Synthesis and Spectroscopic Properties of a New Class of Strongly Fluorescent Dipyrrinones

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Abstract: A new, highly fluorescent ($\Phi_F \geq 0.8$) chromophore has been synthesized in one step from dipyrrinones by reaction with *N*,*N*-carbonyldiimidazole to form the 3*H*,5*H*-dipyrrolo[1,2-*c*:2′,1′-*f*]pyrimidine-3,5-dione nucleus.

The tricyclic dipyrrole ring system, 3*H*,5*H*-dipyrrolo-[1,2-*c*:2′,1′-*f*]pyrimidin-3-one (Figure 1A) has been reported three times since 1986,[1−3] but apparently not earlier. In 1986, Lugtenburg et al.[1] showed how to prepare the tricyclic parent (Figure 1A) from pyrrole-2-aldehyde in three to four steps. Subsequently, we showed how to fabricate analogues[2,3] by inserting the CH_2 methano bridge into a preformed dipyrrinone (Figure 1B)—a convenient but typically low-yield synthesis. Recently, we discovered how to bridge the two dipyrrinone nitrogens more efficiently by inserting a carbonyl group in one step and in very high yield. The reaction successfully produced the first members of a new class of highly fluorescent compounds with the chromophore of Figure 1C.

Dipyrrinones such as kryptopyrromethenone (Figure 1B, **KRP**) and methyl xanthobilirubinate (Figure 1B, **XBRMe**) do not exhibit fluorescence following excitation of their long-wavelength intense absorption band near 420 nm. Rather, their excited states relax by a facile nonradiative decay mechanism: $Z \rightarrow E$ isomerization of the C(4)−C(5) double bond.[2] In earlier investigations of dipyrrinone fluorescence, we observed that a methylene bridge connecting the pyrrole and lactam nitrogens prevented $Z \rightarrow E$ double-bond isomerization, thus minimizing nonradiative decay of the dipyrrinone excited state and leading to strong fluorescence (fluorescence quantum yield, $\Phi_F \sim 0.85$ in cyclohexane[2]). The strong fluorescence observed was consistent with that detected earlier by the Lugtenburg group, which showed that the unsubstituted, parent methano-bridged dipyrrinone (Figure 1A) exhibited a $\Phi_F = 1.0 \pm 0.5$.[1] In a follow-up study comparing fluorescence of methano-, 1,2-ethano-, and 1,3-propano-bridged dipyrrinones, as might be expected, decreased fluorescence was found in the more flexible systems: ethano, $\Phi_F \sim 0.26$; propano, $\Phi_F \sim 1.2 \times 10^{-3}$ as compared to the methano.[3]

In searching for a high yield conversion of dipyrrinones to even more highly fluorescent derivatives, we found success in a one-step reaction with *N*,*N*′-carbonyldiimidazole (CDI). Thus, treatment of a typical dipyrrinone in dry dichloromethane with 5 molar equiv of CDI in the presence of DBU yielded *N*,*N*′-carbonyl-bridged dipyrrinones (Figure 2) in nearly quantitative yield. The resulting 3*H*,5*H*-dipyrrolo[1,2-*c*:2′,1′-*f*]pyrimidine-3,5-diones (see Figure 1C for numbering), to which we attach the generic name "xanthoglows" (after the product **2** formed from xanthobilirubic acid), are new members of the unusual pyrrole-based tricyclic ring system not found outside of the methano-bridged dipyrrinones,[1−3] except apparently only in a fermentation broth natural product, PD125375.[4]

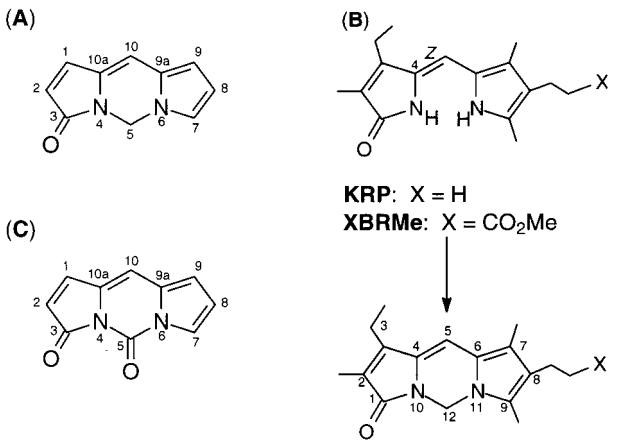

Figure 1. Dipyrrinones and their fluorescent methano-bridged analogues. (A) The unsubstituted parent methano-bridge dipyrrinone: 3*H*,5*H*-dipyrrolo[1,2-*c*:2′,1′-*f*]pyrimidin-3-one. (B) Conversion of kryptopyrromethenone (**KRP**) and methyl xanthobilirubinate (**XBRMe**) to their corresponding *N*,*N*′-methano-bridged analogues. The numbering system used is based on that of 10*H*-dipyrrinones. (C) 3*H*,5*H*-Dipyrrolo-[1,2-*c*: 2′,1′-*f*]pyrimidin-3,5-dione, a new, highly fluorescent chromophore. The number system shown is that of Figure 1A.

The structures of **1**−**8** follow logically from their known precursors and their spectroscopic properties. In addition, X-ray quality crystals of **1** (triclinic space group *P*-1 with cell dimensions $a = 9.1880(10)$ Å, $b = 10.232(2)$ Å and $c = 12.188(2)$ Å and **8** (monoclinic space group $P2(1)/n$ with cell dimensions $a = 8.2590(10)$ Å, $b = 15.3980(10)$ Å, and $c = 13.044(2)$ Å) were grown by slow diffusion of hexane into dichloromethane, and their crystal structures were determined. Both are planar structures, with N(11)−C(6)−C(5)−C(4) torsion angles of 0.9° and 1.39°, respectively, and N(10)−C(4)−C(5)−C(6) torsion angles of 1.0° and 3.06°, respectively (see Figure 2 for numbering system used). The N(10)−C(12)−N(11) angles are 112.4° and 112.1°, respectively (see Figure 2 for number system used). The C(4)−C(5) bond lengths of **1** and **8** are 1.345(7) Å and 1.342(6) Å, respectively, and the C(5)−(C6) bond lengths are 1.426(7) and 1.419(6) Å, respectively—bond distances very similar to those reported for unbridged dipyrrinones[5] and indicative of bond alternation in thesix-membered ring. Crystals of **1** show two molecules in the unit cell, stacked atop one another with imide carbonyls

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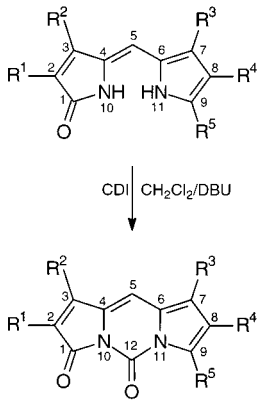

	R^1	R^2	R^3	R^4	R^5
1:	Me	Et	Me	P-Me	Me
2:	Me	Et	Me	P	Me
3:	Me	Et	Me	A-Me	Me
4:	Me	Et	Me	A	Me
5:	Me	Et	P-Me	Me	Me
6:	Me	Et	P	Me	Me
7:	Me	Et	Me	Et	Me
8:	Me	Et	Me	H	Me
9:	Me	Et	Me	$SO_3^-Na^+$	Me

A = CH_2CO_2H, A-Me = $CH_2CH_2CO_2Me$,
P = $CH_2CH_2CO_2H$, P-Me = $CH_2CH_2CO_2Me$.

Figure 2. General reaction for converting 10*H*-dipyrrinones to *N*,*N*′-carbonyldipyrrinones, the xanthoglows of this work. Xanthoglow itself is **2**. The numbering system is based on that of 10*H*-dipyrrinones.

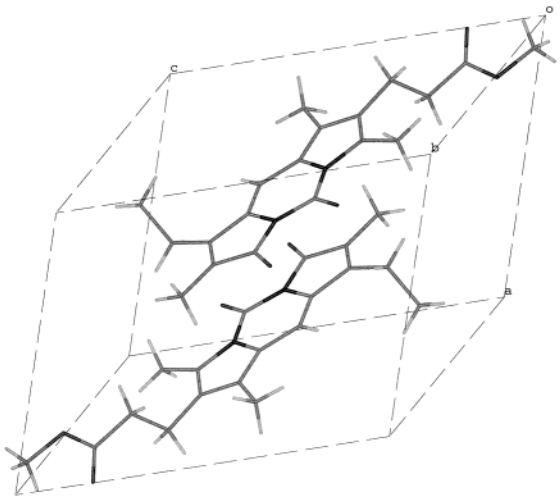

Figure 3. Packing of xanthoglow methyl ester (**1**) molecules in the unit cell. One CH_2Cl_2 molecule per molecule of **1** has been deleted for clarity of representation.

opposed, at an intermolecular distance of ~3.52 Å (Figure 3). Crystals of **8** show two complete molecules in the unit cells along with one dichloromethane molecule per dipyrrinone. The stacking arrangement of **8** is similar to that of **1**, and the interplanar intermolecular distance is ~3.40 Å.

The *N*,*N*′-carbonyl-bridged dipyrrinones gave pronounced hypochromicity and a bathochromically shifted λ_{max} of long wavelength transition (Figure 4), with only a small influence due to changes in solvent type and polarity (Table 1). Solutions of **1**−**8** were strongly fluo-

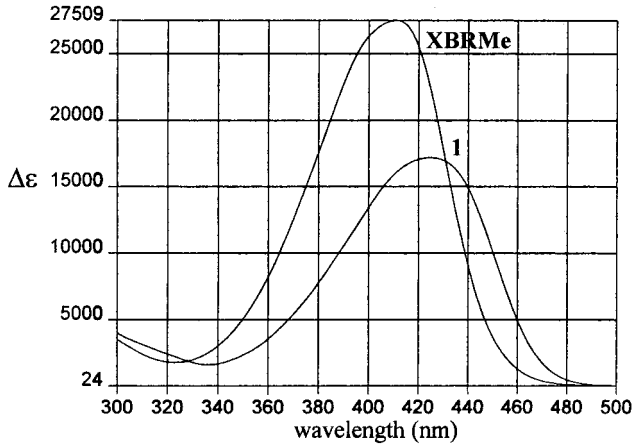

Figure 4. Partial UV−vis absorption spectrum of ~3.1×10^{-5} M **XBRMe** (Figure 1) and its *N*,*N*-carbonyl-bridged analogue **1** in DMSO.

Table 1. UV−Vis Data for *N*,*N*′-Carbonyl-Bridged Dipyrrinones 1−8[a]

bridged dipyrrinone	$\Delta\epsilon^{max}$ (λ^{max}, nm)					
	benzene	$CHCl_3$	$(CH_3)_2CO$	CH_3OH	CH_3CN	$(CH_3)_2SO$
1	15 400 (420)	18 600 (427)	18 600 (420)	17 000 (424)	18 000 (420)	17 200 (425)
2	15 700 (421)	17 000 (428)	15 100 (413)	16 500 (425)	13 700 (408)	17 200 (426)
3	16 900 (416)	17 100 (423)	16 100 (413)	17 100 (420)	15 300 (413)	17 700 (421)
4	14 800 (424)	15 500 (424)	14 800 (417)	15 300 (425)	15 600 (417)	15 800 (423)
5	15 600 (425)	17 400 (429)	15 700 (420)	16 700 (426)	15 700 (420)	18 100 (427)
6	18 300 (419)	17 600 (423)	17 100 (415)	18 100 (421)	17 100 (416)	18 600 (421)
7	15 100 (428)	17 900 (432)	16 700 (422)	17 100 (428)	16 700 (423)	17 300 (428)
8	17 500 (423)	17 200 (420)	16 800 (412)	17 400 (420)	14 100 (409)	17 900 (420)

[a] $\Delta\epsilon$ in L mol^{-1} cm^{-1} at 22 °C and concentrations ~1.5×10^{-5} M.

Table 2. Fluorescence Data for *N*,*N*′-Carbonyl-Bridged Dipyrrinones 1−8[a]

bridged dipyrrinone	C_6H_6			$CHCl_3$			CH_3OH			$(CH_3)_2SO$		
	λ^{exc}	λ^{em}	Φ_F	λ^{exc}	λ^{em}	Φ_F	λ^{exc}	λ^{em}	Φ_F	λ^{exc}	λ^{em}	Φ_F
1	320	470	1.0	330	495	0.95	330	530	0.92	330	505	1.0
2[b]	330	480	0.87	330	490	0.95	330	535	0.86	330	510	1.0
3	300	465	1.0	295	490	1.0	295	525	0.94	295	500	1.0
4[b]	270	465	0.88	295	485	0.96	330	535	0.91	295	505	1.0
5	320	470	1.0	330	495	0.95	330	535	0.82	330	510	1.0
6[b]	315	470	0.84	330	500	1.0	335	540	0.95	330	510	1.0
7	355	500	0.98	355	500	1.0	335	540	0.93	330	510	0.98
8	295	465	1.0	295	490	0.96	275	520	0.89	295	495	0.92

[a] λ^{exc} = excitation wavelength in nm, λ^{em} = emission wavelength in nm, Φ_F = fluorescence quantum yield. [b] Named as follows: **2**, xanthoglow; **4**, nor-xanthoglow; **6**, ψ-xanthoglow.

rescent to the eye. Excitation of the long wavelength band (410−430 nm) produced intense fluorescence between 465 and 540 nm (Table 2), with an unusually large Stokes shift—much larger than that seen in CH_2-bridged[1,2] (Figure 1B) and BF_2-bridged dipyrrinones.[6] The fluorescence quantum yields at room temperature in cyclohexane, determined versus 1,9-diphenylanthracene stan-

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dard, $\Phi_F = 0.90 \pm 0.02$,[7] were typically very large ($\Phi_F \geq 0.95$), even larger than those of the methano-bridged dipyrrinones.[1−3] The strong fluorescence is consistent with radiative de-excitation being the dominant relaxation pathway for return to the ground state because nonradiative pathways cannot be accessed, e.g., photoisomerization from 4*Z* to 4*E* and also molecular rotation about the C(5)−C(6) bond. The very large values of Φ_F might not be anticipated, however.

Further studies are currently underway on derivatives (such as water-soluble **9**, inter alia) of this highly fluorescent chromophore, including their lasing and photophysical properties, their photochemistry, their uses as biological probe fluorophores and pharmacophores, and their metabolism.

Experimental Section[8]

Fluorescence measurements were determined from solutions prepared as follows. Stock solutions of **1**−**8** (~2.25×10^{-4} M) were prepared by dissolving an appropriate amount of the desired *N*,*N*′-carbonyl dipyrrinone in 10 mL of chloroform. Then 100 μL of the stock solution was diluted to 5 mL (volumetric flask) with the selected solvent. The final concentrations of the solutions were ~4.5×10^{-6} M. Fluorescence measurements were then recorded at 20 °C as follows.

The method of choice for the determination of fluorescence quantum yields was to relate the quantum yield of the sample to that of a reference standard.[7] The equation used to relate these quantum yields is given by

$$\Phi_s = [(A_r F_s n_s^2)/(A_s F_r n_r^2)]\Phi_r \quad (1)$$

where the subscript s refers to the sample and the subscript r refers to the reference standard; Φ is quantum yield, *A* is the absorbance at the excitation wavelength, *F* is the integrated emission area across the band, and *n* is the index of refraction (at the sodium D line) of the solvent containing the sample and the reference standard.

The reference standard chosen was 9,10-diphenylanthracene ($\Phi_F = 0.90 \pm 0.02$ in cyclohexane[7]) because its fluorescence emission is in the same range as our samples. Once the excitation and emission spectra had been obtained for all of the samples in all of the desired solvents and the reference standard in cyclohexane, the absorbance (*A*) was determined by measuring the peak height of the excitation curves, and the integrated emission (*F*) determined by photocopying the spectra then cutting out each emission curve and weighing it on an analytic balance. The indices of refraction for the solvents used were taken from the Aldrich catalog.

Calibration of the method against perylene (Φ_F 0.78, cyclohexane)[9] and anthracene (Φ_F 0.27 ± 0.03, ethanol)[7] gave values of Φ_F 0.74 and 0.27 for 4.5×10^{-6} M solutions.

General Procedure for Inserting Bridging Carbonyl. The dipyrrinone (0.250 g) was dissolved in 70 mL of dry dichloromethane to afford a yellow solution: then carbonyldiimidazole (CDI) (0.785 g, or 5 mol equiv), DBU (0.72 mL, or 5 mol equiv), and 4 Å molecular sieves (~1 g) were added, and the mixture was heated at reflux for 12 h. The mixture was cooled, filtered to remove the sieves, and washed successively with water (2 × 100 mL) and brine (100 mL). After the mixture was dried over anhyd. $MgSO_4$, the solvent was removed (rotovap), and the crude yellow product was purified by radial chromatography using CH_2Cl_2 eluent to afford ~0.260 g (95%) of pure product.

Methyl *N*,*N*′-Carbonylxanthobilirubinate (1). Methyl xanthobilirubinate[10] (0.2500 g, 0.7902 mmol) gave 0.255 g (94%) of the bridged product: mp 140−1 °C; IR (thin film) ν 2931, 1760, 1684, 1635, 1535, 1436, 1316, 1291, 1195, 754 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.36 (1H, s), 3.65 (3H, s), 2.72 (2H, t, J = 7.4 Hz), 2.2 (3H, s), 2.51 (2H, q, J = 7.7 Hz), 2.42 (2H, t, J = 7.4 Hz), 2.10 (3H, s), 1.92 (3H, s), 1.19 (3H, t, J = 7.7 Hz) ppm; ^{13}C NMR ($CDCl_3$) δ 173.2, 167.9, 146.7, 143.5, 131.7, 130.6, 126.4, 126.4, 126.0, 120.6, 97.1, 51.9, 34.5, 19.6, 18.1, 14.0, 13.1, 9.2, 8.6 ppm. Anal. Calcd for $C_{19}H_{22}N_2O_4$ (342.40): C, 66.65; H, 6.48; N, 8.18. Found: C, 66.31; H, 6.78; N, 8.22.

***N*,*N*′-Carbonylxanthobilirubic Acid (2).** Methyl ester **1** (0.255 g, 0.745 mmol) was dissolved in 80 mL of THF and 80 mL of 0.1 M NaOH. The solution was stirred at 40 °C for 30 min. The solution was acidified with dilute HCl and then diluted with CH_2Cl_2. The solution was then washed with water (2 × 150 mL) and brine (150 mL) and dried over anhyd $MgSO_4$, and the solvent was removed. The crude yellow product was then purified by radial chromatography (CH_2Cl_2 2% vol/MeOH): mp 256−8 °C; IR (thin film) ν 2918, 1761, 1635, 1538, 1319, 1197, 1120, 755 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 10.20 (br. s, 1H), 6.39 (s, 1H), 2.76 (t, 2H, J = 7.5 Hz), 2.66 (s, 3H), 2.54 (q, 2H, J = 7.7 Hz), 2.50 (t, 2H, J = 7.5 Hz), 2.13 (s, 3H), 1.96 (s, 3H), 1.21 (t, 3H, J = 7.6 Hz) ppm; ^{13}C NMR ($CDCl_3$) δ 177.4, 168.0, 146.7, 143.6, 131.9, 130.7, 126.564, 126.556, 125.8, 120.6, 97.2, 34.3, 19.4, 18.2, 14.1, 13.3, 9.3, 8.7 ppm. Anal. Calcd for $C_{18}H_{20}N_2O_4 \cdot H_2O$ (346.39): C, 62.42; H, 6.40; N, 8.09. Found: C, 62.68; H, 6.08; N, 8.10.

Methyl *N*,*N*′-Carbonyl-nor-xanthobilirubinate (3). Methyl nor-xanthobilirubinate[11] (0.100 g, 0.331 mmol) gave 0.098 g (90%) of the bridged product: mp 236−7 °C; IR (thin film) ν 2922, 1761, 1708, 1535, 1425, 1319, 1117, 753 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.40 (s, 1H), 3.70 (s, 3H), 3.44 (s, 2H), 2.67 (s, 3H), 2.56 (q, 2H, J = 7.5 Hz), 2.13 (s, 3H), 1.96 (s, 3H), 1.21 (t, 3H, J = 7.5 Hz) ppm; ^{13}C NMR ($CDCl_3$) δ 171.5, 167.9, 146.7, 143.5, 132.8, 130.8, 126.6, 126.5, 121.0, 120.6, 97.8, 52.3, 30.0, 18.2, 14.0, 13.3, 9.4, 8.7 ppm. Anal. Calcd for $C_{18}H_{20}N_2O_4$ (328.37): C, 65.84; H, 6.14; N, 8.53. Found: C, 65.92; H, 6.08; N, 8.41.

***N*,*N*′-Carbonyl-nor-xanthobilirubic Acid (4).** Methyl ester **3** (0.098 g, 0.297 mmol) was saponified to give 0.041 g (56%) of the desired acid: mp 220−1 °C; IR (thin film) ν 3205, 2975, 1763, 1686, 1638, 1539, 1434, 1320, 1199, 1064, 755 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ ~11 (br s, 1H), 6.39 (s, 1H), 3.46 (s, 2H), 2.66 (s, 3H), 2.53 (q, 2H, J = 7.5 Hz), 2.12 (s, 3H), 1.95 (s, 3H), 1.20 (t, 3H, J = 7.5 Hz) ppm; ^{13}C NMR ($CDCl_3$) δ 176.6, 167.9, 146.8, 145.5, 133.0, 130.9, 126.7, 126.6, 120.9, 120.0, 97.2, 29.9, 18.2, 14.0, 13.3, 9.4, 8.7 ppm. Anal. Calcd for $C_{18}H_{18}N_2O_4 \cdot {}^1/_2H_2O$ (323.35): C, 63.15; H, 5.92; N, 8.68. Found: C, 63.07; H, 5.59; N, 8.59.

Methyl *N*,*N*′-Carbonyl-R-xanthobilirubinate (5). Methyl R-xanthobilirubinate[12] (1.00 g, 3.16 mmol) gave 0.91 g (85%) of the bridged product: mp 150−1 °C; IR (thin film) ν 2928, 1767, 1732, 1687, 1537, 1434, 1371, 1195, 1120, 756 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.49 (s, 1H), 3.66 (s, 3H), 2.85 (t, 2H, J = 7.5 Hz), 2.63 (s, 3H), 2.55 (q, 2H, J = 8 Hz), 2.51 (t, 2H, J = 7.5 Hz), 1.99 (s, 3H), 1.96 (s, 3H), 1.22 (t, 3H, J = 8 Hz) ppm; ^{13}C NMR ($CDCl_3$) δ 173.3, 168.0, 146.8, 143.6, 131.7, 130.9, 126.5, 126.4, 123.7, 122.5, 97.2, 52.0, 34.6, 19.9, 18.2, 14.1, 13.2, 9.1, 8.7 ppm. Anal. Calcd for $C_{19}H_{22}N_2O_4$ (342.40): C, 66.65; H, 6.48; N, 8.18. Found: C, 66.77:H, 6.64; N, 8.20.

***N*,*N*′-Carbonyl-R-xanthobilirubic Acid (6). Methyl ester 5** (0.750 g, 2.19 mmol) was saponified to give 0.567 g (79%) of the desired acid: mp 236−7 °C; IR (thin film) ν 3304, 2924, 1752, 1735, 1686, 1638, 1528, 1438, 1367, 1320, 1153, 755 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.49 (s, 1H), 2.86 (t, 2H, J = 7.5 Hz), 2.63 (s, 3H), 2.57 (t, 2H, J = 7.5 Hz), 2.56 (q, 2H, J = 8.0 Hz), 2.00 (s, 3H), 1.96 (s, 3H), 1.22 (t, 3H, J = 8.0 Hz) ppm; ^{13}C NMR (DMSO-d_6) δ 173.6, 166.9, 147.2, 142.5, 130.0, 129.7, 126.2, 14.9, 124.2, 122.4, 98.2, 34.3, 19.0, 17.2, 13.7, 12.8, 8.5, 8.1 ppm. Anal. Calcd for $C_{18}H_{20}N_2O_4CH_2O$ (346.39): C, 62.42; H, 6.40; N, 8.09. Found: C, 62.59; H, 6.02; N, 7.95.

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***N,N′*-Carbonylkryptopyrromethenone (7).** Kryptopyrromethenone[13] (0.250 g, 0.968 mmol) gave 0.262 g, 95%) of the bridged product: mp 161−2 °C; IR (thin film) ν 2962, 1761, 1684, 1635, 1533, 1456, 1327, 1306, 1192, 1120, 753 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.37 (1H, s), 2.62 (3H, s), 2.52 (2H, q, J = 7.5 Hz), 2.40 (2H, q, J = 7.5 Hz), 2.10 (3H, s), 1.93 (3H, s), 1.20 (3H, t, J = 7.5 Hz), 1.05 (3H, t, J = 7.5 Hz) ppm; ^{13}C NMR ($CDCl_3$) δ 168.0, 146.6, 143.7, 131.0, 130.3, 129.7, 126.3, 126.2, 120.9, 97.2, 18.1, 17.3, 14.9, 14.1, 13.0, 9.2, 8.6 ppm. Anal. Calcd for $C_{17}H_{20}N_2O_2$ (284.36): C, 71.81; H, 7.09; N, 9.85. Found: C, 72.00; H, 7.03; N, 9.80.

8-Des-ethyl-*N,N′*-carbonylkryptopyrromethenone (8). 8-Des-ethylkryptopyrromethenone[14] (2.00 g, 8.68 mmol) gave 1.55 g (70%) of the bridged product: mp 171−2 °C; IR (thin film) ν 2925, 1763, 1681, 1522, 1310, 1190, 1118 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.40 (1H, s), 6.02 (1H, s), 2.68 (3H, s), 2.54 (2H, q, J = 7.5 Hz), 2.15 (3H, s), 1.96 (3H, s), 1.22 (3H, t, J = 7.5 Hz) ppm; ^{13}C NMR ($CDCl_3$) δ 167.9, 146.8, 143.7, 135.2, 130.6, 127.0, 126.4, 121.1, 117.4, 97.4, 18.1, 15.8, 14.0, 10.9, 8.6 ppm. Anal. Calcd for $C_{15}H_{16}N_2O_2$ (256.31): C, 70.29; H, 6.29; N, 10.93. Found: C, 70.11; H, 6.07; N, 11.01.

Sodium 8-Des-ethyl-*N,N′*-carbonylkryptopyrromethenone-8-sulfonate (9). 8-Des-ethyl-*N,N′*-carbonylkryptopyrromethenone (**8**) (0.05 g, 0.200 mmol) was stirred at 0 °C for 1 h in 2 mL of concentrated sulfuric acid. The solution was then carefully neutralized with aqueous potassium carbonate and extracted with CH_2Cl_2 (3 × 100 mL) to remove any starting material. The water was then removed from the aqueous solution, affording a yellow powder containing the desired product contaminated with inorganic salts. Triturating the mixture with absolute ethanol afforded the more soluble desired fluorophore **9**, only slightly contaminated by inorganic salts, e.g., Na_2SO_4, that resisted complete removal and thus made combustion analysis inaccurate. The sample was pure by ^{13}C NMR, which gave the correct chemical shifts and no signals from contaminants. Compound **9**: mp >300 °C; ^1H NMR (DMSO-d_6) δ 7.02 (1H, s), 2.81 (3H, s), 2.59 (2H, q, J = 7.5 Hz), 2.25 (3H, s), 1.86 (3H, s), 1.14 (3H, t, J = 7.5 Hz) ppm; ^{13}C NMR (DMSO-d_6) δ 166.9, 147.2, 142.9, 134.5, 131.4, 130.3, 125.7, 125.1, 120.0, 98.3, 17.1, 13.7, 13.5, 10.1, 8.1 ppm; HRMS (FAB, 3-NBA) calcd 359.06657 ($C_{15}H_{16}N_2O_5SNa$, MH + Na^+), found 359.06597, Δ = 0.6 mDa, error 3.3 ppm.

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Supporting Information Available: Crystal structure atomic coordinates of **1** and **8**, tables of bond lengths, bond angles, and torsion angles are available from the Cambridge Structural Data File (CDC Nos. 178346 (**1**) and 178347 (**8**). This material is available free of charge via the Internet at http://pubs.acs.org.

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