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Supporting Information

Rapid synthesis of 3-cyanopyridine-derived chromophores with two-dimensional tunability and solvatochromic photophysical properties

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CONTENTS.

General Procedures.

Commercially available reagents were used without further purification; solvents were dried by standard procedures. Light petroleum refers to the fraction with bp 40-60 °C. Flash chromatography was carried out using Merck Kieselgel 60 H silica or Matrex silica 60. Analytical thin layer chromatography was carried out using aluminium-backed plates coated with Merck Kieselgel 60 GF_{254} that were visualised under UV light (at 254 and/or 360 nm). Microwave irradiation experiments were performed using a self-tunable CEM Discover® focused monomodal microwave synthesizer at the given temperature by varying the irradiation power (initial power given in parentheses) and monitoring temperature through the instrument's in-built IR sensor. Infra-red (IR) spectra were recorded in the range 4000-600 cm^{-1} using KBr disks or between NaCl plates and are reported in cm^{-1}. Nuclear magnetic resonance (NMR) spectra were recorded in $CDCl_3$ at 25 °C unless stated otherwise and were reported in ppm; *J* values were recorded in Hz and multiplicities were expressed by the usual conventions. Low-resolution mass spectra (MS) were determined using electrospray ionization (ES) unless otherwise stated. *In vacuo* refers to evaporation at reduced pressure using a rotary evaporator and diaphragm pump, followed by the removal of trace volatiles using a vacuum (oil) pump.

Typical Experimental Procedure for Microwave-Assisted Synthesis of 3-Cyanopyridines 3.

A solution of 3–aminocrotononitrile **1** (0.57 mmol, 1 equiv), 1-phenyl-2-propyn-1-ol **2a** (1.14 mmol, 2 equiv) and barium manganate (1.70 mmol, 3 equiv) in ethanol–acetic acid (5.0 mL) (5:1) was irradiated at 170 °C at an initial power of 150 W (which was moderated to maintain constant temperature) in a sealed Pyrex™ vessel for 15 min in a self-tuned single-mode CEM Discover® microwave synthesizer. The mixture was cooled rapidly to room temperature, by passing compressed air through the microwave cavity for 5 min, and then filtered through Celite. The filtrate was poured into water (15 mL) and extracted with ethyl acetate (8 mL). The aqueous layer was further extracted with ethyl acetate (8 mL) and the organic extracts were combined, washed sequentially with saturated aqueous sodium hydrogen carbonate solution (10 mL) and brine (10 mL), dried (Na_2SO_4) and evaporated *in vacuo*. Purification by flash chromatography on silica, eluting with EtOAc–light petroleum (1:6), gave *3-cyanopyridine* **3a** (0.10 g, 86%).

2-Methyl-6-phenylnicotinonitrile (3a) (0.10 g, 86%) was prepared according to the given procedure using 1-phenyl-2-propyn-1-ol (**2a**) (0.14 mL, 1.14 mmol) and was obtained as colourless crystals, mp 137–139 °C (EtOH) (Lit.,[1] mp 139–140 °C) (Found: MH^+, 195.0916. $C_{13}H_{11}N_2$ [MH^+] requires 195.0917); ν_{max} 2222, 1640, 1579, 1444, 1384, 1285, 783, 741, 694; $\lambda_{max}(CHCl_3)$/nm 224 (log ε 4.62), 302 (log ε 4.18); δ_H (400 MHz; $CDCl_3$) 8.96 (2H, m, 2',6'-H), 7.86 (1H, d, *J* 8.2, 4-H), 7.58 (1H, d, *J* 8.2, 5-H), 7.43 (3H, m, 3',4',5'-H), 2.76 (3H, s, 2-Me); δ_C (100 MHz; $CDCl_3$) 161.6 (C), 159.8 (C), 140.7 (CH), 137.7 (C), 133.1 (C), 130.4 (CH), 129.0 (CH), 127.4 (CH), 117.4 (CH), 106.7 (CN), 23.9 (CH_3); *m/z* (APcI) 195 (MH^+, 100%).

4,6-Bis(4-methoxyphenyl)-2-methylnicotinonitrile (3b) (0.17 g, 88%) was prepared according to the given procedure using 1,3-bis(4-methoxyphenyl)prop-2-yn-1-ol (**2b**)[2] (0.28 mL, 1.14 mmol) and was obtained as colourless crystals, mp 172-173 °C (EtOH) (Lit.,[3] mp 172-173 °C) (Found: MH^+, 331.1435. $C_{21}H_{19}N_2O_2$ [MH^+] requires 331.1447); ν_{max} 3050, 2210, 1640, 1600, 1450, 1314, 1250, 1090, 912; $\lambda_{max}(CHCl_3)$/nm 236 (log ε 4.58), 322 (log ε 4.18); δ_H (400 MHz; $CDCl_3$) 8.08 (2H, d, *J* 8.9, 2',6'-H), 7.63 (2H, d, *J* 8.9, 2'',6''-H), 7.61 (1H, s, 5-H), 7.08 (2H, d, *J* 8.9, 3',5'-H), 7.04 (2H, d, *J* 8.9, 3'',5''-H), 3.94 (3H, s, OMe), 3.92 (3H, s, OMe), 2.90 (3H, s, 2-Me); δ_C (100 MHz; $CDCl_3$) 166.2 (C), 157.2 (C), 156.6 (C), 155.4 (C), 153.1 (C), 147.7 (C), 134.4 (C), 124.9 (C), 124.3 (CH), 123.4 (CH), 112.3 (CH), 111.2 (CH), 108.9 (CH), 106.2 (CN), 59.9 (CH_3), 58.9 (CH_3), 28.9 (CH_3); *m/z* 331 (MH^+, 100%).

2-Methyl-4-[4-(dimethylamino)phenyl]-6-(4-methoxyphenyl)nicotinonitrile (3c) (0.18 g, 92%) was prepared according to the given procedure using 3-[4-(dimethylamino)phenyl]-1-(4-methoxyphenyl)prop-2-yn-1-ol (**2c**) (0.30 mL, 1.14 mmol) and was obtained as luminescent yellow coloured crystals, mp 195-196 °C (EtOH) (Lit.,[3] mp 194-196 °C) (Found: MH^+, 344.1759. $C_{22}H_{22}N_3O$ [MH^+] requires 344.1763); ν_{max} 3042, 2992, 2211, 1634, 1598, 1461, 1300, 1250, 1100, 1004, 920; $\lambda_{max}(CHCl_3)$/nm 240 (log ε 4.56), 374 (log ε 4.15); δ_H (400 MHz; $CDCl_3$) 7.96 (2H, d, *J* 8.9, 2',6'-H), 7.54 (2H, d, *J* 8.9, 2'',6''-H), 7.52 (1H, s, 5-H), 6.94 (2H, d, *J* 8.9, 3',5'-H), 6.76 (2H, d, *J* 8.9, 3'',5''-H), 3.82 (3H, s, OMe), 2.98 (6H, s, NMe_2), 2.88 (3H, s, 2-Me); δ_C (100 MHz; $CDCl_3$) 164.8 (C), 163.6 (C), 161.5 (C), 152.7 (C), 151.5 (C), 150.9 (C), 148.6 (C), 143.3 (C), 129.9 (CH), 128.9 (CH), 124.0 (CH), 116.8 (CH), 114.4 (CH), 106.9 (CN), 55.5 (CH_3), 40.4 (CH_3×2), 24.5 (CH_3); *m/z* 344 (MH^+, 100%).

2-Methyl-4-(4-bromophenyl)-6-(4-methoxyphenyl)nicotinonitrile (3d) (0.19 g, 89%) was prepared according to the given procedure using 3-(4-bromophenyl)-1-(4-methoxyphenyl)prop-2-yn-1-ol (**2d**) (0.33 mL, 1.14 mmol) and was obtained as colourless crystals, mp 224-226 °C (EtOH) (Found: MH^+, 379.2498. $C_{20}H_{16}BrN_2O$ [MH^+] requires 379.0368); ν_{max} 3032, 2972, 2213, 1632, 1588, 1451, 1229, 1240, 1102, 1006, 918; $\lambda_{max}(CHCl_3)$/nm 228 (log ε 4.60), 314 (log ε 4.28); δ_H (400 MHz; $CDCl_3$) 7.98 (2H, d, *J* 8.9, 2',6'-H), 7.64 (2H, d, *J* 8.8, 3'',5''-H), 7.54 (1H, s, 5-H), 6.92 (2H, d, *J* 8.9, 3',5'-H), 6.82 (2H, d, *J* 8.8, 2'',6''-H), 3.82 (3H, s, OMe), 2.90 (3H, s, 2-Me); δ_C (100 MHz; $CDCl_3$) 165.8 (C), 164.8 (C), 162.5 (C), 154.7 (C), 153.5 (C), 152.4 (C), 149.6 (C), 144.4 (C), 130.2 (CH), 129.4 (CH), 125.0 (CH), 118.8 (CH), 116.4 (CH), 105.2 (CN), 55.4 (CH_3), 26.4 (CH_3); *m/z* (ES) 379 (MH^+, 100%), 381 (97).

2-Methyl-6-4-(4-methoxyphenyl)-(2-pyridyl)nicotinonitrile (3e) (0.14 g, 84%) was prepared according to the given procedure using 3-[4-methoxyphenyl]-1-(2-pyridyl)prop-2-yn-1-ol (**2e**) (0.25 mL, 1.14 mmol) and was obtained as colourless crystals, mp 197-199 °C (EtOH) (Lit.,[3] mp 197-199 °C) (Found: MH^+, 302.3419. $C_{19}H_{16}N_3O$ [MH^+] requires 302.1215); ν_{max} 3042, 2982, 2233, 1630, 1568, 1450, 1326, 1230, 1106, 1008, 922; $\lambda_{max}(CHCl_3)$/nm 238 (log ε 4.76), 336 (log ε 4.56); δ_H (400 MHz; $CDCl_3$) 8.72 (1H, d, *J* 6.4, 2'-H), 8.56 (1H, d, *J* 7.9, 5'-H), 8.46 (1H, s, 5-H), 7.88 (1H, m, 4'-H), 7.72 (2H, d, *J* 8.8, 2'',6''-H), 7.48 (1H, m, 3'-H), 7.08 (2H, d, *J* 8.8, 3'',5''-H), 3.90 (3H, s, OMe), 2.96 (3H, s, 2-Me); δ_C (100 MHz; $CDCl_3$) 161.2 (C), 161.0 (C), 159.6 (C), 155.4 (C), 154.4 (C), 149.3 (CH), 137.2 (CH), 130.3 (C), 128.4 (CH), 128.0 (CH), 124.0 (CH), 120.0 (CH), 118.7 (CH), 117.0 (CH), 105.6 (CN), 55.6 (CH_3), 24.4 (CH_3); *m/z* 302 (MH^+, 100%).

2-Methyl-4-[4-(dimethylamino)phenyl]-6-(2-pyridyl)nicotinonitrile (3f) (0.14 g, 80%) was prepared according to the given procedure using 3-[4-(dimethylamino)phenyl]-1-(2-pyridyl)prop-2-yn-1-ol (**2f**) (0.26 mL, 1.14 mmol) and was obtained as luminescent green coloured crystals, mp 263-265 °C (EtOH) (Lit.,[3] mp 263-265 °C) (Found: MH^+, 315.3835. $C_{20}H_{19}N_4$ [MH^+] requires 315.1531); ν_{max} 3046, 2984, 2221, 1632, 1565, 1452, 1323, 1230, 1104, 1006, 920; $\lambda_{max}(CHCl_3)$/nm 246 (log ε 4.68), 385 (log ε 4.38);δ_H (400 MHz; $CDCl_3$) 8.62 (1H, d, *J* 6, 2'-H), 8.42 (1H, d, *J* 8.0, 5'-H), 8.32 (1H, s, 5-H), 7.78 (1H, m, 4'-H), 7.62 (2H, d, *J* 8.8, 2'',6''-H), 7.28 (1H, m, 3'-H), 6.74 (2H, d, *J* 8.8, 3'',5''-H), 2.98 (6H, s, NMe_2), 2.82 (3H, s, 2-Me); δ_C (100 MHz; $CDCl_3$) 160.2 (C), 159.0 (C), 158.6 (C), 153.2 (C), 152.4 (C), 148.2 (CH), 135.8 (CH), 129.8 (C), 127.4 (CH), 127.0 (CH), 122.0 (CH), 119.8 (CH), 116.9 (CH), 115.0 (CH), 106.2 (CN), 40.6 (CH_3×2), 23.6 (CH_3); *m/z* 315 (MH^+, 100%).

2-Methyl-4-(4-bromophenyl)-6-(2-pyridyl)nicotinonitrile (3g) (0.17 g, 87%) was prepared according to the given procedure using 3-(4-bromophenyl)-1-(2-pyridyl)prop-2-yn-1-ol (**2g**) (0.30 mL, 1.14 mmol) and was obtained as colourless crystals, mp 296-298 °C (EtOH) (Found: MH^+, 350.2124. $C_{18}H_{13}BrN_3$ [MH^+] requires 350.0215); ν_{max} 3052, 2988, 2216, 1630, 1558, 1450, 1322, 1228, 1102, 1004, 916; $\lambda_{max}(CHCl_3)$/nm 226 (log ε 4.64), 310 (log ε 4.26); δ_H (400 MHz; $CDCl_3$) 8.68 (1H, d, *J* 6, 2'-H), 8.52 (1H, d, *J* 8.0, 5'-H), 8.40 (1H, s, 5-H), 7.87 (1H, m, 4'-H), 7.72 (2H, d, *J* 8.8, 3'',5''-H), 7.34 (1H, m, 3'-H), 6.80 (2H, d, *J* 8.8, 2'',6''-H), 2.98 (3H, s, 2-Me); δ_C (100 MHz; $CDCl_3$) 164.2 (C), 160.0 (C), 159.6 (C), 156.2 (C), 154.6 (C), 150.2 (CH), 138.8 (CH), 130.8 (C), 128.4 (CH), 127.9 (CH), 124.0 (CH), 120.8 (CH), 119.6 (CH), 118.0 (CH), 104.8 (CN), 26.4 (CH_3); *m/z* 350 (MH^+, 100%), 352(97).

2-Methyl-4-(4-methoxyphenyl)-6-[4-(piperidino)phenyl]nicotinonitrile (3h) (0.19 g, 88%) was prepared according to the given procedure using 3-(4-methoxyphenyl)-1-[4-(piperidino)phenyl]prop-2-yn-1-ol (**2h**) (0.33 mL, 1.14 mmol) and was obtained as light yellow crystals, mp 212-214 °C (EtOH) (Found: MH^+, 384.4854. $C_{25}H_{26}N_3O$ [MH^+] requires 384.1998); ν_{max} 3054, 2994, 2218, 1636, 1560, 1456, 1326, 1230, 1106, 1008, 922; $\lambda_{max}(CHCl_3)$/nm 238 (log ε 4.38), 336 (log ε 4.50); δ_H (400 MHz; $CDCl_3$) 8.00 (2H, d, *J* 8.9, 2',6'-H), 7.82 (2H, d, *J* 8.8, 2''',6'''-H), 7.66 (1H, s, 5-H), 7.02 (2H, d, *J* 8.8, 3''',5'''-H), 6.90 (2H, d, *J* 8.9, 3',5'-H), 3.70 (3H, s, OMe), 3.34 (4H, t, *J* 4.9, 2'',6''-CH_2), 2.88 (3H, s, 2-Me), 1.68 (6H, m, 3'',4'',5''-CH_2); δ_C (100 MHz; $CDCl_3$) 161.2 (C), 161.0 (C), 158.9 (C), 154.4 (C), 148.2 (C), 130.4 (C), 128.5 (CH), 128.4 (CH), 125.8 (C), 118.6 (CH), 117.0 (CH), 114.8 (CH), 114.6 (CH), 106.2 (CN), 55.9 (CH_3), 52.4 (CH_2×2), 25.9 (CH_2×2), 25.5 (CH_2), 24.4 (CH_3); *m/z* 384 (MH^+, 100%).

2-Methyl-4-[4-(dimethylamino)phenyl)-6-[4-(piperidino)phenyl]nicotinonitrile (3i) (0.19 g, 86%) was prepared according to the given procedure using 3-[4-(dimethylamino)phenyl]-1-[4-(piperidino)phenyl]prop-2-yn-1-ol (**2i**) (0.35 mL, 1.14 mmol) and was obtained as luminescent green coloured crystals, mp 214-216 °C (EtOH) (Found: MH^+, 397.5214. $C_{26}H_{29}N_4$ [MH^+] requires 397.2314); ν_{max} 3056, 2998, 2219, 1636, 1562, 1457, 1328, 1231, 1104, 1008, 924; $\lambda_{max}(CHCl_3)$/nm 248 (log ε 4.24), 364 (log ε 4.60); δ_H (400 MHz; $CDCl_3$) 7.98 (2H, d, *J* 8.9, 2',6'-H), 7.62 (2H, d, *J* 8.8, 2''',6'''-H), 7.53 (1H, s, 5-H), 7.00 (2H, d, *J* 8.9, 3',5'-H), 6.84 (2H, d, *J* 8.8, 3''',5'''-H), 3.34 (4H, t, *J* 4.9, 2'',6''-CH_2), 3.08 (6H, s, NMe_2), 2.86 (3H, s, 2-Me), 1.70 (6H, m, 3'',4'',5''-CH_2); δ_C (100 MHz; $CDCl_3$) 160.2 (C), 159.0 (C), 158.6 (C), 153.4 (C), 148.0 (C), 129.4 (C), 127.5 (CH), 127.4 (CH), 124.8 (C), 116.6 (CH), 116.0 (CH), 113.8 (CH), 112.6 (CH), 106.8 (CN), 55.4 (CH_3), 52.6 (CH_2×2), 40.6 (CH_3×2), 26.0 (CH_2×2), 25.8 (CH_2), 24.2 (CH_3); *m/z* 397 (MH^+, 100%).

2-Methyl-4-(4-bromophenyl)-6-[4-(piperidino)phenyl]nicotinonitrile (3j) (0.20 g, 82%) was prepared according to the given procedure using 3-(4-bromophenyl)-1-[4-(piperidino)phenyl]prop-2-yn-1-ol (**2j**) (0.39 mL, 1.14 mmol) and was obtained as light coloured crystals, mp 296-298 °C (EtOH) (Found: MH^+, 432.3558. $C_{24}H_{23}BrN_3$ [MH^+] requires 432.0997); ν_{max} 3052, 2994, 2216, 1630, 1554, 1450, 1320, 1230, 1100, 1004, 918; $\lambda_{max}(CHCl_3)$/nm 220 (log ε 4.48), 312 (log ε 4.10);δ_H (400 MHz; $CDCl_3$) 8.00 (2H, d, *J* 8.9, 2',6'-H), 7.68 (2H, d, *J* 8.8, 3''',5'''-H), 7.60 (1H, s, 5-H), 7.00 (2H, d, *J* 8.8, 2''',6'''-H), 6.90 (2H, d, *J* 8.9, 3',5'-H), 3.36 (4H, t, *J* 4.9, 2'',6''-CH_2), 2.89 (3H, s, 2-Me), 1.72 (6H, m, 3'',4'',5''-CH_2); δ_C (100 MHz; $CDCl_3$) 162.2 (C), 161.0 (C), 160.4 (C), 156.4 (C), 150.0 (C), 132.4 (C), 130.5 (CH), 128.4 (CH), 126.8 (C), 118.6 (CH), 117.0 (CH), 116.8 (CH), 114.6 (CH), 105.0 (CN), 55.6 (CH_3), 52.8 (CH_2×2), 28.0 (CH_2), 25.8 (CH_2×2), 24.8 (CH_3); *m/z* 432 (MH^+, 100%), 434 (97).

Typical Experimental Procedure for Copper(I)-Mediated *N*-Arylation (Table 3).

A solution of pyrrolidine (2 mmol, 2 equiv), Cu(phen)(PPh_3)Br (10 mol%), neocuproine (10 mol%) and potassium *tert*-butoxide (2 mmol, 2 equiv) in toluene (10 mL) was stirred at room temperature for 5 min. A solution of 2-methyl-4-(4-bromophenyl)-6-(4-methoxphenyl)nicotinonitrile (**3d**) (1 mmol, 1 equiv) in toluene (5 mL) was added dropwise and the reaction mixture was heated at reflux overnight. After cooling rapidly to room temperature, the mixture was filtered through Celite. The filtrate was poured into water (15 mL) and extracted with diethyl ether (15 mL). The aqueous layer was further extracted with ether (15 mL) and organic extracts were combined, dried (Na_2SO_4) and evaporated *in vacuo*. Purification by flash chromatography on silica, eluting with EtOAc–light petroleum (1:6), gave the *4-[4-(pyrrolidino)phenyl]-substituted 3-cyanopyridine* **3k** (0.32 g, 86%).

2-Methyl-6-(4-methoxphenyl)-4-[4-(pyrrolidino)phenyl]nicotinonitrile (3k) (0.32 g, 86%) was prepared according to the given procedure using 2-methyl-4-(4-bromophenyl)-6-(4-methoxphenyl)nicotinonitrile (**3d**) (0.38 g, 1.00 mmol) and was obtained as luminescent green coloured crystals, mp 196-198 °C (EtOH) (Found: MH^+, 370.4588. $C_{24}H_{24}N_3O$ [MH^+] requires 370.1841); ν_{max} 3044, 2998, 2218, 1639, 1599, 1464, 1302, 1254, 1106, 1008, 922; $\lambda_{max}(CHCl_3)$/nm 252 (log ε 4.48), 386 (log ε 4.03); δ_H (400 MHz; $CDCl_3$) 7.98 (2H, d, *J* 8.9, 2',6'-H), 7.52 (2H, d, *J* 8.8, 2'',6''-H), 7.50 (1H, s, 5-H), 6.98 (2H, d, *J* 8.9, 3',5'-H), 6.70 (2H, d, *J* 8.8, 3'',5''-H), 3.82 (3H, s, OMe), 3.20 (4H, t, *J* 6.6, 2''',5'''-CH_2), 2.86 (3H, s, 2-Me), 1.96 (4H, t, *J* 6.6, 3''',4'''-CH_2); δ_C (100 MHz; $CDCl_3$) 162.8 (C), 160.6 (C), 161.2 (C), 150.7 (C), 150.5 (C), 150.8 (C), 146.6 (C), 143.0 (C), 129.4 (CH), 128.6 (CH), 124.0 (CH), 116.8 (CH), 114.6 (CH), 107.0 (CN), 55.5 (CH_3), 46.4 (CH_2×2), 28.6 (CH_2×2), 24.2 (CH_3); *m/z* 370 (MH^+, 100%).

2-Methyl-4-[4-(pyrrolidino)phenyl]-6-(2-pyridyl)nicotinonitrile (3l) (0.25 g, 72%) was prepared according to the given procedure using 2-methyl-4-(4-bromophenyl)-6-(2-pyridyl)nicotinonitrile (**3g**) (0.35 g, 1.00 mmol), catalysed by Cu(neocup)(PPh_3)Br[4] (10 mol%), and was obtained as luminescent green coloured crystals, mp 266-268 °C (EtOH) (Found: MH^+, 341.1780. $C_{22}H_{21}N_4$ [MH^+] requires 341.1766); ν_{max} 3048, 2988, 2216, 1634, 1569, 1458, 1329, 1232, 1105, 1008, 923; $\lambda_{max}(CHCl_3)$/nm 258 (log ε 4.60), 397 (log ε 4.16); δ_H (400 MHz; $CDCl_3$) 8.64 (1H, d, *J* 6.4, 2'-H), 8.42 (1H, d, *J* 8.0, 5'-H), 8.31 (1H, s, 5-H), 7.78 (1H, m, 4'-H), 7.60(2H, d, *J* 8.8, 2'',6''-H), 7.28 (1H, m, 3'-H), 6.60 (2H, d, *J* 8.8, 3'',5''-H), 3.20 (4H, t, *J* 6.6, 2''',5'''-CH_2), 2.82 (3H, s, 2-Me), 1.96 (4H, t, *J* 6.6, 3''',4'''-CH_2); δ_C (100 MHz; $CDCl_3$) 160.0 (C), 158.0 (C), 158.6 (C), 152.2 (C), 151.4 (C), 148.0 (CH), 133.8 (CH), 129.6 (C), 126.8 (CH), 127.0 (CH), 121.0 (CH), 119.4 (CH), 116.8 (CH), 114.8 (CH), 106.6 (CN), 46.4 (CH_2×2), 28.6 (CH_2×2), 23.6 (CH_3); *m/z* (APcI) 341 (MH^+, 100%).

2-Methyl-4-[4-(pyrrolidino)phenyl)]-6-[4-(piperidino)phenyl]nicotinonitrile (3m) (0.37 g, 88%) was prepared according to the given procedure using 2-methyl-4-(4-bromophenyl)-6-[4-(piperidino)phenyl]nicotinonitrile **(3j)** (0.44 g, 1.00 mmol) and was obtained as luminescent yellow coloured crystals, mp 216-218 °C (EtOH) (Found: MH^+, 423.2532. $C_{28}H_{31}N_4$ [MH^+] requires 423.2549); ν_{max} 3058, 2999, 2220, 1637, 1564, 1459, 1329, 1233, 1106, 1008, 926; $\lambda_{max}(CHCl_3)$/nm 252 (log ε 4.20), 370 (log ε 4.58); δ_H (400 MHz; $CDCl_3$) 7.98 (2H, d, *J* 8.9, 2',6'-H), 7.60 (2H, d, *J* 8.8, 2''',6'''-H), 7.58 (1H, s, 5-H), 7.00 (2H, d, *J* 8.9, 3',5'-H), 6.68 (2H, d, *J* 8.8, 3''',5'''-H), 3.48 (4H, t, *J* 6.6, 2'''',5''''-CH_2), 3.34 (4H, t, *J* 4.9, 2'',6''-CH_2), 2.88 (3H, s, 2-Me), 2.06 (4H, t, *J* 6.6, 3'''',4''''-CH_2), 1.70 (6H, m, 3'',4'',5''-CH_2); δ_C (100 MHz; $CDCl_3$) 159.8 (C), 159.0 (C), 158.4 (C), 153.3 (C), 148.1 (C), 129.2 (C), 126.9 (CH), 127.3 (CH), 124.5 (C), 116.4 (CH), 115.8 (CH),

113.6 (CH), 112.4 (CH), 107.2 (CN), 55.2 (CH_3), 52.6 (CH_2×2), 50.4 (CH_2×2), 28.6 (CH_2×2), 26.0 (CH_2), 25.8 (CH_2×2), 24.0 (CH_3); *m/z* (APcI) 423 (MH^+, 100%).

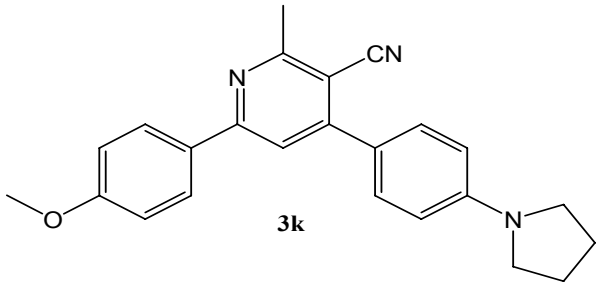
Photophysical Analysis.

a. General Measurements.

Electronic absorption spectra were measured upon 2.5×10^{-8} mol L^{-1} solutions in aerated cyclohexane, chloroform, methanol, acetonitrile and DMSO for selected compounds at room temperature from 200 to 600 nm on a Varian Cary 500 Scan UV-vis NIR spectrophotometer using Cary WinUV Scan Application software. Steady-state luminescence analyses were processed using the same 2.5×10^{-8} mol L^{-1} solutions as for the absorption measurements. A Perkin-Elmer Luminescence Spectrometer LS55 with FL Winlab v. 4.00.02 software was used over the range 300-800 nm. Radiative lifetimes were measured using a JobinYvon-Horiba Fluorolog spectrometer fitted with a JY TBX picosecond photodetection module. Aerated solution samples for luminescence lifetime decays were irradiated using a pulsed NanoLED configured for 355 nm or 372 nm output and emission detected at emission maxima. Data sets were obtained using the JY-Horiba FluorHub single photon counting module and lifetimes determined using the provided decay analysis software package, v6.1. Fluorescence quantum yields, Φ_F, were measured in various solvents using 2.5×10^{-8} mol L^{-1} fluorescein in 0.1 mol L^{-1} NaOH as the reference standard (Φ_F = 0.79).[5] Each chromophore was diluted with the appropriate solvent until the absorbance [λ_{max}(ICT)] at 320-400 nm was calibrated between 0.05 and 0.01.[6] The fluorescence spectra were then recorded with excitation wavelengths between 320-400 nm. The peak was integrated using Microsoft Excel. This process was repeated three times at different optical densities. The integrated intensity was plotted against the absorbance of each sample. The slopes of the resulting lines were calculated using Microsoft Excel. The quantum yield was then determined by the following equation, taking into account the respective refractive indices: [7]

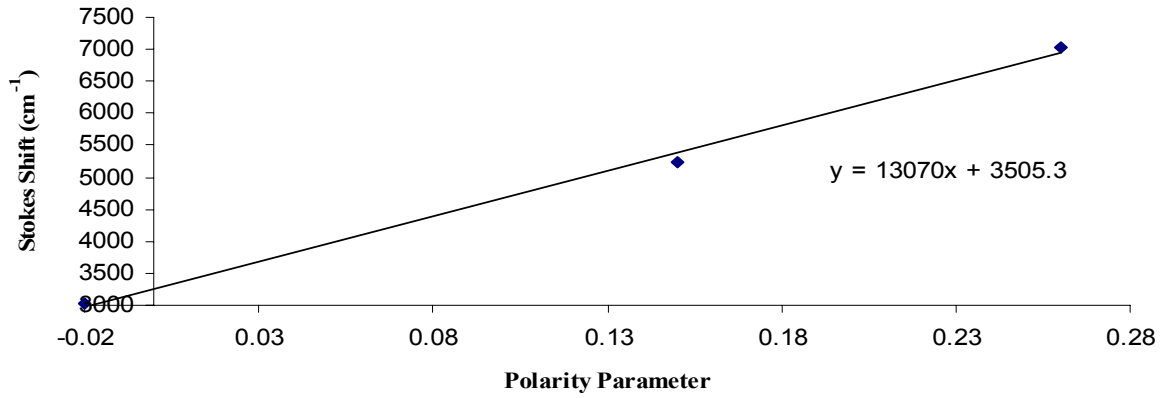
$$\phi_{sample} = \phi_{std} \frac{(Slope_{sample})}{(Slope_{std})} \frac{(\eta^2_{sample})}{(\eta^2_{std})}$$

b. The Difference of The Dipole Moment between The Ground and Excited States (3k)



3k

Lippert-Mataga Plot: 3k in Various Solvets



Solvent	ε	n	Δf	$\Delta\upsilon_{st}$ (cm^{-1})	Slope (cm^{-1})	$\Delta\mu_{eg}$ (D)
Cyclohexane	2.02	1.426	-0.02	3364	**13070**	**17.6**
Chloroform	4.89	1.446	0.15	5160		
DMSO	46.71	1.479	0.26	7089		

The change of the dipole moment $\Delta\mu_{eg}$ between the ground and the excited states can be calculated using the Lippert-Mataga equation, where:

$$\Delta\upsilon_{st} = \frac{2\Delta\mu_{eg}^2}{hca^3}\Delta f + const \quad \&$$

$$\Delta f = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}$$

From the slope of the plot shown above, the magnitude of $\Delta\mu_{eg}$ can be obtained as **17.6 D** by estimating the cavity radius ***a*** equals to **6.06 Å** from the molecular volume as calculated from the molecular weight of **3k** and the molecular density for general D-A type molecules,[8] which equals to 0.95 g cm^{-3}.

c. Solvatochromic Properties of Nicotinonitrile 3k

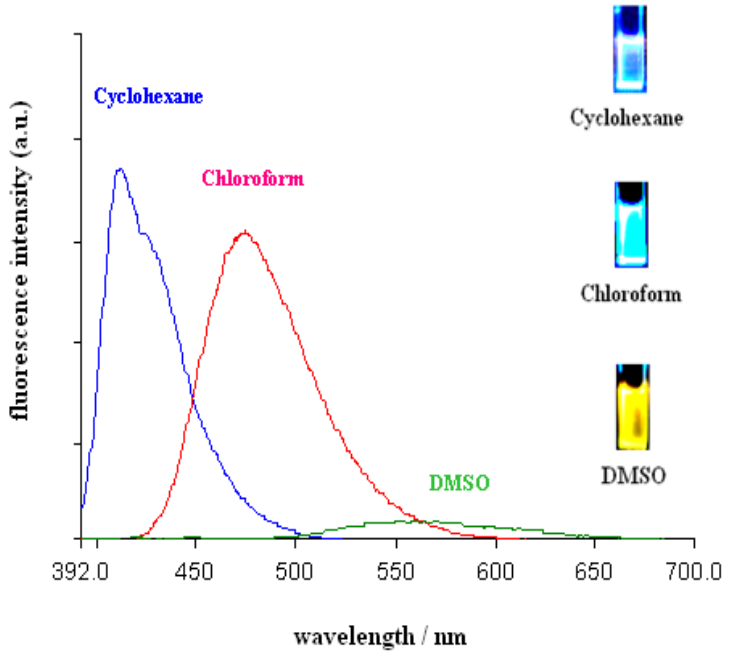


Fig. 1 Room temperature solvatochromic behaviour of **3k**. Inset: visualization of solutions of **3k** (2.5×10^{-6} M) in various solvents irradiated at 380 nm using a handheld UV lamp.

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