

Synthesis and NMR characterisation of the reference dyes

The dyes used as references for yellow (1), magenta (2), and cyan (3) colour (Fig. 1) were prepared according to procedures previously reported in the literature and their molecular structures were checked by recording their ^1H and ^{13}C NMR spectra using a Bruker *Avance Neo 400* spectrometer. The synthesis and the NMR characterisation for each compound is described below.

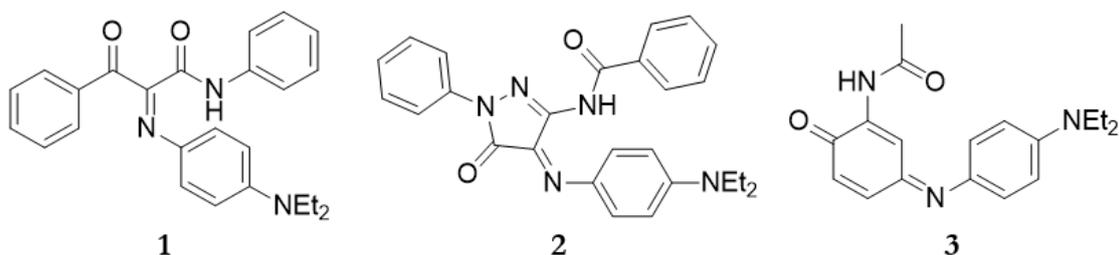


Figure 1: Structure of the dyes used as reference for yellow (1), magenta (2) and cyan (3) colour.

2-((4-(Diethylamino)phenyl)imino)-3-oxo-N,3-diphenylpropanamide (1), the dye chosen as a reference for yellow colour, was prepared adapting a procedure reported by Sano [19]. In a 100 mL round-bottomed flask, 2-benzoylacetanilide (470 mg, 1.97 mmol) and *N,N*-diethylbenzene-1,4-diamine (693 μL , 4.18 mmol) were added while stirring to a 2 wt% NaOH aqueous solution (30 mL). A solution of ammonium persulfate (450 mg, 1.98 mmol) in deionized water (20 mL) was then added dropwise during 1 h maintaining a continuous magnetic stirring. The mixture was allowed to stir for additional 30 min after the end of the addition. An orange solid formed during the reaction. The mixture was extracted with CH_2Cl_2 (4 \times 25 mL), the organic layers combined, and the solvent evaporated under vacuum. The residue (1.05 g) was recrystallized from EtOH (5 mL) affording the product as an orange solid in 36% yield (280 mg, 0.70 mmol). NMR analyses of the compound are in accordance with previous reports [18].

^1H NMR (400 MHz, CDCl_3) δ 9.43 (br s, 1H, NH), 7.89 (d, $J = 7.7$ Hz, 2H, Ar-H), 7.71 (d, $J = 7.9$ Hz, 2H, Ar-H), 7.56 (t, $J = 7.4$ Hz, 1H, Ar-H), 7.43 (t, $J = 7.7$ Hz, 2H, Ar-H), 7.35 (t, $J = 7.9$ Hz, 2H, Ar-H), 7.17 (d, $J = 9.1$ Hz, 2H, Ar-H), 7.12 (t, $J = 7.4$ Hz, 1H, Ar-H), 6.49 (d, $J = 9.1$ Hz, 2H, Ar-H), 3.32 (q, $J = 7.1$ Hz, 4H, CH_2CH_3), 1.12 ppm (t, $J = 7.1$ Hz, 6H, CH_2CH_3).

^{13}C NMR (100 MHz, CDCl_3) δ 198.6 (C), 161.4 (C), 151.2 (C), 148.6 (C), 137.6 (C), 134.8 (C), 134.5 (CH), 132.2 (C), 129.21 (CH), 129.20 (CH), 129.0 (CH), 127.4 (CH), 124.4 (CH), 119.5 (CH), 111.4 (CH), 44.6 (CH_2), 12.8 ppm (CH_3).

N-(4-((4-(Diethylamino)phenyl)imino)-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-3-yl)benzamide (2), the dye chosen as a reference for magenta colour, was prepared according to a procedure reported by Vittum [20]. *N*-(5-Oxo-1-phenyl-4,5-dihydro-1H-pyrazol-3-yl)benzamide (4) used in the synthesis of the dye was prepared by benzoylation of commercial 5-amino-2-phenyl-1H-pyrazol-3(2H)-one as reported before [21]. Pyrazolone 4 (317 mg, 1.14 mmol), EtOAc (60 mL) and 4% aqueous ammonia (60 mL) were added to a solution of *N,N*-diethylbenzene-1,4-diamine (265 μL , 1.59 mmol) in EtOH (60 mL). A solution of AgNO_3 in deionized water (30 mL) was then added over 25 minutes

while stirring. The mixture was allowed to stir at room temperature for an additional hour after the end of the addition. The reaction mixture was filtered on filter paper and the residue washed twice with EtOAc (3 mL). The biphasic mixture was extracted with EtOAc (4 × 60 mL), and the combined organic phases dried over Na₂SO₄ and filtered. Evaporation of the solvent under vacuum afforded the crude product which was purified by flash column chromatography on silica gel (eluent CH₂Cl₂ + 1% Et₃N). The product was obtained as a dark purple solid in 86 % yield (431 mg, 0.98 mmol). NMR analyses of the compound are in accordance with previous reports [18].

¹H NMR (400 MHz, CDCl₃) δ 8.88 (br s, 1H, NH), 8.45 (d, *J* = 9.4 Hz, 2H, Ar-*H*), 8.10 (d, *J* = 7.8 Hz, 2H, Ar-*H*), 7.99 (d, *J* = 7.4 Hz, 2H, Ar-*H*), 7.61 (t, *J* = 7.3 Hz, 1H), 7.55 (d, *J* = 7.4 Hz, 2H), 7.42 (t, *J* = 7.8 Hz, 3H, Ar-*H*), 7.18 (t, *J* = 7.4 Hz, 1H, Ar-*H*), 6.74 (d, *J* = 9.4 Hz, 2H, Ar-*H*), 3.53 (q, *J* = 7.1 Hz, 4H), 1.28 ppm (t, *J* = 7.1 Hz, 6H).

¹³C NMR (100 MHz, CDCl₃) δ 163.5 (C), 152.9 (C), 152.3 (C), 144.1 (C), 138.9 (C), 135.3 (C), 135.2 (CH), 134.0 (C), 133.8 (C), 132.6 (CH), 129.1 (CH), 128.7 (CH), 127.6 (CH), 124.9 (CH), 119.2 (CH), 111.5 (CH), 45.4 (CH₂), 12.9 ppm (CH₃).

***N*-(3-((4-(Diethylamino)phenyl)imino)-6-oxocyclohexa-1,4-dien-1-yl)acetamide (3)**, the dye chosen as a reference for cyan colour, was prepared adapting a procedure reported in [22]. AgNO₃ aqueous solution (2.80 g, 17.0 mmol in 15.7 mL) was added to a NaCl (1.14 g, 19.6 mmol) solution in deionized water (23.5 mL) under vigorous stirring. A silver chloride suspension was obtained to which Na₂CO₃·H₂O (1.86 g, 15.0 mmol) and subsequently a solution of *N*-(2-hydroxyphenyl)acetamide (314 mg, 2.08 mmol) in EtOH (15.7 mL) were added. Finally, a solution of *N,N*-diethylbenzene-1,4-diamine (330 μL, 1.98 mmol) in 0.13 M HCl (15.3 mL) was added dropwise over 15 minutes and the reaction mixture stirred for additional 1 h 20 min. EtOAc (50 mL) was then added and the solid removed by filtration on filter paper. The organic phase was separated and the product extracted with EtOAc (2 × 50 mL). The combined organic phases were washed with brine (2 × 50 mL), dried over Na₂SO₄, filtered and the solvent was evaporated under vacuum. The crude was purified by filtration on a short column of silica gel (eluent CH₂Cl₂ + 2% Et₃N) and then recrystallized from Et₂O (8 mL). The product was obtained as a dark crystalline solid with golden reflection in 68 % yield (444 mg, 1.42 mmol). NMR analyses of the compound are in accordance with previous reports [18].

¹H NMR (400 MHz, C₆D₆) 8.92 (d, *J* = 2.6 Hz, 1H, quinone-*H*), 7.94 (br s, 1H, NH), 7.48 (d, *J* = 9.1 Hz, 1H, 2H, Ar-*H*), 7.32 (dd, *J* = 9.8 and 2.6 Hz, 1H, quinone-*H*), 6.53 (d, *J* = 9.8 Hz, 1H, quinone-*H*), 6.41 (d, *J* = 9.1 Hz, 1H, 2H, Ar-*H*), 2.76 (q, *J* = 7.1 Hz, 4H, CH₂CH₃), 1.35 (s, 3H, COCH₃), 0.73 ppm (t, *J* = 7.1 Hz, 6H, CH₂CH₃).

¹H NMR (400 MHz, CDCl₃) δ 8.43 (d, *J* = 2.5 Hz, 1H, quinone-*H*), 8.23 (br s, 1H, NH), 7.31 (dd, *J* = 9.8 and 2.5 Hz, 1H, quinone-*H*), 7.22 (d, *J* = 9.0 Hz, 2H, Ar-*H*), 6.75 (d, *J* = 9.0 Hz, 2H, Ar-*H*), 6.69 (d, *J* = 9.8 Hz, 1H, quinone-*H*), 3.44 (q, *J* = 7.1 Hz, 4H, CH₂CH₃), 2.20 (s, 3H, COCH₃), 1.22 ppm (t, *J* = 7.1 Hz, 6H, CH₂CH₃).

¹³C NMR (100 MHz, CDCl₃) δ 181.1 (C), 169.4 (C), 152.4 (C), 148.8 (C), 143.8 (CH), 139.8 (C), 135. (C), 127.9 (CH), 127.6 (CH), 112.1 (CH), 109.9 (CH), 44.7 (CH₂), 25.0 (CH₃), 12.9 ppm (CH₃).

References

Please, consider the reference list in the main text of the paper.