

## Supporting Information

### Synthesis of dyes CC101-CC103

Compounds **1**, **2**, **3**, **5a**, **5b** and **5c** were synthesized following the literatures.<sup>1,2,3</sup>

#### (E)-ethyl 2-cyano-2-(2-methyl-4H-chromen-4-ylidene)acetate (**4**).

Under N<sub>2</sub> atmosphere, a mixture of **3** (13.1 g, 81.9 mmol), ethyl 2-cyanoacetate (11.3 g, 100 mmol), ammonium acetate (1.54 g), acetic acid (6 mL) was refluxed in toluene (50 mL) for 18 h. Then water was added into the reaction mixture and the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was removed by rotary evaporation. The residue was purified by column chromatography on silica gel to give **3** as yellow liquid (12.9 g, 62%).  
<sup>1</sup>H-NMR (400 MHz, Acetone-d<sub>6</sub>) δ 8.07 (d, *J* = 7.9 Hz, 1H), 7.75 (t, *J* = 8.7 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 1H), 7.48 – 7.37 (t, *J* = 8.1 Hz, 1H), 6.15 (s, 1H), 4.30 – 4.19 (q, *J* = 11.2 Hz, 2H), 2.41 (s, 3H), 1.07 (m, *J* = 12.2 Hz, 3H).  
GCT/TOF HRMS-EI (m/z): [M]<sup>+</sup> calcd for C<sub>15</sub>H<sub>13</sub>NO<sub>3</sub>, 255.0895; found, 255.0894.

#### (Z)-ethyl 2-cyano-2-(2-((E)-2-(1,2,2,4-tetramethyl-1,2,3,4-tetrahydroquinolin-6-yl)vinyl)-4H-chromen-4-ylidene)acetate (**6a**).

**4** (500 mg, 1.96 mmol), **5a** (434 mg, 2 mmol) and piperidine (0.5 mL) were refluxed in acetonitrile (30 mL) for 8 h. The reaction solution was removed by rotary evaporation. The residue was purified by column chromatography on silica gel to give **6a** as red liquid (650 mg, 73%).  
<sup>1</sup>H-NMR (400 MHz, Acetone-d<sub>6</sub>) δ 7.50 – 7.38 (m, *J* = 16.5 Hz, 7H), 7.09 (d, *J* = 16.1 Hz, 1H), 7.00 (d, *J* = 16.1 Hz, 1H), 6.18 (s, 1H), 4.24 (q, *J* = 11.2 Hz, 2H), 2.96 – 2.94 (m, 4H), 1.85 (d, *J* = 13.0 Hz, 2H), 1.25 (s, 6H), 1.07 (m, *J* = 12.2 Hz, 6H). GCT/TOF HRMS-EI (m/z): [M]<sup>+</sup> calcd for C<sub>29</sub>H<sub>30</sub>N<sub>2</sub>O<sub>3</sub>, 454.2256; found, 454.2254.

#### (Z)-ethyl 2-cyano-2-(2-((E)-2-(7-methoxy-1,2,2,4-tetramethyl-1,2,3,4-tetrahydroquinolin-6-yl)vinyl)-4H-chromen-4-ylidene)acetate (**6b**).

A procedure similar to that for **6a** but with compound **5b** (780 mg, 2 mmol) instead of compound **5a**. **6b** as red liquid (711 mg, 75%).  
<sup>1</sup>H-NMR (400 MHz, Acetone-d<sub>6</sub>) δ 7.84 (s, 1H), 7.50 – 7.38 (m, 4H), 7.09 (d, *J* = 16.1 Hz, 1H), 7.00 (d, *J* = 16.1 Hz, 1H), 6.76 (s, 1H), 6.18 (s, 1H), 4.24 (q, *J* = 11.2 Hz, 2H), 3.89 (s, 3H), 2.96 – 2.94 (m,

4H), 1.85 (d,  $J = 13.0$  Hz, 2H), 1.25 (s, 6H), 1.07 (m,  $J = 12.2$  Hz, 6H). GCT/TOF HRMS-EI (m/z):  $[M]^+$  calcd for  $C_{30}H_{32}N_2O_4$ , 484.2362; found, 484.2364.

**(Z)-ethyl2-cyano-2-(2-((E)-2-(2,4-dihexyl-7-methoxy-1,2-dimethyl-1,2,3,4-tetrahydroquinolin-6-yl)vinyl)-4H-chromen-4-ylidene)acetate (6c).**

A procedure similar to that for **6a** but with compound **5c** (494 mg, 2 mmol) instead of compound **5a**. **6c** as red liquid (856 mg, 70%).  $^1H$ -NMR (400 MHz, Acetone- $d_6$ )  $\delta$  7.84 (s, 1H), 7.55 – 7.37 (m, 4H), 7.08 (d,  $J = 16.0$  Hz, 1H), 6.99 (d,  $J = 16.1$  Hz, 1H), 6.75 (s, 1H), 6.20 (s, 1H), 4.30 – 4.19 (q,  $J = 11.2$  Hz, 2H), 3.90 (s, 3H), 2.98 – 2.94 (m, 4H), 1.85 (d,  $J = 13.0$  Hz, 2H), 1.59 – 1.45 (m,  $J = 16.2$  Hz, 7H), 1.32 – 1.25 (m,  $J = 13.2$  Hz, 19H), 0.88 (t,  $J = 11$  Hz, 6H). GCT/TOF HRMS-EI (m/z):  $[M]^+$  calcd for  $C_{40}H_{52}N_2O_4$ , 624.3927; found, 624.3927.

**(Z)-2-cyano-2-(2-((E)-2-(1,2,2,4-tetramethyl-1,2,3,4-tetrahydroquinolin-6-yl)vinyl)-4H-chromen-4-ylidene)acetic acid (7a).**

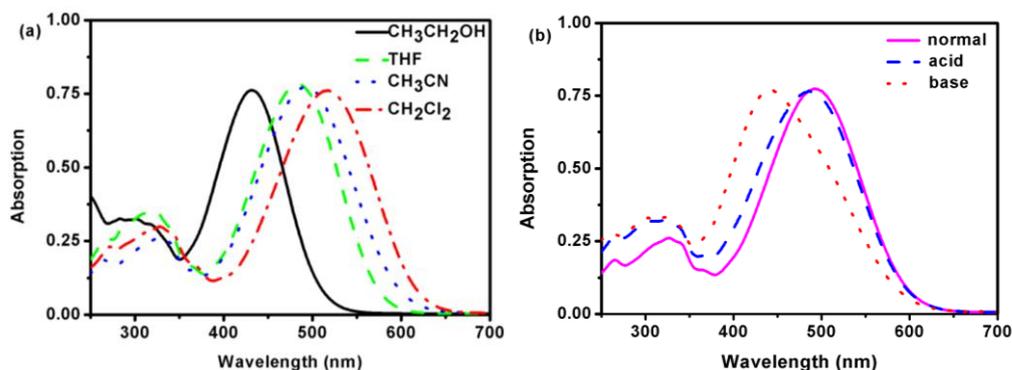
**6a** (650 mg, 1.43 mmol) and 2 M aqueous solution of LiOH (5 mL) were heated to 40 °C over night. Then water was added into the reaction mixture and the mixture was extracted with  $CH_2Cl_2$ . The organic layer was removed by rotary evaporation. The residue was purified by column chromatography on silica gel to give **7a** as red solid (530 mg, 87%).  $^1H$ -NMR (400 MHz, Acetone- $d_6$ )  $\delta$  7.50 – 7.38 (m,  $J = 16.5$  Hz, 7H), 7.09 (d,  $J = 16.1$  Hz, 1H), 7.00 (d,  $J = 16.1$  Hz, 1H), 6.18 (s, 1H), 2.96 – 2.94 (m, 4H), 1.85 (d,  $J = 13.0$  Hz, 2H), 1.25 (s, 6H), 1.07 (m,  $J = 12.2$  Hz, 3H). GCT/TOF HRMS-EI (m/z):  $[M]^+$  calcd for  $C_{27}H_{26}N_2O_3$ , 426.1943; found, 426.1942.

**(Z)-2-cyano-2-(2-((E)-2-(7-methoxy-1,2,2,4-tetramethyl-1,2,3,4-tetrahydroquinolin-6-yl)vinyl)-4H-chromen-4-ylidene)acetic acid (7b).**

A procedure similar to that for **7a** but with compound **6b** (711 mg, 1.5 mmol) instead of compound **6a**. **6b** as red liquid (580 mg, 85%).  $^1H$ -NMR (400 MHz, Acetone- $d_6$ )  $\delta$  7.84 (s, 1H), 7.50 – 7.38 (m, 4H), 7.09 (d,  $J = 16.1$  Hz, 1H), 7.00 (d,  $J = 16.1$  Hz, 1H), 6.76 (s, 1H), 6.18 (s, 1H), 3.89 (s, 3H), 2.96 – 2.94 (m, 4H), 1.85 (d,  $J = 13.0$  Hz, 2H), 1.25 (s, 6H), 1.07 (m,  $J = 12.2$  Hz, 3H). GCT/TOF HRMS-EI (m/z):  $[M]^+$  calcd for  $C_{28}H_{28}N_2O_4$ , 456.2049; found, 456.2049.

**(Z)-2-cyano-2-(2-((E)-2-(2,4-dihexyl-7-methoxy-1,2-dimethyl-1,2,3,4-tetrahydroquinolin-6-yl)vinyl)-4H-chromen-4-ylidene)acetic acid (7c).**

A procedure similar to that for **7c** but with compound **6c** (856 mg, 1.4 mmol) instead of compound **6a**. **6c** as red liquid (650 mg, 78%). <sup>1</sup>H-NMR (400 MHz, Acetone-d<sub>6</sub>) δ 7.84 (s, 1H), 7.55 – 7.37 (m, 4H), 7.08 (d, *J* = 16.0 Hz, 1H), 6.99 (d, *J* = 16.1 Hz, 1H), 6.75 (s, 1H), 6.20 (s, 1H), 3.90 (s, 3H), 2.98 – 2.94 (m, 4H), 1.85 (d, *J* = 13.0 Hz, 2H), 1.59 – 1.45 (m, *J* = 16.2 Hz, 7H), 1.32 – 1.25 (m, *J* = 13.2 Hz, 16H), 0.88 (t, *J* = 11 Hz, 6H). GCT/TOF HRMS-EI (*m/z*): [M]<sup>+</sup> calcd for C<sub>37</sub>H<sub>46</sub>N<sub>2</sub>O<sub>3</sub>, 566.3508; found, 566.3508.

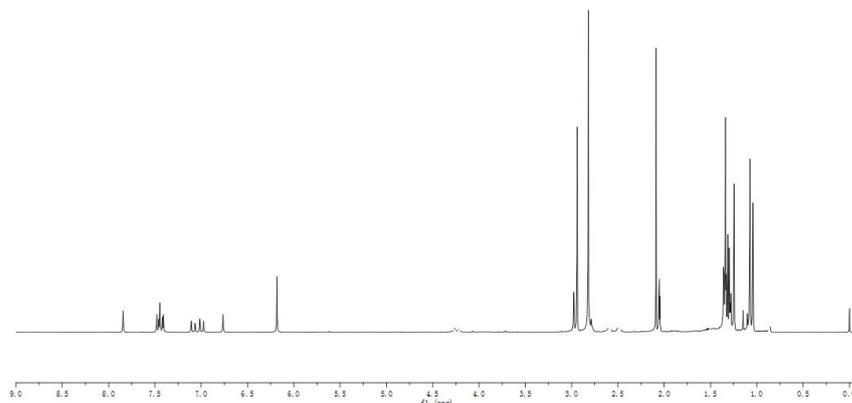


**Fig.S1** a) UV-Vis spectra of CC101 in different solvents (CH<sub>3</sub>CH<sub>2</sub>OH, THF, CH<sub>3</sub>CN and CH<sub>2</sub>Cl<sub>2</sub>); b) UV-Vis spectra of CC101 in CH<sub>3</sub>CN in the presence of acid (acetic acid, 2 × 10<sup>-5</sup> M) or base (LiOH, 2 × 10<sup>-5</sup> M)

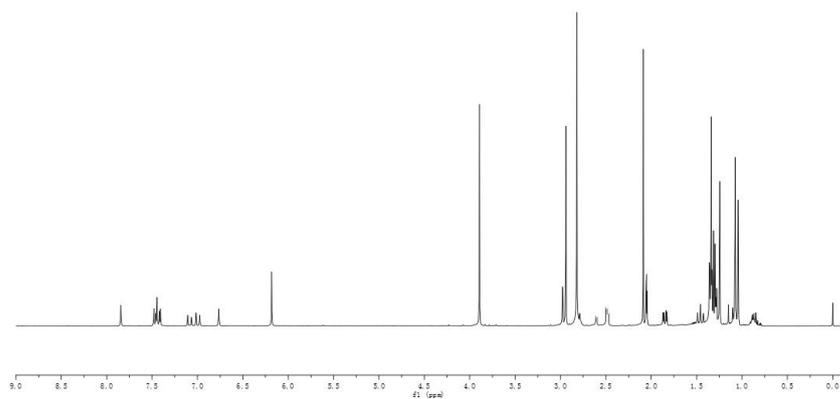
dye	$\lambda_{\max}$ (nm)	oscillator strength <i>f</i>
<b>CC101</b>	384	0.3055
	495	1.0698
<b>CC102</b>	381	0.2763
	490	1.0847
<b>CC103</b>	381	0.2980
	492	1.0933

**Fig.S2** Computed excitation wavelength and oscillator strength at a B3LYP/6-31G(d) level under vacuum condition.

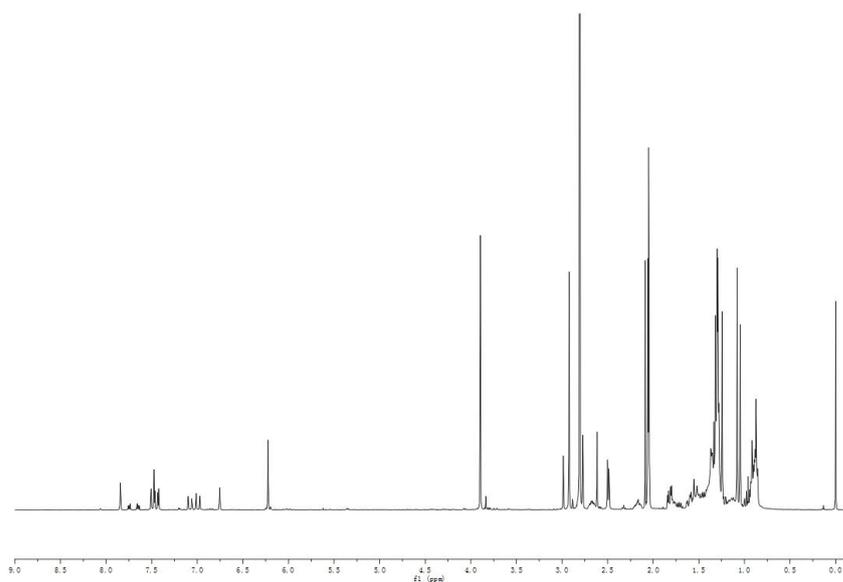
Compound **7a**



Compound 7b



Compound 7c



Reference

[1] Urs Séquin, *Helvetica Chimica Acta*, 1981, 64, 2654-2664.

[2] Yan Hao, Xichuan Yang, Jiayan Cong, Anders Hagfeldt, Licheng Sun, *Tetrahedron*, 2012, 68, 552-558.

[3] Ming Cheng, Xichuan Yang, Jiajia Li, Cheng Chen, Jianghua Zhao, Yu Wang, Licheng Sun, *Chem. Eur. J.*, 2012, 18, 16196-16202.