Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C. This journal is © The Royal Society of Chemistry 2015

#### **Supporting Information**

# Solid State Red Biphotonic Excited Emission from Small Dipolar Fluorophores

Martin Ipuy,<sup>§</sup> Yuan-Yuan Liao,<sup>§</sup> Erwann Jeanneau,<sup>∫</sup> Patrice L. Baldeck,<sup>§</sup> Yann Bretonnière,<sup>§\*</sup> and Chantal Andraud <sup>§</sup>

<sup>§</sup> Laboratoire de Chimie de l'ENS de Lyon
CNRS UMR 5182, Ecole Normale Supérieure de Lyon, Université Lyon I.
46 allée d'Italie, 69364 Lyon cedex, France.

<sup>1</sup> Centre de Diffractométrie Henri Longchambon
Université Lyon I.
43 boulevard du 11 Novembre 1918, 69622 Villeurbanne Cedex, France.

\* To whom correspondence should be addressed. E-mail: yann.bretonniere@ens-lyon.fr

# Contents

Synthesis	р.3	
General remarks	p.3	
2,3-dimethoxybenzaldehyde (3d)	p.4	
Methyl 3,5-dimethoxybenzoate (5i)	p.4	
3,5-dimethoxybenzaldehyde (3i)	p.5	
References	p.5	
Crystallography	p.6	
Complementary spectroscopic data		
Compound 1a-1m characterization		
<sup>1</sup> H and <sup>13</sup> C NMR spectra	p.30	

## **Synthesis**

#### **General remarks**

Commercially available materials were purchased from Sigma-Aldrich, Alfa and Acros and used as received. Analytical thin-layer chromatography (TLC) was carried out on Merck 60 F254 precoated silica gel plate (0.2 mm thickness). Visualization was performed using a UV lamp. Column chromatography was carried out using Merck silica gel 60 (35-70 µm). Microwave syntheses were conducted in 20 mL sealed tube on a Biotage Initiator 2.5 single-mode reactor using external IR temperature control. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded at room temperature on a Bruker AC 500 spectrometer. <sup>13</sup>C NMR spectra were recorded with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as internal standard. For proton, data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad), coupling constants in Hz. Infrared spectra (IR) were recorded on a FT-IR spectrophotometer and are reported as wavelength numbers ( $v/cm^{-1}$ ). Low resolution mass spectra were taken on Agilent 6120 Quadrupole LCMS System. High resolution mass spectrometry measurements and elemental analysis were performed at the Service Central d'Analyse du CNRS (Lyon, France). Melting points were recording on a calibrated Koffler bench.

**TCF** was synthesized according to known literature procedures <sup>1</sup> from 3hydroxy-3-methylbutanone and 2 equivalent of malononitrile using a Soxhlet apparatus in anhydrous ethanol in the presence of minimal amount of Lithium ethoxide as catalyst.

2,3-dimethoxybenzyl alcohol (**4d**) was oxidized by PCC to afford the 2,3dimethoxybenzaldehyde (**3d**). 3,5-dimethoxybenzaldehyde **3i** was synthesized according to Jana *et al.*<sup>2</sup> from 2,5-dihydroxybenzoic acid (**4i**) by alkylation with dimethylsulfate to give the ester (**5i**), followed by reduction to the benzyl alcohol with LiAlH<sub>4</sub> and oxidation to the aldehyde with PCC in good overall yield (60 %).

3



**2,3-dimethoxybenzaldehyde (3d).** To a solution of (2,3-dimethoxyphenyl)methanol (2 g, 12 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (8 mL) was added PCC (3.88 g, 1.5 eq, 18 mmol). The solution was stirred vigorously at room temperature for 24 h. The mixture was filtered through a pad of Celite®

rinsing with dichloromethane (100 mL). After evaporation of the solvent, the crude product was dissolved in EtOAc, washed twice with 1 M NaCl (2×15 mL), once with 1 M aqueous HCl (10 mL), twice with saturated aqueous NaHCO<sub>3</sub> (2×10 mL) and finally twice with brine (2×10 mL). The organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated to give the product as a slightly yellow solid (1.12 g, yield=56 %). <sup>1</sup>H NMR (DMSO-d6, 500 MHz,  $\delta$ /ppm) 10.46 (s, 1 H, OH), 7.45 (dd, *J*=7.0 Hz, *J*=2.5 Hz, 1 H), 7.18 (dd, *J*=7.0 Hz, *J*=2.5 Hz, 1 H), 7.16 (t, *J*=7.0 Hz, 1 H), 4.02 (s, 3 H), 3.94 (s, 3 H); <sup>13</sup>C NMR (DMSO-d6, 125 MHz,  $\delta$ /ppm) 190.3, 153.2, 152.9, 129.9, 124.3, 119.3, 118.2, 62.5, 56.2; IR (v/cm<sup>-1</sup>) 2938, 2873, 2834, 1684, 1583, 1478, 1262, 1242, 1220, 996; Anal. calcd for C<sub>9</sub>H<sub>10</sub>O<sub>3</sub>: C, 65.05; H, 6.07; found: C 65.36, H 6.18; MS (ES, m/z) [M+Na]<sup>+</sup> 189.1; m.p. 50-52°C.



**Methyl 3,5-dimethoxybenzoate (5i).** To 3,5dihydroxybenzoic acid (5 g, 1 eq, 32.4 mmol) and  $K_2CO_3$ (18 g, 4 eq, 130 mmol) in acetone (100 mL) was added dimethyl sulfate (10.6 mL, 3.5 eq,112 mmol) and the mixture was stirred at reflux for 4 h. The reaction mixture

was cooled to room temperature and the solid filtered off and thoroughly rinsed with acetone (2×100 mL). After most of the acetone was removed under vacuum, the residue was diluted with 1 M aqueous NaOH (50 mL), stirred for 5 min and extracted three times with Et<sub>2</sub>O (100 mL then 2×50 mL). The combined organic phases were washed with 1 M HCl, aqueous NaHCO<sub>3</sub>, then dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated under vacuum to give **5i** as a slightly yellow powder. Used without further purification for the next step (4.8 g, yield=78%). Spectoscopic data are in agreement with the literature.<sup>2</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz,  $\delta$ /ppm) 7.17 (s, 2 H), 6.63 (s, 1 H), 3.94 (s, 3 H), 3.81 (s, 6 H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>,  $\delta$ /ppm) 167.0, 160.8 (2 C), 132.1, 107.2 (2 C), 105.9, 58.7, 55.7 (2 C); IR (v/cm<sup>-1</sup>): 2969, 2901, 1717, 1594, 1455, 1240, 1199, 1155, 1063, 982, 758; Anal. calcd for C<sub>10</sub>H<sub>12</sub>O<sub>4</sub>: C 61.22, H 6.16; found: C 60.93, H 6.08; MS (ES<sup>-</sup>, m/z): 198.1 for [M+H]<sup>+</sup>; m.p. 34-36°C.



**3,5-dimethoxybenzaldehyde (3i).** A solution of **5i** (4 g, 1 eq, 20.4 mmol) in dry diethyl ether (5 mL) was added dropwise at 0 °C to a suspension of LiAlH<sub>4</sub> (775 mg, 20.4 mmol, 1 eq) in dry diethyl ether (80 mL). The solution was stirred at 0 °C for 1 h and then quenched by slow

addition of a saturated aqueous Na<sub>2</sub>SO<sub>4</sub> solution. The solid was filtered off and washed with diethyl ether (100 mL). The filtrate was evaporated to afford pure (3,5dimethoxyphenyl)methanol as colorless oil (2.4 g). It was then dissolved in  $CH_2CI_2$ (8 mL) and PCC (6.59 g, 1.5 eq, 31 mmol) was added. The solution was stirred vigorously at room temperature for 24 h. The mixture was filtered through a pad of Celite® rinsing with 100 mL of dichloromethane. After evaporation of the solvent, the crude product was dissolved in EtOAc, washed twice with 1 M NaCl (2×15 mL), once with 1 M aqueous HCI (10 mL), twice with saturated aqueous NaHCO<sub>3</sub> (2×10 mL) and finally twice with brine (2×10 mL). The organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated to give 3i as a slightly yellow solid (2.57 g, yield=76 % for the 2 steps). Spectroscopic data are in agreement with literature.<sup>2</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz,  $\delta$ /ppm) 9.91 (s, 1 H), 7.01 (d, 2 H, J = 2.3 Hz), 6.70 (t, 1 H, J = 2.3 Hz), 3.84 (s, 6 H, -OCH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, δ/ppm) 192.0, 161.4 (2 C), 138.5, 107.3 (2 C), 107.2, 55.8 (2 C); IR (v/cm<sup>-1</sup>) 3073, 2942, 2848, 1693, 1590, 1467, 1297, 1205, 1157; Anal. calcd for C<sub>9</sub>H<sub>10</sub>O<sub>3</sub>: C 65.05, H 6.07; found: C 64.88, H 6.22; MS (ES<sup>-</sup>, m/z) 189.1 for [M+Na]<sup>+</sup>; m.p. 46-48°C.

#### References

(1) He, M., Leslie, T. M., and Sinicropi, J. A. (2002) α-Hydroxy Ketone Precursors Leading to a Novel Class of Electro-optic Acceptors. *Chem. Mater. 14*, 2393-2400.

(2) Jana, N., and Nanda, S. (2012) Asymmetric Total Syntheses of Cochliomycin A and Zeaenol. *Eur. J. Org. Chem. 2012*, 4313-4320.

# Crystallography

Table SI-1 provides some geometric data (selected bond lengths and angles definied in Figure SI-1) for all compounds.



**Figure SI-1.** Molecular structure showing the selected bonds and angles, common to all compounds.

**Table SI-1.** Selected Bond Distances (Å) and Torsion Angle (°) for all compounds.

	<b>a</b> <sub>1</sub>	<b>b</b> <sub>1</sub>	<b>a</b> <sub>2</sub>	<i>b</i> <sub>2</sub>	<b>a</b> <sub>3</sub>	<i>b</i> <sub>3</sub>	α
1c	1.463(3)	1.344(3)	1.435(3)	1.366(3)	1.445(3)	1.368(3)	0
1d	1.456(3)	1.351(2)	1.431(2)	1.364(2)	1.443(3)	1.368(3)	8.7
1e	1.433(4)	1.355(4)	1.421(4)	1.367(3)	1.430(3)	1.367(4)	1.8
1g	1.448(4)	1.353(4)	1.425(4)	1.369(4)	1.434(4)	1.363(4)	12.6
1i	1.469(2)	1.342(2)	1.433(2)	1.361(2)	1.448(2)	1.365(2)	0
1j	1.441(3)	1.356(3)	1.430(3)	1.366(3)	1.435(3)	1.373(3)	2.5
1m	1.429(3)	1.357(3)	1.417(3)	1.378(3)	1.429(3)	1.379(3)	6.2

CCDC 1429526 (1c), 1429527 (1d), 1429528 (1e), 1429529 (1g), 1429531 (1i), 1429530 (1j), and 1429532 (1m) contain the crystallographic data for this paper (cif). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.



Figure SI-2. Emission of compounds 1a, 1b, 1d, 1g and 1j in ethylene glycol.



Figure SI-3. Emission of compounds 1c, 1e, 1f, 1j and 1m in ethylene glycol.



**Figure SI-4.** Emission of a 10  $\mu$ M solution of **1h** in various solvents under a handle UV lamp (365 nm) showing the enhancement of fluorescence due to an increase of viscosity. From left to right: THF, ethylene glycol, glycerol/methanol (90/10) and frozen glycerol/methanol (90/10).



**Figure SI-5.** Absorption spectra of **1b** (50  $\mu$ M) in THF/water mixture with different water fraction ( $f_w$ ). The corresponding emission spectra are given in the main text, Fig. 3a.



**Figure SI-6.** Absorption (top) and fluorescence (bottom) spectra of **1b** at 50  $\mu$ M in THF/water mixture with different water fraction ( $f_w$ ). Insets: change of peak intensity with  $f_w$ .



**Figure SI-7.** Absorption (top) and fluorescence (bottom) spectra of **1c** at 50  $\mu$ M in THF/water mixture with different water fraction ( $f_w$ ). Insets: change of peak intensity with  $f_w$ .



**Figure SI-8.** Absorption (top) and fluorescence (bottom) spectra of **1d** at 50  $\mu$ M in THF/water mixture with different water fraction ( $f_w$ ). Insets: change of peak intensity with  $f_w$ .



**Figure SI-9.** Absorption (top) and fluorescence (bottom) spectra of **1e** at 50  $\mu$ M in THF/water mixture with different water fraction ( $f_w$ ). Insets: change of peak intensity with  $f_w$ .



**Figure SI-10.** Absorption (top) and fluorescence (bottom) spectra of **1f** at 50  $\mu$ M in THF/water mixture with different water fraction ( $f_w$ ). Insets: change of peak intensity with  $f_w$ .



**Figure SI-11.** Absorption spectra of **1g** (50  $\mu$ M) in THF/water mixture with different water fraction ( $f_w$ ). The corresponding emission spectra are given in the main text, Fig. 3b.



**Figure SI-12.** Absorption spectra of **1h** (50  $\mu$ M) in THF/water mixture with different water fraction ( $f_w$ ). The corresponding emission spectra are given in the main text, Fig. 3d.



**Figure SI-13.** Absorption (top) and fluorescence (bottom) spectra of **1i** at 50  $\mu$ M in THF/water mixture with different water fraction ( $f_w$ ). Insets: change of peak intensity with  $f_w$ .



**Figure SI-14.** Absorption (top) and fluorescence (bottom) spectra of **1j** at 50  $\mu$ M in THF/water mixture with different water fraction ( $f_w$ ). Insets: change of peak intensity with  $f_w$ .



**Figure SI-15.** Absorption (top) and fluorescence (bottom) spectra of **1k** at 50  $\mu$ M in THF/water mixture with different water fraction ( $f_w$ ). Insets: change of peak intensity with  $f_w$ .



**Figure SI-16.** Absorption spectra of **1b** (50  $\mu$ M) in THF/water mixture with different water fraction ( $f_w$ ). The corresponding emission spectra are given in the main text, Fig. 3d.



**Figure SI-17.** Absorption (top) and fluorescence (bottom) spectra of **1m** at 50  $\mu$ M in THF/water mixture with different water fraction ( $f_w$ ). Insets: change of peak intensity with  $f_w$ .



**Figure SI-18.** Excitation spectra of monomethoxy compounds **1a-1c** at 50  $\mu$ M in THF/water mixture giving the maximum emission.

![](_page_20_Figure_2.jpeg)

**Figure SI-19.** Excitation spectra of dimethoxy compounds **1d**, **1e**, **1g**, **1h**, and **1i** at 50  $\mu$ M in THF/water mixture giving the maximum emission.

![](_page_21_Figure_0.jpeg)

**Figure SI-20.** Excitation spectra of trimethoxy compounds **1j** and **1m** at 50  $\mu$ M in THF/water mixture giving the maximum emission.

![](_page_21_Figure_2.jpeg)

Figure SI-21. Solid state excitation (dots) and emission spectra of 1a.

![](_page_22_Figure_0.jpeg)

Figure SI-22. Solid state excitation (dots) and emission spectra of 1b.

![](_page_22_Figure_2.jpeg)

Figure SI-23. Solid state excitation (dots) and emission spectra of 1c.

![](_page_23_Figure_0.jpeg)

Figure SI-24. Solid state excitation (dots) and emission spectra of 1d.

![](_page_23_Figure_2.jpeg)

Figure SI-25. Solid state excitation (dots) and emission spectra of 1e.

![](_page_24_Figure_0.jpeg)

Figure SI-26. Solid state excitation (dots) and emission spectra of 1f.

![](_page_24_Figure_2.jpeg)

Figure SI-27. Solid state excitation (dots) and emission spectra of 1g.

![](_page_25_Figure_0.jpeg)

Figure SI-28. Solid state excitation (dots) and emission spectra of 1h.

![](_page_25_Figure_2.jpeg)

Figure SI-29. Solid state excitation (dots) and emission spectra of 1i.

![](_page_26_Figure_0.jpeg)

Figure SI-30. Solid state excitation (dots) and emission spectra of 1j.

![](_page_26_Figure_2.jpeg)

Figure SI-31. Solid state excitation (dots) and emission spectra of 1k.

![](_page_27_Figure_0.jpeg)

Figure SI-32. Solid state excitation (dots) and emission spectra of 1I.

![](_page_27_Figure_2.jpeg)

Figure SI-33. Solid state excitation (dots) and emission spectra of 1m.

![](_page_28_Figure_0.jpeg)

Figure SI-34. Fluorescence intensity at 600 nm vs Laser power for compound 1a showing the quadratic dependence and the two-photon character of the excitation ( $\lambda_{exc}$ =800 nm)

# Compound 1a-1m characterization <sup>1</sup>H and <sup>13</sup> C NMR spectra

![](_page_30_Figure_0.jpeg)

#### Figure SI-35. <sup>1</sup>H NMR spectrum of **1a** (DMSO-d6, 500 MHz)

![](_page_31_Figure_0.jpeg)

#### Figure SI-36. <sup>13</sup>C NMR spectrum of **1a** (DMSO-d6, 125 MHz)

![](_page_32_Figure_0.jpeg)

#### Figure SI-37. <sup>1</sup>H NMR spectrum of 1b (DMSO-d6, 500 MHz)

![](_page_33_Figure_0.jpeg)

#### Figure SI-38. <sup>13</sup>C NMR spectrum of 1b (DMSO-d6, 125 MHz)

![](_page_34_Figure_0.jpeg)

## Figure SI-39. <sup>1</sup>H NMR spectrum of 1c (DMSO-d6, 500 MHz)

![](_page_35_Figure_0.jpeg)

#### Figure SI-40. <sup>13</sup>C NMR spectrum of 1c (DMSO-d6, 125 MHz)

![](_page_36_Figure_0.jpeg)

#### Figure SI-41. <sup>1</sup>H NMR spectrum of 1d (DMSO-d6, 500 MHz)

![](_page_37_Figure_0.jpeg)

#### Figure SI-42. <sup>13</sup>C NMR spectrum of 1d (DMSO-d6, 125 MHz)

![](_page_38_Figure_0.jpeg)

#### Figure SI-43. <sup>1</sup>H NMR spectrum of **1e** (DMSO-d6, 500 MHz)

![](_page_39_Figure_0.jpeg)

#### Figure SI-44. <sup>13</sup>C NMR spectrum of 1e (DMSO-d6, 125 MHz)

![](_page_40_Figure_0.jpeg)

## Figure SI-45. <sup>1</sup>H NMR spectrum of 1f (DMSO-d6, 500 MHz)

![](_page_41_Figure_0.jpeg)

#### Figure SI-46. <sup>13</sup>C NMR spectrum of 1f (DMSO-d6, 125 MHz)

![](_page_42_Figure_0.jpeg)

## Figure SI-47. <sup>1</sup>H NMR spectrum of **1g** (DMSO-d6, 500 MHz)

![](_page_43_Figure_0.jpeg)

#### Figure SI-48. <sup>13</sup>C NMR spectrum of 1g (DMSO-d6, 125 MHz)

![](_page_44_Figure_0.jpeg)

#### Figure SI-49. <sup>1</sup>H NMR spectrum of 1h (DMSO-d6, 500 MHz)

![](_page_45_Figure_0.jpeg)

#### Figure SI-50. <sup>13</sup>C NMR spectrum of 1h (DMSO-d6, 125 MHz)

![](_page_46_Figure_0.jpeg)

## Figure SI-51. <sup>1</sup>H NMR spectrum of 1i (DMSO-d6, 500 MHz)

![](_page_47_Figure_0.jpeg)

#### Figure SI-52. <sup>13</sup>C NMR spectrum of 1i (DMSO-d6, 125 MHz)

![](_page_48_Figure_0.jpeg)

#### Figure SI-53. <sup>1</sup>H NMR spectrum of 1j (DMSO-d6, 500 MHz)

![](_page_49_Figure_0.jpeg)

#### Figure SI-54. <sup>13</sup>C NMR spectrum of 1j (DMSO-d6, 125 MHz)

![](_page_50_Figure_0.jpeg)

![](_page_50_Figure_1.jpeg)

![](_page_51_Figure_0.jpeg)

#### Figure SI-56. <sup>13</sup>C NMR spectrum of 1k (DMSO-d6, 125 MHz)

![](_page_52_Figure_0.jpeg)

## Figure SI-57. <sup>1</sup>H NMR spectrum of 1I (DMSO-d6, 500 MHz)

![](_page_53_Figure_0.jpeg)

#### Figure SI-58. <sup>13</sup>C NMR spectrum of 1I (DMSO-d6, 125 MHz)

![](_page_54_Figure_0.jpeg)

#### Figure SI-59. <sup>1</sup>H NMR spectrum of 1m (DMSO-d6, 500 MHz)

![](_page_55_Figure_0.jpeg)

#### Figure SI-60. <sup>13</sup>C NMR spectrum of 1m (DMSO-d6, 125 MHz)