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Tetrahedron Letters 49 (2008) 1860–1864
Tetrahedron Letters

Synthesis of fluorescent rhodamine dyes using an extension of the Heck reaction

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Received 2 October 2007; revised 4 January 2008; accepted 7 January 2008
Available online 11 January 2008

Abstract

Both benzo[*b*]thiophene and indole containing rhodamine dyes were synthesized according to a new pathway requiring a Heck-type coupling and a Pictet–Spengler reaction. The electron-rich indolic dye was shown to have noteworthy absorption and emission maximum.

Keywords: Rhodamine; Benzo[*b*]thiophene; Indole; Fluorescent dyes; Heck-type coupling; Pictet–Spengler reaction

Rhodamine dyes are used in various biological applications from biology to material sciences. They represent an important family of long-wavelength visible dyes with absorption maxima about 600 nm. However, their fluorescence detection sensitivity is compromised due to their excitation and emission spectra which often overlap significantly with cellular autofluorescence, dramatically limiting their usefulness in live cells. Therefore, many research groups focused on the development of new long-wavelength rhodamine dyes with absorption beyond 600 nm avoiding the undesired autofluorescence of biological species.

Different groups synthesized various rigidified rhodamine dyes with additional conjugation of the π system to shift their absorption and emission maxima. For example, different pentacyclic rhodamine dyes were developed by Drexhage/Arden-Jacob and co-workers[1,2] and Benson et al. (Fig. 1).[3]

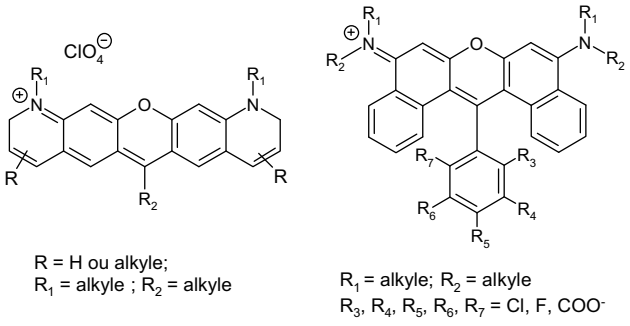

Fig. 1. Pentacyclic rhodamine dyes.

More recently, Liu et al. synthesized rhodamine dyes with different aryl or heteroaryl moieties to rigidify the system and improved the fluorescence characteristics (Fig. 2).[4] The synthesis is based on a Suzuki coupling of different arylboronic acids with *p*-bromo-*m*-nitroanisole followed by a Bischler–Napieralski reaction to afford different quinoline derivatives as intermediates of rhodamine derivatives. These new dyes showed absorptions beyond 600 nm and high fluorescence quantum yields.[5]

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doi:10.1016/j.tetlet.2008.01.021

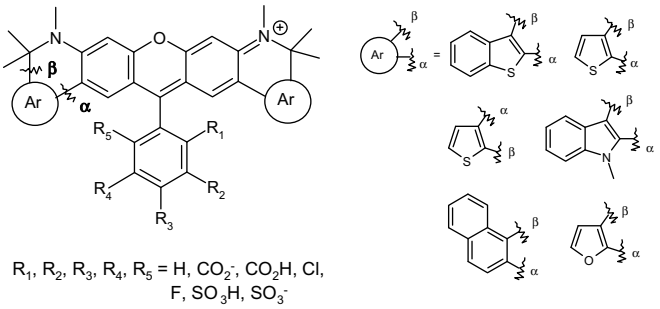


Fig. 2. Aryl and heteroaryl rhodamine dyes.

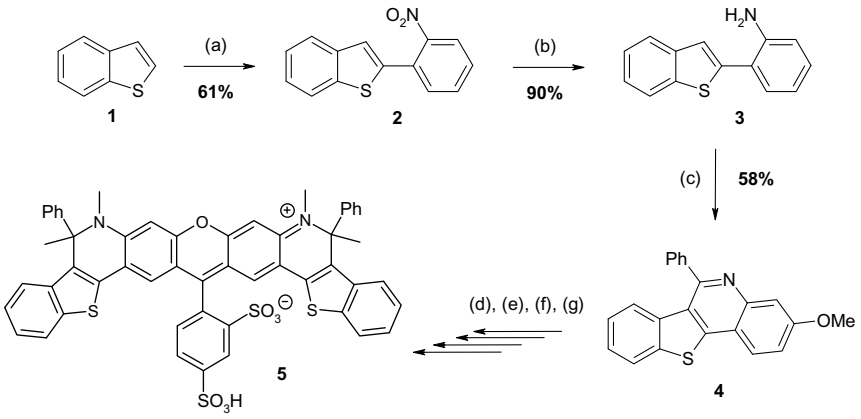
To facilitate the access of new rigid rhodamines in fewer steps and to avoid the use of the required boronic acids involved in the Suzuki cross coupling, we described here an alternative pathway to the synthesis of a benzothiophene containing rhodamine dyes. Our methodology was based on the previously works developed in our laboratory concerning a direct pallado-catalyzed arylation at the 2 position of 3-substituted benzo[*b*]thiophene and the access to benzothieno[3,2-*c*]quinolines analogues by Pictet–Spengler reaction.[6] We assumed that the design of a rhodamine dye containing an electron-richest moiety than benzo[*b*]thiophene moiety would improve its fluorescence properties. Hence, we applied our methodology to the synthesis of an indole rhodamine dye, which showed noteworthy fluorescence characteristics.

The synthesis of benzo[*b*]thiophenic rhodamine derivative **6** started from benzothieno[3,2-*c*]quinoline **4** (Scheme 1). Recently, we developed the access to benzothieno[3,2-*c*]-quinolines in three steps from benzo[*b*]thiophene **1**·**6c**. The first step involved the Heck-type coupling of benzo[*b*]-thiophene **1** with the *p*-methoxy-*o*-nitrophenyl bromide. 2-(*p*-Methoxy-*o*-nitrophenyl) benzo[*b*]thiophene **2** was selectively obtained in a yield of 61%. After reduction of the nitro group, the corresponding 2-(benzo[*b*]thiophen-2-yl)aniline **3** was involved in a Pictet–Spengler reaction with benzaldehyde, affording 3-methoxy-6-phenylbenzothieno-[3,2-*c*]quinoline **4**. Compound **4** was then turned into rhodamine derivative **6** according to the pathway developed by Liu et al.[5] After quaternization of **2** with *p*-TsOMe, the ammonium salt **3** was converted into the tertiary amine **4** by reaction with MeMgCl at room temperature. Aminophenol **5** was then obtained by demethylation of **4** with BBr_3. Condensation of **5** with 4-formyl-1,3-benzenesulfonic acid, disodium salt afforded the rhodamine **6** as a pearly blue solid in a good isolated yield of 92%.

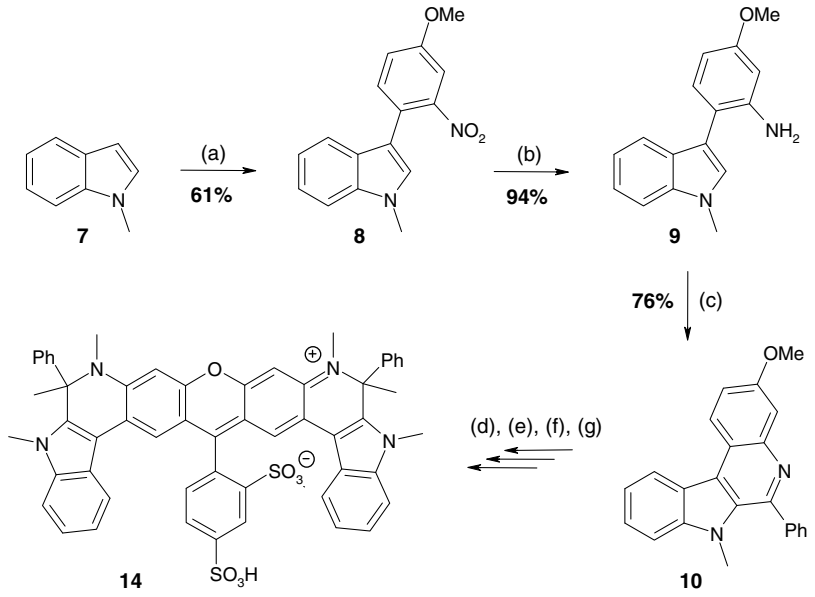
Also, we synthesized an indolo-rhodamine according to the same pathway. The first step concerned the Heck-type coupling of the indole moiety with *p*-bromo-*o*-nitroanisole. Few years ago, Lane and Sames described the C-2 selective arylation of *N*-methylindole with *para*-substituted aryl iodides under similar conditions to ours.[7] Nevertheless, the 3-aryl-*N*-methylindole was the major product with an *ortho*-substituted aryl iodide, probably due to the steric hindrance.

With a labile protecting group of the indole moiety such as a phenylsulfonyl group, our coupling conditions were not successful. From commercially *N*-methylindole **7**, 3-(*p*-methoxy-*o*-nitrophenyl)-*N*-methylindole **8** was selectively obtained in a yield of 61%,[8] in agreement with Sames results. The regioisomers mixture was obtained in an overall yield of 75% in a 8:2 ratio. The hydrogenation of **8** in the presence of a catalytic amount of Pd/C under 10 atm. of hydrogen at room temperature gave the corresponding 5-methoxy-(*N*-methylindol-3-yl)aniline **9**.[9] We then realized the Pictet–Spengler reaction with benzaldehyde. The use of TFA was not required to obtain the cyclized compound **10**.[10] As described with benzo[*b*]thiophene derivatives,[6] indolo[3,2-*c*]quinoline **10** was directly obtained in a yield of 76%, probably due to an in situ oxidation of the corresponding dihydro-indolo[3,2-*c*]quinoline **10**.

Indolo[3,2-*c*]quinoline **10** was then turned into the rhodamine derivative **14** according to the previously described procedure. All the intermediates were obtained in good isolated yields (Scheme 2).[11–14]



Scheme 1. Reagents and conditions: (a) 5 mol % $Pd(OAc)_2$, 10 mol % PPh_3, 3 equiv K_2CO_3, 1.1 equiv ArBr, DMF, 130 °C, overnight (61%); (b) 1 mol % Pd/C (10%), H_2 10 bars, ethanol, rt, overnight (90%); (c) refluxing toluene then 1 equiv TFA, toluene, 80 °C, O_2, 1.5 h (58%); (d) 5 equiv *p*-TsOMe, chlorobenzene, reflux, overnight; (e) 4 equiv MeMgCl, THF, rt, in the dark, overnight; (f) 3 equiv BBr_3, DCM, rt, in the dark, overnight; (g) 0.5 equiv 4-formyl-1,3-benzenedisulfonic acid, disodium salt, TFA, DMF, rt, in the dark then 120 °C, in the dark, overnight.



Scheme 2. Reagents and conditions: (a) 5 mol % $Pd(OAc)_2$, 10 mol % PPh_3, 3 equiv K_2CO_3, DMF, 130 °C, 4 h; (b) 1 mol % Pd/C (10%), H_2 10 bars, ethanol, rt, overnight; (c) refluxing toluene, 24 h; (d) 5 equiv *p*-TsOMe, chlorobenzene, reflux, overnight (83%); (e) 4 equiv MeMgCl, THF, rt, in the dark, overnight (95%); (f) 3 equiv BBr_3, DCM, rt, in the dark, overnight (70%); (g) 0.5 equiv 4-formyl-1,3-benzenedisulfonic acid, disodium salt, TFA, DMF, rt, in the dark then 120 °C, in the dark, overnight (95%).

Several photophysical characteristics, (Absorption and emission maxima, fluorescence quantum yields (ϕ_f), lifetime (τ)), were determined in methanol and DMSO for both rhodamines **5** and **14**.[15] We compared them to those of rhodamine 101 which was chosen as a reference and to rhodamine **15** synthesized by Liu et al. (Fig. 3). [5] Results are summarized in Table 1.

Rhodamines **5** and **15** differ only by the presence of a phenyl group at the α-position of the nitrogens. As expected, these rhodamines exhibited similar absorption characteristics in methanol with a slightly higher extinction coefficient for **5** compared to **15**. Nevertheless, the presence of the phenyl groups decreases the fluorescence quantum yield from 0.81 for **15** to 0.64 for **5** and increases the Stokes shift from 17 nm to 25 nm. These results indicate that the substitution at the α-position of the nitrogens will promote the molecular reorganization between the Franck–Condon excited-state and the emitting one. This has, for consequence, an emission occurring at lower energy for **5** but also an increase of the nonradiative deactivation process presumably by the rotation of the phenyl groups and hence a lower quantum yield.

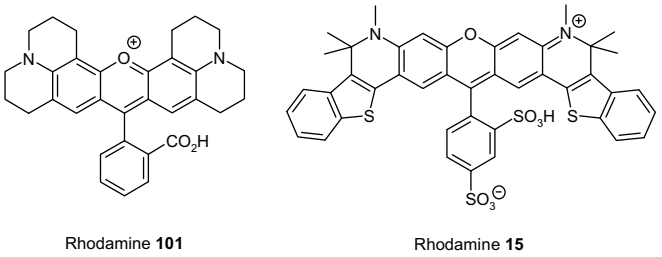


Fig. 3. Structures of rhodamines 101 and **15**.

Table 1
Photophysical characteristics of rhodamines 101, **5**, **14** and **15** in methanol and DMSO at 20 °C

Rhodamine	Solvent	λ_{max}^{abs}/nm ε/(M^{-1} cm^{-1})	λ_{max}^{em}/nm	$\Delta\lambda$[a]/nm	ϕ_f[b]	τ/ns
Rhodamine 101	MeOH	568 (126,000)	587	19	1	4.21
	DMSO	567 (52,000)	619	52	1	3.7
Rhodamine **15**[5]	MeOH	616 (143,000)	633	17	0.89	—[c]
Benzothiophene	MeOH	613 (200,000)	638	25	0.64	3.18
5	DMSO	617 (83,000)	664	47	0.50	3.0
Indolique **14**	MeOH	634 (76,000)	672	38	0.16	2.37
	DMSO	627 (31,000)	683	56	0.15	3.0

[a] $\Delta\lambda$ stokes shift $\Delta\lambda = \lambda_{max}^{em} - \lambda_{max}^{abs}$.
[b] See experimental part.
[c] Not determined.

On the other hand, rhodamine **14** showed absorption and emission maxima that are remarkably red-shifted versus **5** with a shoulder until 750 nm (Fig. 4). This difference can be explained by the introduction of an electron-rich *N*-methylindole moiety instead of the benzo[*b*]thiophene moiety. However, the fluorescence quantum yield was four times lower.

In DMSO, the fluorescence quantum yields of **5** and **14** slightly decrease (0.50 and 0.15, respectively). Emission maxima were observed, respectively, at 664 and 683 nm with stokes shifts more pronounced of 47 and 56 nm.

We have also investigated the emission lifetime of all the rhodamines in methanol and DMSO, $C = 1.5 \times 10^{-3}$ mM. At this low concentration rate, we avoid any self-absorption phenomenon or intermolecular quenching that was evidenced for rhodamines.[16] The fluorescence decay of the compounds are mono-exponential (Fig. 5) and are in qualitative agreement with that already published for rho-

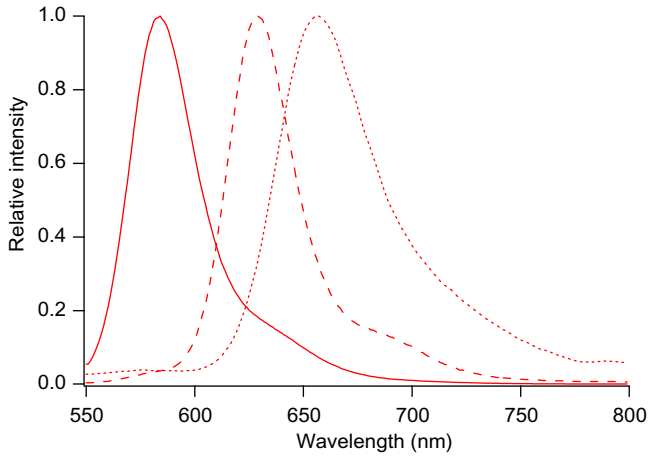


Fig. 4. Normalized emission spectra of rhodamines 101 strait line, **5** dashed line and **14** dotted line.

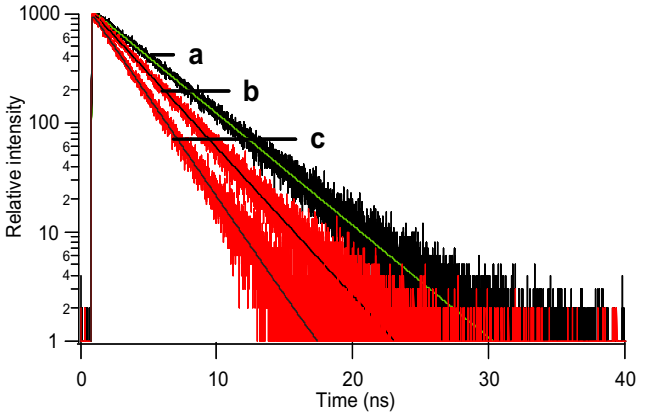


Fig. 5. Emission lifetime of rhodamine 101 (a), **5** (b) and **14** (c) in methanol recorded at the maximum of emission after excitation at 400 nm.

damine 101.[17,18] The modified rhodamines **5** and **14** exhibit shorter fluorescence lifetime of 3.2 ns and 2.4 ns, respectively, (Table 1) versus the standard rhodamine 101.

In summary, we developed a new methodology for the synthesis of heterocyclic rhodamines. The indolic rhodamine proved to have long-wavelength absorption and emission. The access to these compounds could be extended to other heterocycles thus open new routes for the synthesis of new rhodamines. These dyes could be interesting for biological applications.

Acknowledgement

The authors thank the 'Ministère de la Recherche et de l'Enseignement Supérieur' for the grant to E.D.'s PhD.

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8. Preparation and characterization for **8**: In anhydrous DMF (1.5 mL) were successively added PPh_3 (39 mg, 0.15 mmol, 0.1 equiv), K_2CO_3 (622 mg, 4.5 mmol, 3 equiv), *N*-methylindole **7** (0.200 mL, 1.5 mmol) and *p*-bromo-*m*-nitroanisole (383 mg, 1.65 mmol, 1.1 equiv). The mixture was heated at 100 °C and $Pd(OAc)_2$ (17 mg, 0.075 mmol, 0.05 equiv) was added. The reaction was heated at 130 °C for 4 h. After cooling at room temperature, the suspension was filtered over Celite (rinsed with CH_2Cl_2). The resulting organic layer was washed with brine, dried over $MgSO_4$, filtered and solvents were removed under reduced pressure. The crude product was purified by flash chromatography (heptane/CH_2Cl_2 = 7:3) to afford **8** in 61% yield (260 mg) as a red solid; mp 112–114 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.83 (s, 3H), 3.91 (s, 3H), 7.12–7.38 (m, 6H), 7.47 (d, 1H, J = 7.9 Hz), 7.53 (d, 1H, J = 8.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 33.1 (CH_3), 56.0 (CH_3), 107.6 (C), 108.9 (CH), 109.8 (CH), 110.8 (C), 118.8 (CH), 119.1 (CH), 120.2 (CH), 121.6 (C), 122.3 (CH), 127.0 (C), 127.8 (CH), 133.6 (CH), 136.9 (C), 158.3 (C); Anal. Calcd for $C_{16}H_{14}N_2O_3$: C, 68.08; H, 5.00; N, 9.92. Found: C, 67.92; H, 5.07; N, 10.01; MS (ESI$^+$): m/z = 283 (MH^+).
9. Preparation and characterization data for **9**: A suspension of 3-(*p*-methoxy-*o*-nitrophenyl)-*N*-methylindole **8** (226 mg, 0.8 mmol) and Pd/C (10%) (8.5 mg, 0.008 mmol, 1 mol %) in EtOH (4 mL) was stirred overnight at room temperature under 10 bars of hydrogen. The reaction mixture was filtered over Celite (rinsed with CH_2Cl_2). Solvents were removed under reduced pressure. The crude product was purified by flash chromatography (CH_2Cl_2/heptane = 7:3) to afford **9** in 94% yield (190 mg) as a white solid; mp 110–112 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.74 (br s, 2H), 3.83 (s, 3H), 3.84 (s, 3H), 6.44 (m, 2H), 7.13–7.32 (m, 4H), 7.39 (d, 1H, J = 8.1 Hz), 7.62 (d, 1H, J = 7.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 32.9 (CH_3), 55.3 (CH_3), 101.1 (CH), 104.0 (CH), 109.5 (CH), 112.9 (C), 113.6 (C), 119.5 (CH), 120.4 (CH), 122.0 (CH), 127.2 (C), 127.6 (CH), 132.1 (CH), 137.1 (C), 145.8 (C), 159.7 (C); Anal. Calcd for $C_{16}H_{16}N_2O$: C, 76.16; H, 6.39; N, 11.10. Found: C, 76.13; H, 6.52; N, 10.99; MS (ESI$^+$): m/z = 253 (MH^+).
10. Preparation and characterization data for **10**: A solution of 5-methoxy-(*N*-methylindol-3-yl)phenylamine **9** (2.43 g, 9.6 mmol) and benzaldehyde (1.03 mL, 10.1 mmol, 1.05 equiv) was refluxed in anhydrous toluene (10 mL) under inert atmosphere for a day. The reaction mixture was concentrated in vacuo. The resulting crude product was purified by flash chromatography (cyclohexane/AcOEt: 9:1) to afford **10** in 76% yield (2.47 g) as a pale yellow solid; mp 166–168 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.51 (s, 3H), 4.00 (s, 3H), 7.39–7.46 (m, 2H), 7.52–7.63 (m, 5H), 7.69–7.72 (m, 3H), 8.62 (d, 1H, J = 7.9 Hz), 8.69 (d, 1H, J = 9.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 33.5 (CH_3), 55.9 (CH_3), 109.4 (CH), 110.7 (CH), 119.2 (C), 119.7 (CH), 120.8 (CH), 122.0 (C), 123.5 (C), 123.6 (CH), 124.2 (CH), 127.4 (CH), 128.8 (2CH), 129.1 (CH), 129.8 (2CH), 132.0 (C), 140.7 (C), 142.4 (C), 144.1 (C), 148.4 (C), 158.0 (C); Anal. Calcd for $C_{23}H_{18}N_2O$: C, 81.63; H, 5.36; N, 8.28. Found: C, 81.78; H, 5.78; N, 7.80; MS (ESI$^+$): m/z = 339 (MH^+).
11. Preparation and characterization data for **11**: To a suspension of 3-methoxy-7-methyl-6-phenylindolo[2,3-*c*]quinoline **10** (2.37 g, 7 mmol) in chlorobenzene (35 mL) was added *p*-TsOMe (6.52 g, 35 mmol, 5 equiv) and the mixture was refluxed overnight. After cooling at room temperature, the resulting precipitate was collected by filtration

to afford **11** in 83% yield (3.04 g) as a yellow solid; mp 246–248 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.18 (s, 3H), 3.17 (s, 3H), 4.12 (s, 3H), 4.51 (s, 3H), 6.88 (d, 2H, $J = 8.1$ Hz), 7.50–7.59 (m, 5H), 7.71–7.77 (m, 6H), 7.90 (d, 1H, $J = 2.3$ Hz), 8.62 (d, 1H, $J = 8.3$ Hz), 8.81 (d, 1H, $J = 9.2$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.3 (CH_3), 32.4 (CH_3), 42.7 (CH_3), 57.1 (CH_3), 100.9 (CH), 111.3 (CH), 119.0 (C), 119.7 (C), 122.7 (CH), 122.8 (CH), 125.0 (CH), 125.8 (CH), 125.9 (2CH), 128.2 (2CH), 129.0 (C), 130.0 (2CH), 130.1 (2CH), 130.4 (C), 130.7 (C), 131.8 (CH), 132.1 (CH), 137.2 (C), 138.3 (C), 144.4 (C), 144.7 (C), 146.0 (C), 162.2 (C); Anal. Calcd for $C_{31}H_{28}N_2O_4S$: C, 70.97; H, 5.38; N, 5.34; S, 6.11. Found: C, 71.17; H, 5.46; N, 5.28; S, 5.89; MS (ESI$^+$): $m/z = 353$ ($M^+ - p$TsO$^-$).

12. Preparation and characterization data for **12**: To a suspension of 3-methoxy-5-methyl-6-phenylindolo[2,3-*c*]quinolinium tosylate **11** (3.04 g, 5.8 mmol) in anhydrous THF (40 mL) was added MeMgCl (3 M in THF, 7.7 mL, 23.2 mmol, 4 equiv) at 0 °C under inert atmosphere. The reaction was stirred at room temperature and in the dark for a day. It was then poured into ice and acidified with a 2 M HCl aqueous solution. The solution was extracted with CH_2Cl_2. The resulting organic layer was washed with brine, dried over $MgSO_4$, filtered and solvents were removed under reduced pressure. The crude product was purified by flash chromatography (cyclohexane/$CH_2Cl_2 = 7:3$) to afford **12** in 95% yield (2.11 g) as a white solid; mp 162–164 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.92 (s, 3H), 2.60 (s, 3H), 3.02 (s, 3H), 3.90 (s, 3H), 6.33 (d, 1H, $J = 2.4$ Hz), 6.50 (dd, 1H, $J = 2.4$, 8.3 Hz), 7.24–7.29 (m, 3H), 7.36–7.45 (m, 3H), 7.64–7.67 (m, 2H), 7.91 (d, 1H, $J = 8.3$ Hz), 8.20 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.9 (CH_3), 30.7 (CH_3), 32.2 (CH_3), 55.4 (CH_3), 63.9 (C), 99.2 (CH), 100.8 (CH), 107.2 (C), 109.3 (CH), 114.7 (C), 120.2 (CH), 120.6 (CH), 121.7 (CH), 122.4 (CH), 123.1 (C), 127.8 (CH), 128.5 (2CH), 128.6 (2CH), 137.8 (C), 138.4 (C), 143.3 (C), 145.2 (C), 158.5 (C); Anal. Calcd for $C_{25}H_{24}N_2O$: C, 81.49; H, 6.57; N, 7.60. Found: C, 81.42; H, 6.76; N, 7.48; MS (ESI$^+$): $m/z = 369$ (MH^+).

13. Preparation and characterization data for **13**: To a solution of 3-methoxy-5,6,7-trimethyl-6-phenyl-5,6-dihydro-indolo[2,3-*c*]quinoline **12** (192 mg, 0.5 mmol) in anhydrous CH_2Cl_2 (5 mL) was added at 0 °C under inert atmosphere BBr_3 (1 M in CH_2Cl_2, 1.5 mL, 1.5 mmol, 3 equiv). The reaction mixture was stirred at room temperature and in the dark overnight. Methanol is then slowly added at 0 °C to quench the residual BBr_3. The reaction mixture was extracted with CH_2Cl_2. The resulting organic layer was washed with a saturated $NaHCO_3$ aqueous solution and brine, dried over $MgSO_4$, filtered and solvents were removed under reduced pressure. The crude product was purified by flash chromatography (CH_2Cl_2/cyclohexane = 9:1) to afford **13** in 70% yield (125 mg) as a green solid; mp 144–146 °C; ^{1}H NMR (300 MHz, $(CD_3)_2SO$): δ 1.86 (s, 3H), 2.53 (s, 3H), 2.97 (s, 3H), 6.16 (d, 1H, $J = 2.2$ Hz), 6.31 (dd, 1H, $J = 2.2$, 8.1 Hz), 7.14–7.21 (m, 2H), 7.34–7.49 (m, 4H), 7.58–7.61 (m, 2H), 7.69 (d, 1H, $J = 8.1$ Hz), 8.08 (m, 1H), 9.03 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.6 (CH_3), 31.8 (CH_3), 38.7 (CH_3), 63.4 (C), 99.4 (CH), 103.7 (CH), 106.4 (C), 109.7 (CH), 112.0 (C), 119.9 (2CH), 121.4 (CH), 122.1 (CH), 122.2 (C), 127.7 (CH), 128.2 (2CH), 128.4 (2CH), 136.9 (C), 137.9 (C), 142.8 (C), 144.7 (C), 156.0 (C); HRMS (ESI$^+$) calcd for $C_{24}H_{23}N_2O$: 355.1810. Found: 355.1811.

14. Preparation and characterization data for **14**: To a solution of 3-hydroxy-5,6,7-trimethyl-6-phenyl-5,6-dihydro-indolo[2,3-*c*]quinoline **13** (148 mg, 0.4 mmol, 2 equiv) in DMF (2 mL) were added 4-formyl-1,3-benzenedisulfonic acid, disodium salt (62 mg, 0.2 mmol) and TFA (0.2 mL). The reaction mixture was stirred at room temperature and in the dark overnight. It was then heated at 120 °C in the dark for 24 h. The resulting reaction mixture was concentrated in vacuo. The crude product was purified by flash chromatography ($CHCl_3$/MeOH: 95:5) to afford **14** in 95% yield (178 mg) as a pearly blue solid; mp >250 °C; ^{1}H NMR (300 MHz, CD_3OD): δ 2.91 (s, 6H), 3.07 (s, 6H), 3.35 (s, 3H), 3.60 (s, 3H), 6.95 (d, 2H, $J = 2.1$ Hz), 7.11–7.27 (m, 6H), 7.34–7.52 (m, 13H), 7.69–7.75 (m, 2H), 8.21 (dd, 1H, $J = 1.7$, 7.9 Hz), 9.01 (d, 1H, $J = 1.5$ Hz); ^{13}C NMR (125 MHz, CD_3OD): δ 24.5 (CH_3), 24.6 (CH_3), 31.2 ($2CH_3$), 34.6 ($2CH_3$), 67.1 (C), 67.2 (C), 96.6 (CH), 96.7 (CH), 105.6 (C), 105.7 (2C), 110.7 (2CH), 110.8 (CH), 117.4 (C), 117.5 (C), 120.3 (CH), 120.4 (CH), 120.5 (CH), 121.0 (CH), 121.2 (CH), 121.3 (CH), 122.7 (2CH), 122.9 (C), 123.6 (2C), 124.2 (2CH), 127.4 (CH), 128.8 (CH), 129.3 (2CH), 129.8 (CH), 129.9 (CH), 130.2 (2CH), 130.3 (CH), 131.6 (CH), 133.8 (C), 140.1 (2C), 140.3 (2C), 143.0 (2C), 146.8 (C), 148.7 (C), 152.4 (C), 152.5 (C), 155.8 (C), 158.2 (C), 158.3 (C); Anal. Calcd for $C_{55}H_{44}N_4O_7S_2$, $1.5CHCl_3$, H_2O: C, 59.83; H, 4.22; N, 4.94; S, 5.95. Found: C, 60.54; H, 4.95; N, 4.59; S, 5.65; MS (ESI$^+$): $m/z = 935$ (MH^+), (ESI$^-$): $m/z = 937$ (MH^-).

15. *Absorbance and emission*: UV–visible spectra were obtained using a Cary 1 absorption spectrophotometer on a 1 cm path length quartz cell. The steady-state emission spectra were recorded on a Photon Technology International (PTI) SE-900M spectrofluorimeter and recorded in a 1cm quartz cell. Emission quantum yield ϕ_L were determined at 20 °C in methanol, according to Eq. 1,

$$\phi_L^S = \frac{I_L^S}{I_L^{Ref}} \frac{(1 - 10^{-OD^{Ref}})}{(1 - 10^{-OD^S})} \phi_L^{Ref} \quad (1)$$

where I_L, the emission intensity, was calculated from the spectrum area $\int I(\lambda)d\lambda$, OD represents the optical density at the excitation wavelength. The superscripts 'S' and 'Ref' refer, respectively, to the sample and to the standard. Rhodamine 101 ($\phi_L^{Ref} = 1$ in methanol) was used as the standard.The luminescence lifetime of the complexes was performed after irradiation at $\lambda = 400$ nm obtained by the second harmonic of a Titanium: Sapphire laser (picosecond Tsunami laser spectra physics 3950-M1BB) at a 8MHZ repetition rate. The Fluotime 200 from AMS technologies is used for decay acquisition. It consists of a GaAs microchannel plate photomultiplier tube (Hamamatsu model R3809U-50) followed by a time-correlated single photon counting system from picoquant (PicoHarp300). The ultimated time resolution of the system was closed to 30 ps. These measurements were recorded using the technical support from the chemistry platform 'NanoBio campus' in Grenoble (France).

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