbonyl group throughout the polymer backbone, causing polysulfonamides to undergo an excited-state intramolecular proton-transfer (ESIPT) process and emit

**Scheme 1. Iridium-Catalyzed Direct C−H Amidation (Polymerization)**




**Received:** February 16, 2020

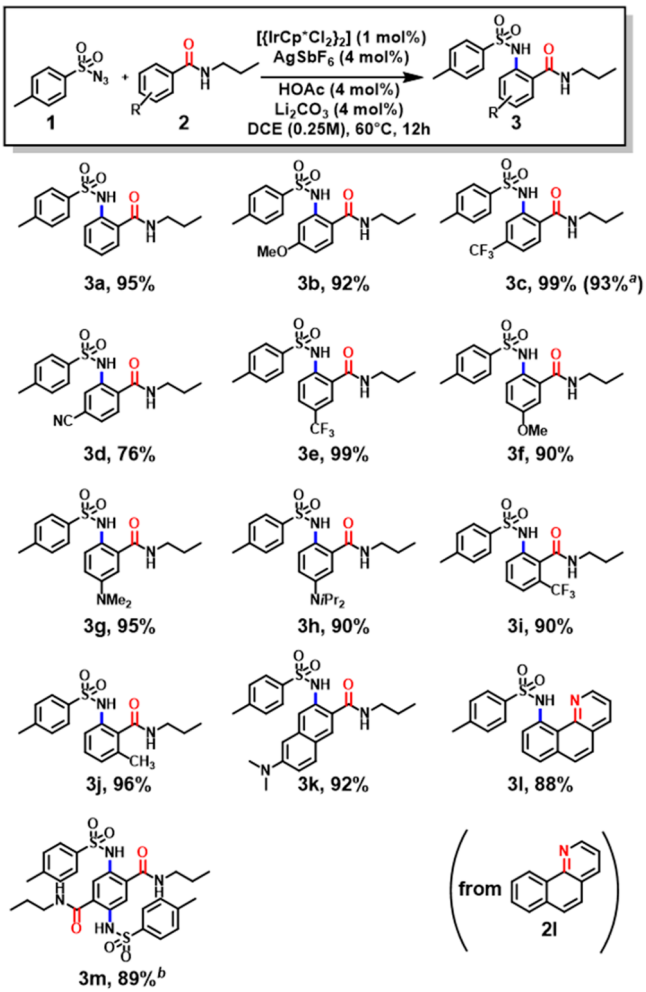
blue-light with high quantum yields. This process occurs when photoexcited molecule emits light with a very large Stokes shift by transfer of protons, leading to keto−enol tautomerization.

Inspired by versatile C−H activation chemistry[24,46,50−54] and numerous examples[8,57−69] of fluorescent molecules by the ESIPT process, we envisioned a new strategy to prepare a series of multicolor fluorophores simply by controlling the electronic properties of functional groups. Herein, we report the DCA as an efficient synthetic strategy to give diverse fluorescent molecules in good-to-quantitative yields from a common reagent, tosyl azide (**1**), under a single set of synthetic conditions (Scheme 1c). By adjusting the electronic characters of the substituents, it was possible to tune our synthesis to produce a broad range of multicolor fluorescent compounds, emitting light between blue and red, and even emitting white light.

To investigate the scope of DCA, we reacted various arenes containing *ortho*-directing groups (**2a−2m**) with the common reagent **1** under the optimal conditions determined in our previous studies.[55,56] High synthetic yields were consistently achieved and were largely unaffected by the position of substituents (*para*-, *meta*-, or *ortho*-) and their electronic variation in benzamides, **2** (Scheme 2). First, nonsubstituted *N*-propylbenzamide (**2a**) was successfully amidated in an excellent yield (95%). Also, amidations of *para*-substituted substrates such as **2b**, containing the electron-donating group (EDG, methoxy), as well as **2c** and **2d** bearing electron-withdrawing groups (trifluoromethyl and nitrile, respectively) proceeded in good-to-quantitative yields (76%−99%). Furthermore, **2e** with electron-withdrawing $-CF_3$ group at the *meta* position underwent DCA with reagent **1** in 99% yield, and **2f−2h** with EDGs (−OMe and amino groups) at *meta* positions resulted in excellent yields (90%−95%). In addition, the reactions of *ortho*- functionalized *N*-propylbenzamides containing $-CF_3$ group (**2i**) and the methyl group (**2j**) were also obtained in excellent yields (90% and 96%, respectively), regardless of electronic properties. To broaden the substrate scope, we tested DCA of compounds having extended $\pi$-systems (**2k** and **2l**) and isolated the desired products in high yields (92% and 88%, respectively). Notably, unlike in the previously reported method,[67] which required prefunctionalization of $NH_2$ at the 10-position of **2l** to synthesize the red-emitting **3l**, this DCA could directly synthesize the same compound in a high yield from commercially available **2l** in a single step similar to other successful DCA using different catalysts.[39,50] Lastly, the terephthalamide derivative (**2m**) containing two amides selectively underwent the desired bis-amidation in the presence of 2.0 equiv of **1** in a high yield (89%) without additional side reactions that would result in tri- and tetra-amidation products.

All reactions proceeded regioselectively at the *ortho* position to the directing group to exclusively afford the mono-amidation per directing group without bis-amidation, even though benzamide derivatives (**2a−2h**, **2k**, and **2m**) have two chemically equivalent *ortho* C−H bonds to the directing group. These results suggest that, after the first DCA, favorable intramolecular hydrogen bonds between the sulfonamide N−H and adjacent carbonyl group would restrict $C_{aryl}-C_{carbonyl}$ bond rotation, thereby suppressing the second amidation. Moreover, steric repulsions between two N−H bonds of sulfonamide and amide might further hinder the second amidation (Figure 1). Furthermore, although compounds **2e−2h**, **2k**, and **2m** (after the first amidation) each possess two

**Scheme 2. Scope of Direct C−H Amidation***




*Reaction conditions: **1** (0.2 mmol), **2** (0.2 mmol), [{IrCp*$Cl_2$}$_2$] (2 $\mu$mol), $AgSbF_6$ (8 $\mu$mol), HOAc (8 $\mu$mol), $Li_2CO_3$ (8 $\mu$mol) in DCE (0.8 mL) at 60 °C for 12 h (isolated yields). [a]The isolated yield in 1 mmol scale. [b]**1** (0.4 mmol) in DCE (1.6 mL).

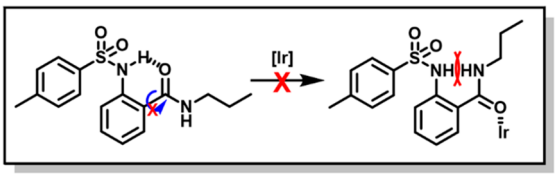



**Figure 1.** Proposed models for suppression of the second amidation.

nonsymmetric *ortho* C−H bonds, the reactions were again highly regioselective, occurring at the sterically more-accessible site.

After preparing the DCA products (**3a−3m**) with excellent efficiency, we next studied their optical properties in THF solutions (see Figure 2 and Table 1). First, the nonsubstituted **3a** exhibited blue emission ($\lambda_{max,em}$ = 472 nm) with $\lambda_{max,abs}$ at 308 nm. When EWGs were attached at the *para* positions (**3c** and **3d**), red-shifts were observed in both the absorptions ($\lambda_{max,abs}$ = 310 and 316 nm) and the emissions ($\lambda_{max,em}$ = 484 and 492 nm), resulting in bright-blue and cyan fluorescence, respectively. On the other hand, the spectra of compound **3b** bearing an EDG at the *para* position underwent blue-shifts in both the absorption ($\lambda_{max,abs}$ = 301 nm) and the emission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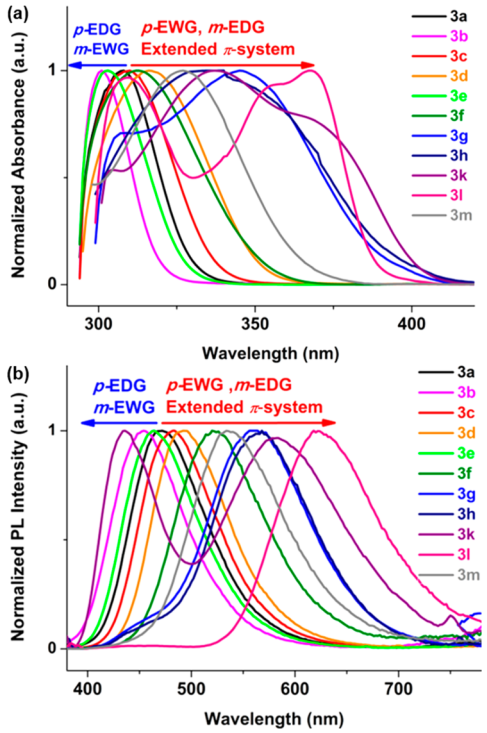


**Figure 2.** (a) Normalized absorption and (b) emission spectra in THF solutions (10 $\mu$M) at 298 K. The excitation wavelengths were 308, 301, 310, 316, 303, 312, 345, 340, 337, 368, and 327 nm for **3a**, **3b**, **3c**, **3d**, **3e**, **3f**, **3g**, **3h**, **3k**, **3l**, and **3m**, respectively.

**Table 1. Photophysical Properties of 3a−3m**

| compound (solvent) | $\lambda_{max,\ abs}$ [a] (nm) | $\lambda_{max,\ em}$ [b] (nm) | $\Phi_{rel,\ PL}$ [c] | CIE coordinates ($x$, $y$) |
|---|---|---|---|---|
| **3a** (THF) | 308 | 472 | 0.16 | 0.166, 0.236 |
| **3b** (THF) | 301 | 454 | 0.05 | 0.161, 0.154 |
| **3c** (THF) | 310 | 484 | 0.15 | 0.177, 0.299 |
| **3d** (THF) | 316 | 492 | 0.14 | 0.198, 0.390 |
| **3e** (THF) | 303 | 464 | 0.13 | 0.162, 0.200 |
| **3f** (THF) | 312 | 520 | 0.11 | 0.300, 0.518 |
| **3g** (THF) | 345 | 562 | 0.07 | 0.398, 0.469 |
| **3h** (THF) | 340 | 568 | 0.12 | 0.413, 0.485 |
| **3h** (MeOH) | 340 | 422, 554 | 0.04 | 0.310, 0.348 |
| **3i** (THF) | 294 | 508 | $2.4 \times 10^{-3}$ | 0.275, 0.458 |
| **3j** (THF) | 296 | 480 | $2.2 \times 10^{-3}$ | 0.204, 0.302 |
| **3k** (THF) | 337 | 436, 584 | $1.5 \times 10^{-2}$ | 0.351, 0.321 |
| **3l** ($CHCl_3$) | 368 | 616 | $2.4 \times 10^{-2}$ | 0.577, 0.413 |
| **3l** (THF) | 368 | 618 | $1.4 \times 10^{-2}$ | 0.583, 0.389 |
| **3m** (THF) | 327 | 534 | 0.20 | 0.357, 0.538 |

[a]Absorption maxima in solutions (10 $\mu$M) at 298 K. [b]Emission maxima in solutions (10 $\mu$M) at 298 K. [c]Determined by using quinine sulfate dihydrate in 0.5 M $H_2SO_4$ as a fluorescence standard.

($\lambda_{max,em}$ = 454 nm) and thus emitted a dark-blue light. In contrast to the trend observed with *para* substituents, increased electron-withdrawing power at the *meta* position (**3e**) gave blue-shifted spectra in both absorption ($\lambda_{max,abs}$ = 303 nm) and emission ($\lambda_{max,em}$ = 464 nm), in comparison to the nonsubstituted **3a**. Similarly, an increase in the electron-donating power (**3f**−**3h**) led to red-shifts for both the absorption ($\lambda_{max,abs}$ = 312−345 nm) and emission ($\lambda_{max,em}$ = 520−568 nm), resulting in green-to-yellow emissions. Each corresponding excitation spectrum was almost identical to the absorption spectrum (see Figure S4 in the Supporting Information). This indicates that the same ground-state species was responsible for the emission excluding any artifact caused by impurity.

In cases involving substituents at the *para* position to the carbonyl group, electronic contributions to lowest unoccupied molecular orbitals (LUMOs) seem to be greater than those to highest occupied molecular orbitals (HOMOs) in both the normal (N) and tautomer (T) forms. This is well-supported by time-dependent density-functional theory (TD-DFT) calculation of **3a**, which show that $\pi$-electron densities of the LUMOs at the *para* position are greater than those of the HOMOs in both the N and T forms (Figure 3). Therefore,

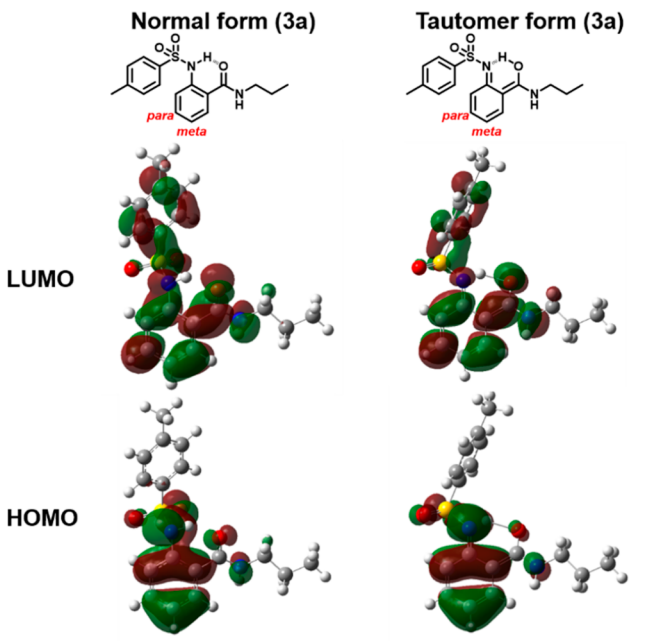


**Figure 3.** Calculated frontier orbitals of normal and tautomer forms of **3a** (by B3LYP/6-31++G(d,p)/IEFPCM).

EWGs would stabilize energy levels of excited states more than those of ground states, thereby resulting in red-shifted spectra. In contrast, $\pi$-electron densities on the HOMOs at the *meta*-position are more dominant than those on the LUMOs. Thus, EWGs would lower the HOMO levels more than the LUMO levels and increase both energy differences ($\Delta E_N$ and $\Delta E_T$), thereby showing blue-shifted spectra. Conversely, the EDGs at the *meta* or *para* position would show the opposite effect, based on the same logic. This argument was further supported by experimentally measuring HOMO and LUMO levels by cyclic voltammetry and UV-vis spectroscopy, as well as TD-DFT calculation ($S_0 \rightarrow S_1$ transition; see Figure S1 in the Supporting Information).

Interestingly, *ortho*-substituted products (**3i** and **3j**) showed negligible fluorescence, regardless of the electronic nature of the substituents (Table 1 and Figure S3 in the Supporting Information). In $CD_2Cl_2$, the chemical shifts of their N−H protons appeared at relatively upfield region ($\delta$ 7.93 and $\delta$ 8.11 ppm, respectively), whereas those of compounds **3a**−**3k** appeared at downfield region ($\delta$ 9.58−11.49 ppm), because of the formation of strong intramolecular bonds (Figure 4). Based on these observations, we concluded that steric repulsion between the amide group and the *ortho* substituents


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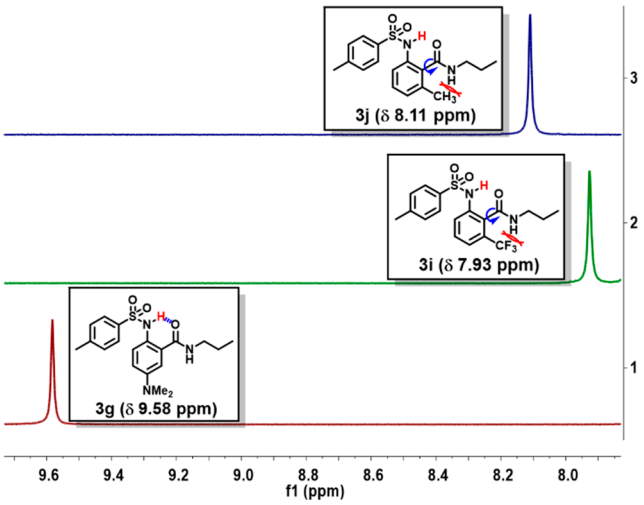


**Figure 4.** $^{1}$H nuclear magnetic resoannce (NMR) spectra of the N−H protons of **3g**, **3i**, and **3j**.

in **3i** and **3j** prevented the formation of intramolecular hydrogen bonding, thereby inhibiting the ESIPT process.

A fluorophore containing the extended $\pi$-system, **3k**, showed a more red-shifted absorption spectrum ($\lambda_{max,abs}$ = 337 nm) than that of **3a**. Interestingly, the purplish-pink fluorescence was characterized by dual emission ($\lambda_{max,em}$ = 436 and 584 nm) that likely resulted from thermal equilibrium between the excited states of the normal (N*) and the tautomer (T*) forms (see Figure 2b and Table 1, as well as Figures 5c and 5d). Upon monitoring at the respective photoluminescence (PL) bands, the excitation spectra were identical each other, and also similar to the absorption spectrum, suggesting that dual emission originated from the identical excited species (see Figure S5a in the Supporting Information).[70,71] The absorption and emission spectra of another example of the extended $\pi$-system, **3l**, underwent even greater red-shifts ($\lambda_{max,abs}$ = 368 nm and $\lambda_{max,em}$ = 618 nm, corresponding to red-emission). In the case of the bis-amidated **3m** containing two directing groups, the second directing group acts as EWG at *para* position, and the second sulfonamide group acts as EDG at *meta* position. Thus, because of the synergistic effect of two substituents, red-shifted emission ($\lambda_{max,em}$ = 534 nm) occurred, resulting in a yellowish-green color.

During the investigation on the effect of various solvents on the ESIPT process, we observed some notable solvatochromisms (see Table 1, as well as Figures 5a and 5d). For example, in less-polar chloroform, **3l** produced an orange emission with chromaticity coordinates of (0.58, 0.43) via positive solvatochromism. Interestingly, when compound **3h** was dissolved in methanol (MeOH), white-light emission occurred with chromaticity coordinates of (0.31, 0.35) resulting from simultaneous emissions of the N* form at 422 nm and the T* form at 554 nm. This dual emission is rationalized by the partial ESIPT quenching through hydrogen bonding between the protic solvent, MeOH, and the ESIPT molecule (Figure 5b).[72−74] In other words, some molecules of **3h** emitted light at the longer wavelength (554 nm), as a result of the ESIPT process, while other molecules underwent intermolecular hydrogen bonding with MeOH to emit the shorter wavelength light (442 nm). This rationale is supported by a series of experiments involving the comparison of fluorescence in various solvents with varying degree of hydrogen-bond donors, as well as excitation spectra monitored at the respective PL bands (see Figures S5b and S6 in the Supporting Information for details). These results clearly indicate that this DCA is an efficient and modular synthetic method synthesizing numerous ESIPT molecules capable of emitting a broad range of colors in the visible-light spectrum, even including white light.

In conclusion, this Ir-catalyzed DCA has proved to be a very efficient method to prepare multicolor fluorophores (up to 99% of yields), regardless of the positions of substituents and their electronic characters under uniform and mild conditions. Since the reaction efficiency is not influenced by the electronic

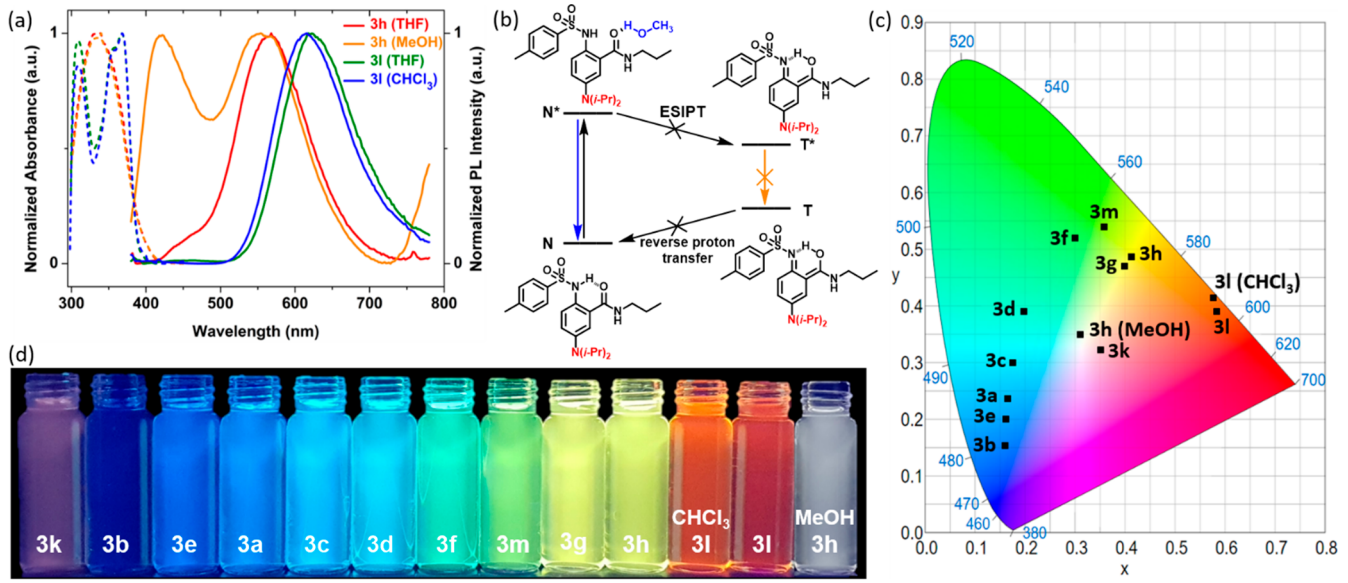


**Figure 5.** (a) Normalized absorption (dashed lines) and emission spectra (solid lines) of **3h** ($\lambda_{ex}$ = 340 nm) and **3l** ($\lambda_{ex}$ = 368 nm) in solutions (10 $\mu$M) at 298 K. (b) Proposed mechanism for the white-light emission of **3h** in methanol; white-light emission appears in MeOH because ESIPT is partially quenched by intermolecular hydrogen bonds with a protic solvent. (c) Emission color coordinates of **3a**−**3h** and **3k**−**3m** in solutions in the CIE 1931 chromaticity diagram. (d) Photograph of **3a**−**3h** and **3k**−**3m** in solution under 365 nm UV irradiation.


https://dx.doi.org/10.1021/acs.orglett.0c00618
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nature of the functional groups, the energy levels of HOMOs and LUMOs can be readily controlled. As a result, we were able to produce a broad range of multicolor fluorescent compounds capable of emitting light between blue and red, even including white light using only a single synthetic strategy and a common coupling reagent. We are currently studying white-light emission by other polymeric materials.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c00618.

Experimental procedures, characterizations, $^{1}H$ and $^{13}C$ NMR spectra for new compounds, and other supporting experiments (PDF)

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

We are thankful for financial support from the National Research Foundation of Korea through the following grants: Creative Research Initiative Grant and the Nano-Material Technology Development Program.

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