Electronic Supplementary Information

Dicyanovinyl-based fluorescent sensors for dual mechanism amine sensing

Guanran Zhang, Alex S. Loch, Jos C. M. Kistemaker, Paul L. Burn* and Paul E. Shaw*

Centre for Organic Photonics & Electronics, School of Chemistry and Molecular Biosciences, The University of Queensland, Queensland 4072, Australia

Materials synthesis

Anhydrous acetonitrile for electrochemical experiments, dichloromethane, and pyridine were prepared by stirring over calcium hydride before distillation and storage over 4Å molecular sieves. Anhydrous tetrahydrofuran for electrochemical experiments was prepared by stirring over lithium aluminium hydride before distillation. Thin-layer chromatography (TLC) was performed on aluminium-backed silica gel 60 F254 plates. Column chromatography was performed by using Davisil LC60A 40−63 μm silica gel. When solvent mixtures are used, the proportions are given by volume. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AV500 or AS500 spectrometers in deuterated chloroform referenced to 7.26 ppm for ^{1}H and 77.0 ppm for ^{13}C. Chemical shifts (δ) are reported in parts per million (ppm) and are referenced to the residual solvent. Coupling constants (*J*) are given to the nearest 0.5 Hz. Peak multiplicities are reported as singlet (s), doublet (d), triplet (t) or multiplet (m). Peak assignments are reported as BT = benzothiadiazolyl H, Bu = *n*-butyl H, Fl = fluorenyl H, Pr = *n*-propyl H, Im = imine H, and Vin = vinyl H. High-resolution electrospray ionization accurate mass measurements (ESI−MS) were recorded in positive mode on an Orbitrap Elite MS (ESI−Orbitrap) via an HESI source. Infrared absorption spectra were recorded on a PerkinElmer Spectrum 100 FT−IR spectrometer as solid samples by using an ATR attachment. Elemental analysis was performed using a Thermo Scientific FlashSmart CHNS/O elemental analyzer. Differential scanning calorimetry (DSC) was performed on a PerkinElmer Pyris Diamond DSC. Melting points were measured in a glass capillary in a Büchi Melting Point B−545 apparatus and are uncorrected. Cyclic voltammetry measurements were performed using a Bioanalytical Systems Inc., Cell Stand C3 instrument with a glassy carbon working electrode, a platinum wire auxiliary electrode, and a $Ag/AgNO_3$ reference electrode in anhydrous acetonitrile. The sample solution contained 0.1 M tetra-*n*-butylammonium perchlorate as the electrolyte and ≈1 mM of sample dissolved in anhydrous dichloromethane or tetrahydrofuran. The solution was deoxygenated by purging with argon. $E_{1/2}$s are referenced against the ferrocene/ferrocenium couple in anhydrous dichloromethane or tetrahydrofuran under the same working conditions. The glassy

carbon electrode was polished between measurements with a polishing pad and rinsed with methanol and acetone before being wiped dry.

7-(Benzo[*c*][1,2,5]thiadiazol-4-yl)-9,9-di-*n*-propyl-*9H*-fluorene-2-carbaldehyde 3

A solution of 9,9-di-*n*-propyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-*9H*-fluorene-2-carbaldehyde[1] (885 mg, 2.12 mmol), 4-bromobenzo[*c*][1,2,5]thiadiazole[2] (401 mg, 1.86 mmol), and potassium carbonate (1.66 g, 12.0 mmol) in *tert*-butanol (5 mL), toluene (15 mL), and water (10 mL) was stirred and deoxygenated by placing under vacuum and backfilling with argon 6 times. Tetrakis(triphenylphosphine)palladium(0) (110 mg, 0.10 mmol) was added and the solution was again deoxygenated by placing under vacuum and backfilling with argon 3 times. The stirred reaction mixture was then heated at reflux under argon in the dark overnight. The reaction mixture was allowed to cool to room temperature and diluted with diethyl ether (20 mL) and water (10 mL). The layers were separated, and the aqueous layer extracted with diethyl ether (3 × 10 mL). The combined organic extracts were washed with water (2 × 10 mL), brine (20 mL), dried over anhydrous sodium sulfate, and filtered through a silica plug. The plug was washed with diethyl ether (*ca.* 50 mL), the filtrate collected, and the solvent removed. The crude residue was purified by column chromatography over silica using a dichloromethane:*n*-hexane mixture (0:1 to 1:0) as eluent to afford the crude product as a cyan coloured solid, after removal of the solvent. The solid was recrystallised from a diethyl ether:*n*-hexane mixture to afford **3** as a cyan coloured crystalline solid (390 mg, 51%); mp: 140 °C; mp (DSC, first heating scan): 119 °C, 145 °C; IR (solid) ν/cm^{-1}: 1692 (CHO); UV−vis: λ_{max}(dichloromethane)/nm 306 (log ε/dm^3 mol^{-1} cm^{-1} 4.37), 316 (4.40), 334 (4.38), 365 (4.26); UV−vis: λ_{max}(134 ± 4 nm neat film)/nm 207sh (log α/cm^{-1} 5.06), 223sh (4.89), 314 (4.92), 337 (4.89), 374 (4.77); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.67−0.84 (10H, m, PrH), 2.05−2.11 (4H, m, PrH), 7.72 (1H, dd, J = 7.0, 8.5 Hz, BTH), 7.79 (1H, dd, J = 1.0, 7.0 Hz, BTH), 7.88−7.91 (2H, m, FlH), 7.92−7.94 (2H, m, FlH), 7.95 (1H, dd, J = 0.5, 1.5 Hz, FlH), 8.02−8.05 (2H, m, FlH and BTH), 10.09 (1H, s, CHO); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 14.4, 17.3, 42.5, 55.7, 120.2, 120.7, 121.0, 123.1, 124.0, 127.8, 128.6, 129.6, 130.7, 134.6, 135.5, 137.9, 139.7, 147.0, 152.0, 152.6, 153.5, 155.7, 192.3; HRMS (ESI-MS) m/z: $[M + H]^+$ Calcd for $C_{26}H_{25}N_2OS$ 413.1682 (100%); Found: 413.1682 (100%); Anal. Calcd for $C_{26}H_{24}N_2OS$: C, 75.7; H, 5.9; N, 6.8. Found: C, 75.8; H, 5.95; N, 6.7. T_g (DSC): 47 °C (second scan, scan rate 200 °C min^{-1}); PL: λ_{max}(dichloromethane)/nm 483. PL: λ_{max}(134 ± 4 nm neat film)/nm 483. PLQY: (sol., dichloromethane) 32 ± 3%. PLQY: (134 nm neat film) 33 ± 3%. $E_{1/2red(1)}$ -2.0 V, $E_{1/2red(2)}$ -2.6 V.

2-[(7-{Benzo[*c*][1,2,5]thiadiazol-4-yl}-9,9-di-*n*-propyl-*9H*-fluoren-2-yl)methylene]malononitrile K12b

A mixture of **3** (98 mg, 0.24 mmol) and malononitrile (24 mg, 0.36 mmol) in anhydrous pyridine (0.1 mL) and anhydrous toluene (1 mL) was stirred at 60 °C under argon in the dark for 1 h. The reaction mixture was allowed to cool to room temperature and the solvent removed. The residue was taken up in the minimum amount of diethyl ether and the crude solid precipitated by the addition of *n*-hexane. The solid was collected, washed with *n*-hexane (*ca.* 10 mL) and purified by column chromatography over silica using a diethyl ether:*n*-hexane mixture (0:1 to 1:5) as eluent followed by a dichloromethane:*n*-hexane mixture (0:1 to 1:1) as eluent to afford the crude product as a yellow coloured solid, after removal of the solvent. Subsequent reprecipitations from a diethyl ether:*n*-hexane mixture afforded **K12b** as a yellow crystalline solid (77 mg, 70%); mp: 178 °C; mp (DSC first heating scan): 185 °C; IR (solid) ν/cm^{-1}: 2226 (CN); UV−vis: λ_{max}(dichloromethane)/nm 235sh (log ε/dm^3 mol^{-1} cm^{-1} 4.12), 248sh (3.93), 275 (3.90), 302sh (3.97), 309 (4.02), 316 (4.06), 406 (4.52); UV−vis: λ_{max}(174 ± 16 nm neat film)/nm 228sh (log α/cm^{-1} 4.78), 245sh (4.62), 277 (4.57), 312 (4.66), 318 (4.67), 406 (5.04), 420sh (5.02); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.65−0.86 (10H, m, PrH), 2.01−2.12 (4H, m, PrH), 7.73 (1H, dd, J = 7.0, 8.5 Hz, BTH), 7.79 (1H, dd, J = 1.0, 7.0 Hz, BTH), 7.84 (1H, s, VinH), 7.88 (1H, d, J = 8.0 Hz, FlH), 7.90−7.94 (2H, m, FlH), 7.97−7.98 (2H, m, FlH), 8.03−8.05 (2H, m, FlH and BTH); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 14.4, 17.3, 42.3, 55.9, 80.7, 113.3, 114.3, 120.8, 120.9, 121.2, 124.2, 124.9, 127.9, 128.8, 129.6, 129.8, 131.0, 134.3, 138.6, 139.2, 147.5, 152.5, 152.8, 153.5, 155.7, 159.9; HRMS (ESI-MS) m/z: $[M + H]^+$ Calcd for $C_{29}H_{25}N_4S$ 461.1794 (100%). Found: 461.1791 (100%). Anal. Calcd for $C_{29}H_{24}N_4S$: C, 75.6; H, 5.25; N, 12.2. Found: C, 75.3; H, 5.3; N, 12.2. T_g (DSC): 60 °C (second scan, scan rate 200 °C min^{-1}). PL: λ_{max}(dichloromethane)/nm 485. PL: λ_{max}(176 ± 16 nm neat film)/nm 511. $E_{1/2red(1)}$ -1.6 V, $E_{1/2red(2)}$ -2.0 V.

Note: the imines were very susceptible to hydrolysis and hence were studied without purification.

***N*-butyl-1-[7-(9,9-di-*n*-propyl-*9H*-fluoren-2-yl)benzo[*c*][1,2,5]thiadiazol-4-yl]methanimine 1**

Synthesis from 7-(9,9-di-*n*-propyl-*9H*-fluoren-2-yl)benzo[*c*][1,2,5]thiadiazole-4-carbaldehyde:

A mixture of 7-(9,9-di-*n*-propyl-*9H*-fluoren-2-yl)benzo[*c*][1,2,5]thiadiazole-4-carbaldehyde (55 mg, 0.13 mmol) and *n*-butylamine (0.05 mL, 0.51 mmol) in anhydrous dichloromethane (4 mL) was stirred overnight at room temperature in the absence of light under argon. The solvent was removed and the gum further dried on high vacuum to give **1** as a bright yellow-green film (*c.a.* 100%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.67−0.82 (10H, m, PrH), 1.00 (3H, t, *J* = 7.5 Hz, BuH), 1.43−1.50 (2H, m, BuH), 1.77−1.82 (2H, m, BuH), 1.98−2.08 (4H, m, PrH), 3.81 (2H, td, *J* = 1.5, 7.0 Hz, BuH), 7.32−7.42 (3H, m, FH), 7.75−7.79 (1H, m, FlH), 7.84−7.87 (2H, m, FlH and BTH), 7.95 (1H, m, FlH), 8.00 (1H, dd, *J* = 1.5, 8.0 Hz, FlH), 8.30 (1H, d, *J* = 7.5 Hz, BTH), 9.15 (1H, dd, *J* = 1.5, 1.5 Hz, ImH); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 13.9, 14.5, 17.3, 20.6, 33.1, 42.7, 55.5, 62.2, 119.7, 120.0, 123.0, 123.9, 126.9, 127.1, 127.4, 127.5, 127.6, 128.4, 135.8, 136.5, 140.5, 141.8, 151.2, 151.3, 153.9, 154.5, 156.8; LRMS (ESI-MS) m/z: $[M + H]^+$ Calcd for $C_{30}H_{34}N_3S$ 468.3 (100%). Found: 468.5 (100%).

Synthesis from **K12**:

A mixture of **K12**[3] (21 mg, 0.05 mmol) and *n*-butylamine (0.45 mL, 0.46 mmol) in anhydrous dichloromethane (4 mL) was stirred overnight at room temperature in the absence of light under argon. The solvent was removed and the gum further dried on high vacuum to give **1** as a bright yellow/green film (*c.a.* 100%) that had an identical NMR and MS to that previously synthesised.

1-[7-(Benzo[c][1,2,5]thiadiazol-4-yl)-9,9-di-*n*-propyl-9H-fluoren-2-yl]-*N*-butylmethanimine 2

Synthesis from **3**:

A mixture of **3** (66 mg, 0.16 mmol) and *n*-butylamine (0.05 mL, 0.51 mmol) in anhydrous dichloromethane (4 mL) was stirred overnight at room temperature in the absence of light under argon. The solvent was removed and the gum further dried on high vacuum to give **2** as a bright green film (*c.a.* 100%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.67−0.71 (6H, m, PrH), 0.71−0.82 (4H, m, PrH), 0.98 (3H, t, *J* = 7.5 Hz, BuH), 1.40−1.48 (2H, m, BuH), 1.71−1.77 (2H, m, BuH), 2.01−2.10 (4H, m, PrH), 3.66 (2H, dt, *J* = 1.5, 7.0 Hz, BuH), 7.68 (1H, dd, *J* = 1.5, 8.0 Hz, FlH), 7.71 (1H, dd, *J* = 7.0, 8.5 Hz, BTH), 7.77−7.79 (2H, m, FlH and BTH), 7.81 (1H, brs, FlH), 7.86 (1H, dd, *J* = 0.5, 8.0 Hz, FlH), 7.91 (1H, dd, *J* = 0.5, 1.5 Hz, FlH), 7.94−8.02 (2H, m, FlH and BTH),^{13}C NMR (125 MHz, $CDCl_3$) δ: 14.0, 14.5, 17.3, 20.6, 33.2, 42.6, 55.6, 61.7, 119.9, 120.1, 120.4, 121.8, 123.9, 127.6, 128.2, 128.4, 129.6, 134.9, 135.5,

136.7, 140.7, 143.1, 151.7, 151.8, 153.6, 155.7, 161.3; HRMS (ESI-MS) m/z: $[M + H]^+$ Calcd for $C_{30}H_{34}N_3S$ 468.2468 (100%). Found: 468.2460 (100%).

Synthesis from **K12b**:

A mixture of **K12b** (70 mg, 0.15 mmol) and *n*-butylamine (0.05 mL, 0.51 mmol) in anhydrous dichloromethane (1 mL) was stirred overnight at room temperature in the absence of light under argon. The solvent was removed and the gum further dried on high vacuum to give **2** as a bright green film (*c.a.* 100%) that had an identical NMR and MS to that previously synthesised.

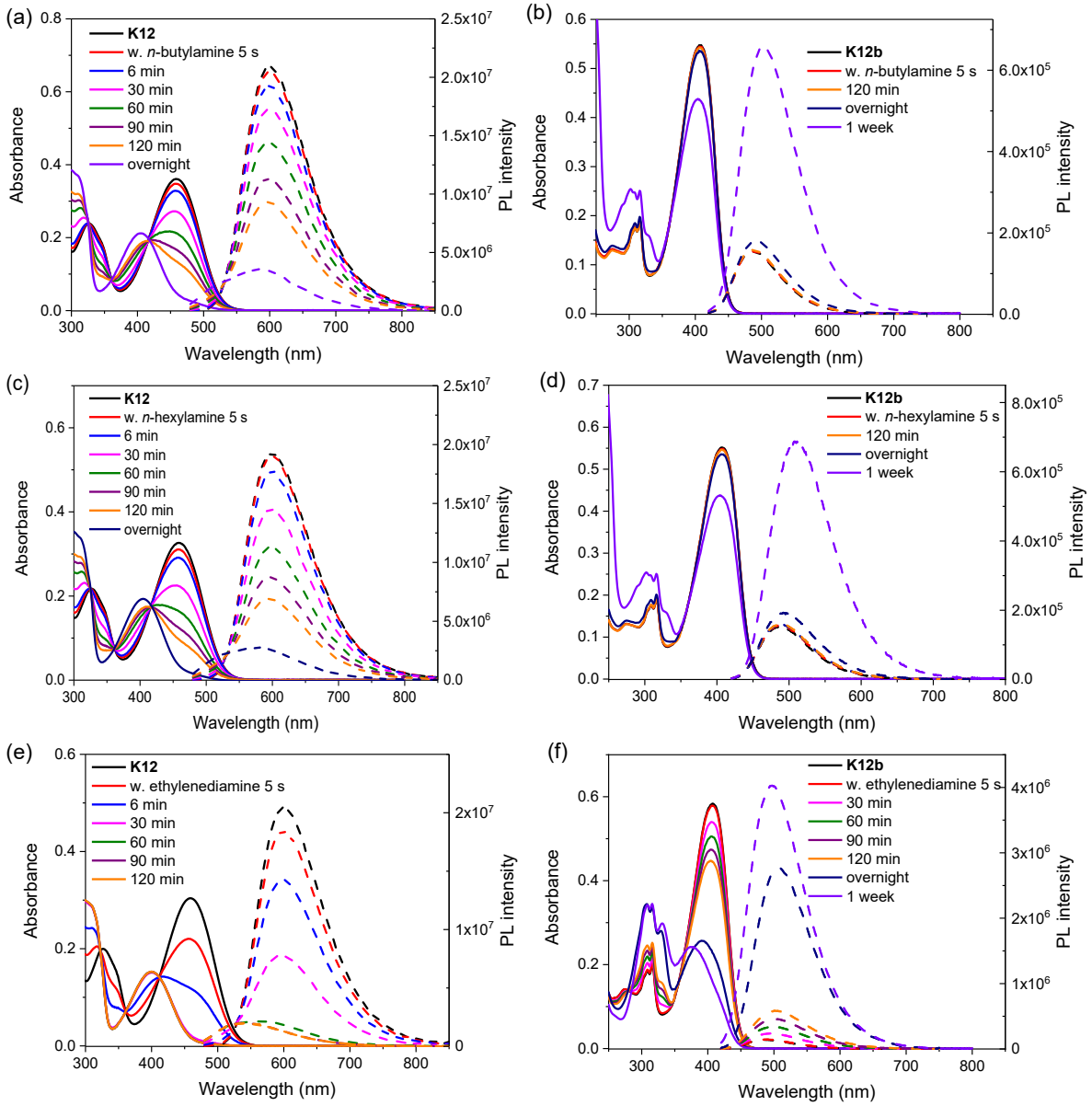


Figure S1 Absorption and PL spectra measured over time of **K12** and **K12b** anhydrous dichloromethane solutions (10 μM) with 10 eq. of *n*-butylamine (a & b), hexylamine (c & d) and 5 eq. of ethylenediamine (e & f). All PL spectra of **K12** and **K12b** solutions were excited at 458 nm and 408 nm, respectively.

Table S1 Reaction rate between **K12** and **K12b** and the four tested amines, obtained from exponential fitting of the data in **Figure 2**.

	***n*-Butylamine**	***n*-Hexylamine**	**Cadaverine**	**Ethylenediamine**
K12	0.008 s^{-1}	0.01 s^{-1}	0.08 s^{-1}	0.2 s^{-1}
K12b	2×10^{-7} s^{-1}	4×10^{-7} s^{-1}	2×10^{-5} s^{-1}	2×10^{-5} s^{-1}

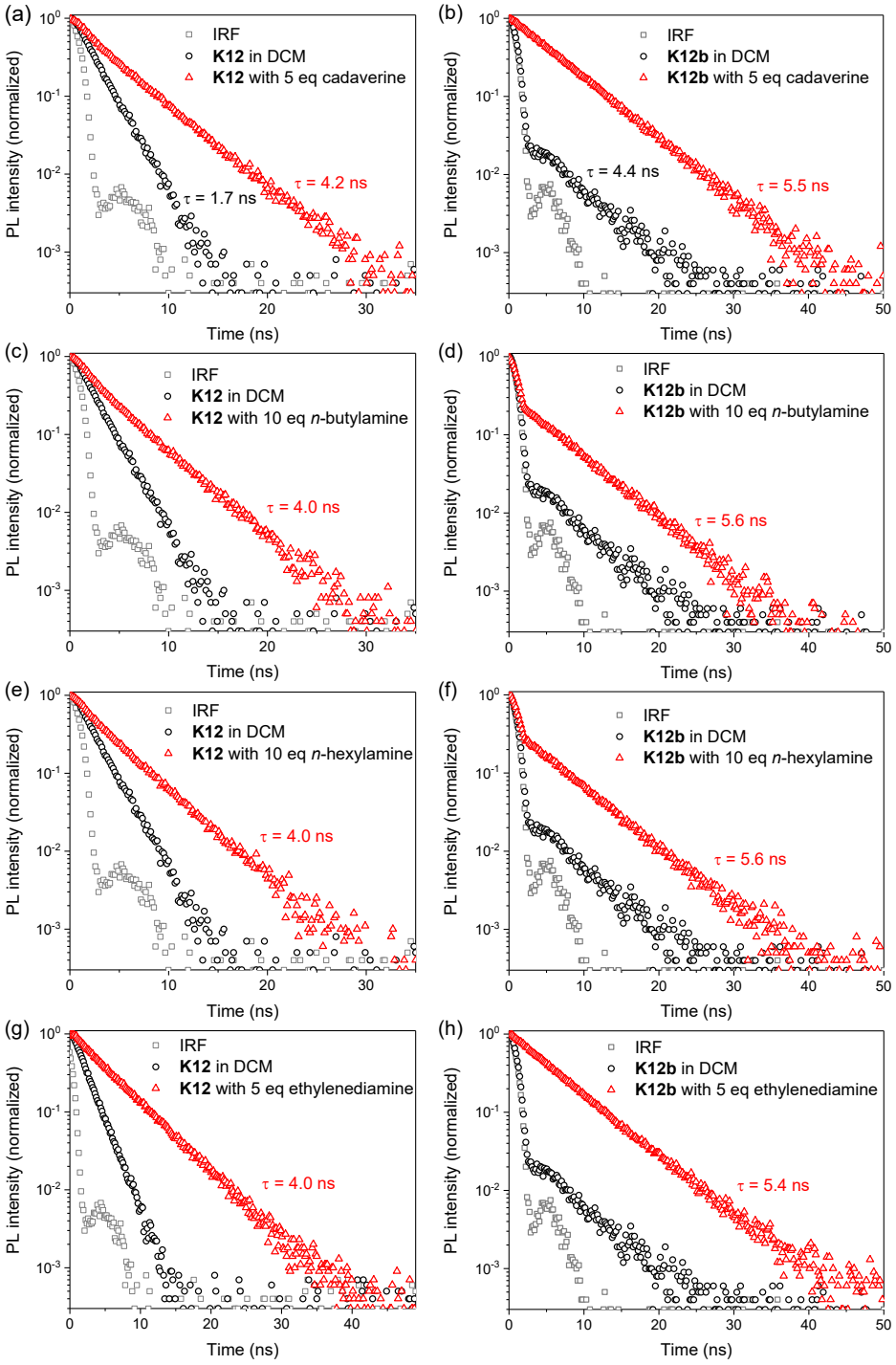


Figure S2 PL decay transients of **K12** (excited at 441 nm, PL decay monitored at 600 nm) and **K12b** (excited at 375 nm, PL decay monitored at 500 nm) anhydrous dichloromethane solutions before and after adding 5 eq. of cadaverine (a & b), 10 eq. of *n*-butylamine (c & d), 10 eq. *n*-hexylamine (e & f) and 5 eq. ethylenediamine (g & h). The fast component in the PL decay of **K12b** samples was attributed to the overlap with the instrument response.

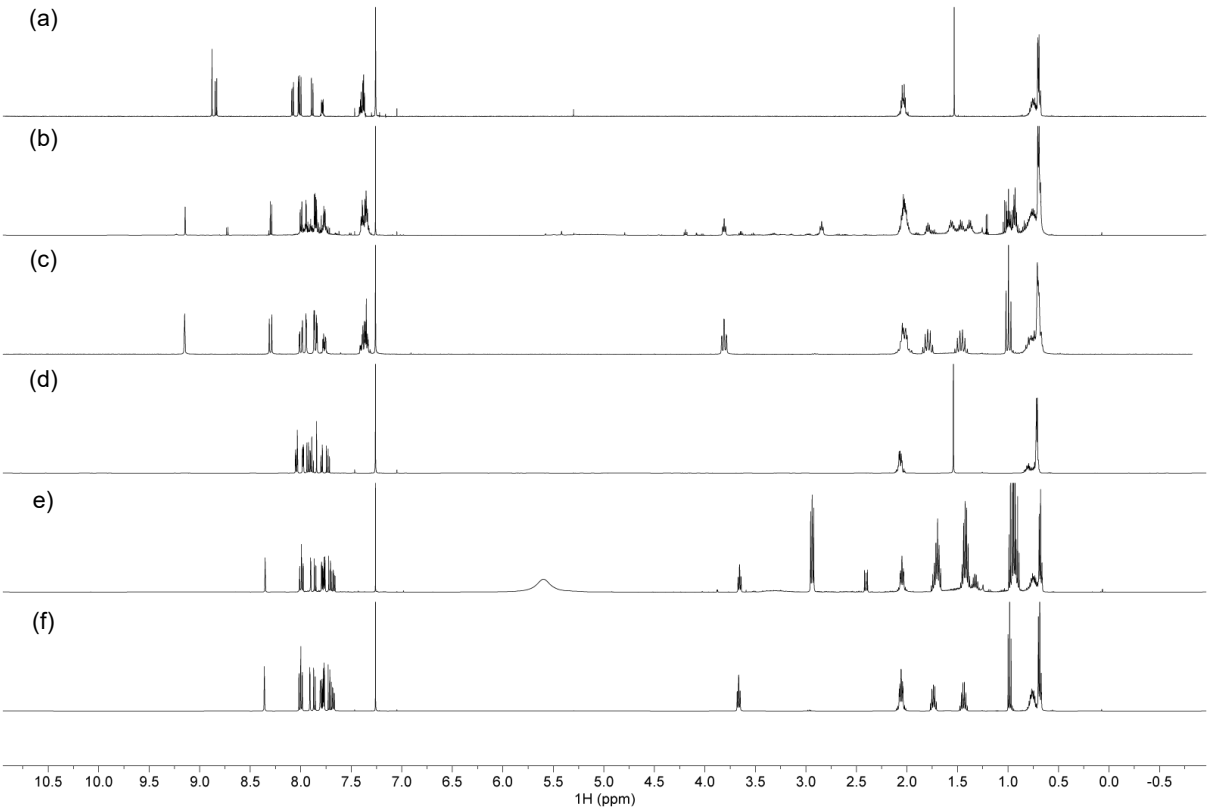
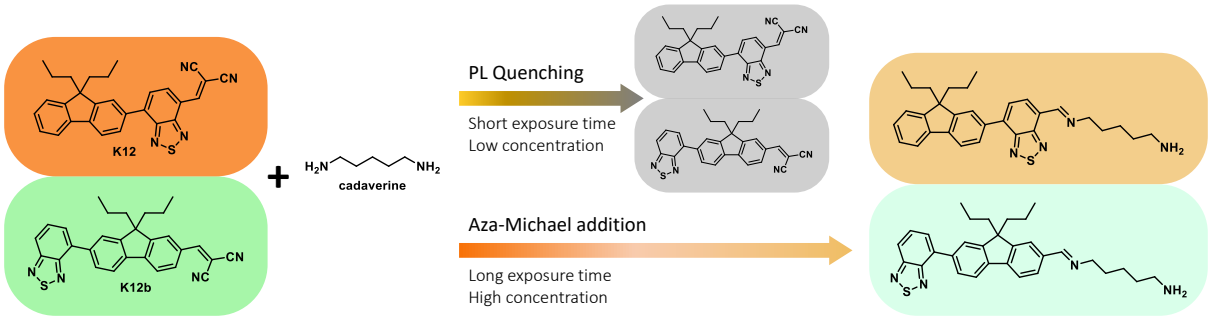


Figure S3 ^{1}H NMR (500 MHz) spectra of **K12** (a), the product of **K12** and *n*-butylamine (b), **1** (c), **K12b** (d), the product of **K12b** and *n*-butylamine (e), and **2** (f).



Scheme S1 Illustration of the different sensing mechanisms in **K12** and **K12b** films with cadaverine over different time scales. With short exposure time or low cadaverine concentration the PL is quenched (illustrated by the grey boxes). At longer exposure times or high cadaverine concentration an aza-Michael addition occurs with subsequent imine formation, which lead to a change in colour of the emission and PL intensity (illustrated by the coloured boxes on the right).

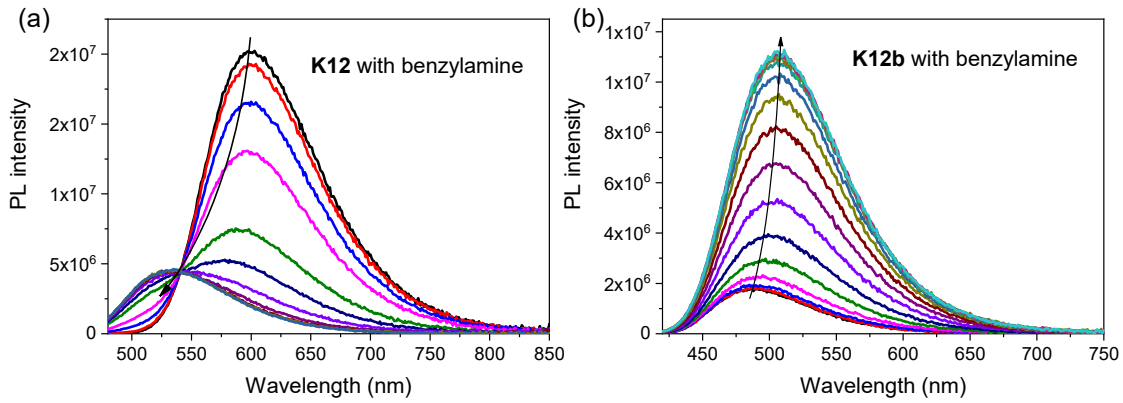


Figure S4 Changes in the PL spectra of **K12** (a) and **K12b** (b) solutions at 10 μM concentration upon increasing benzylamine amine concentrations from 0 – 0.1 M in anhydrous dichloromethane with 5 mM increments.

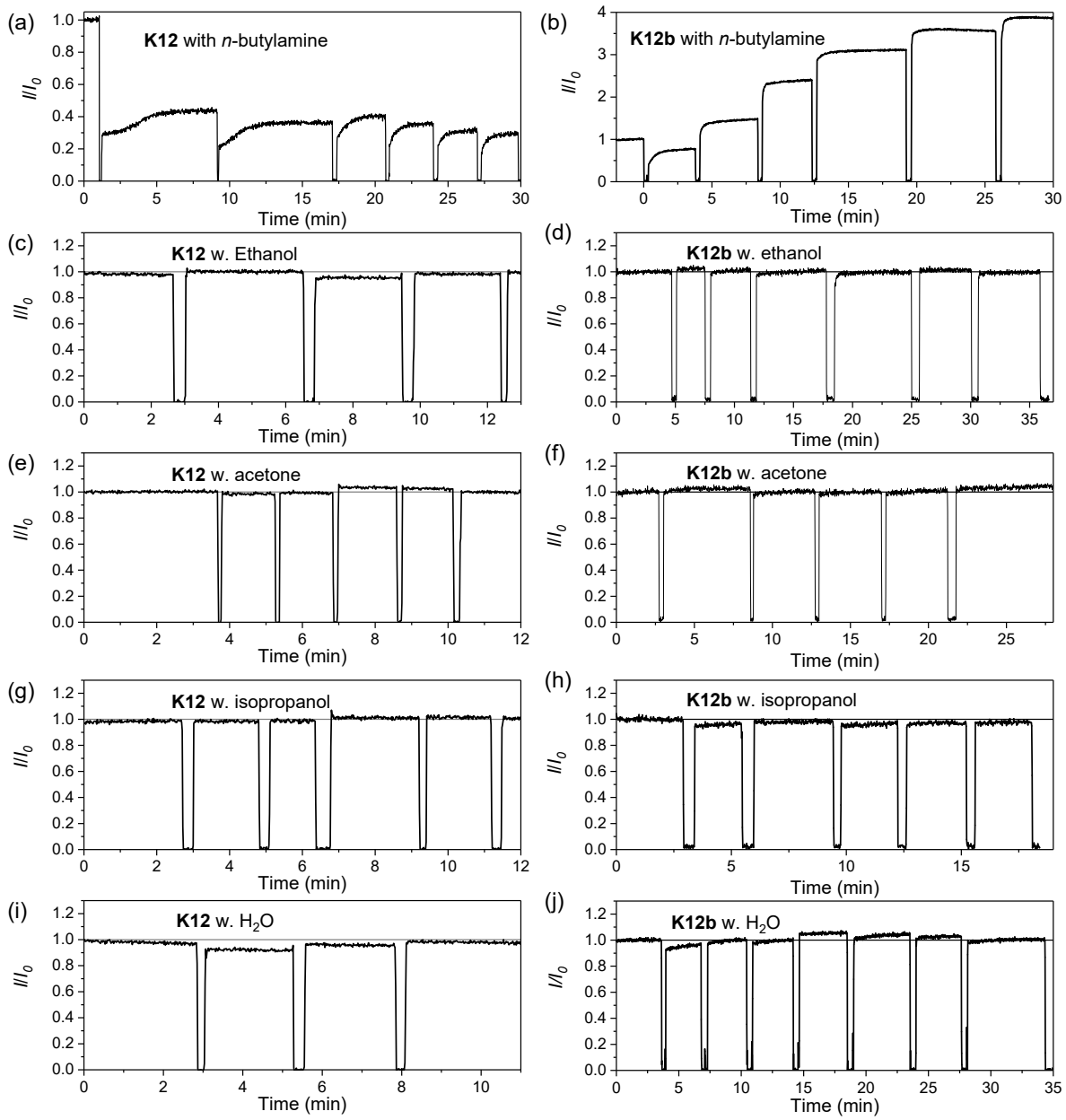


Figure S5 PL peak intensity change of **K12** and **K12b** thin films when exposed to headspace vapours of *n*-butylamine (a & b), ethanol (c & d), acetone (e & f), *iso*-propanol (g & h), and water (i & j). To measure the PL response kinetics, the films were removed from the measurement chamber, exposed to the analyte saturated headspace vapour for 10 seconds (corresponding to where I/I_0 rapidly decreased to zero) before being placed back into the optical chamber for PL measurements.

Determining the Limit of Detection (LOD) towards cadaverine vapour

The LOD was determined using a commonly used method:

$$[LOD]=3\sigma/k$$

where σ is the standard deviation of the signal from a blank measurement, and k is the fitted slope from the linear dependence of fluorescence quenching ratios versus analyte concentration. The standard deviation σ of the PL signal was determined for each sensor film under continuous excitation in air (absence of the analyte) for 20 minutes (**Figure S6a**), and σ was found to be 0.00585 and 0.0135 for **K12** and **K12b** films, respectively. The slope k was determined from the quenching ratio after 60 minutes exposure of cadaverine vapour. The low concentration cadaverine vapour was generated using an Owlstone V-OVG calibration gas generator containing a cadaverine filled permeation tube. The vapour concentration was calculated from the permeation rate, which in turn can be tuned by changing the oven temperature. The permeation rate at 50 ºC was determined by recording the weight loss of the permeation tube

over time, and the permeation rate at elevated temperatures were calculated using the empirical equation:

$$\ln q_{T1} = \ln q_{T2} - 6794\left(\frac{1}{T1} - \frac{1}{T2}\right)$$

where $q_{T1,2}$ are the permeation rates at the two temperatures, T1 and T2 (temperature in Kelvin).

The permeation rate and vapour concentration at different temperatures are listed in **Table S2**.

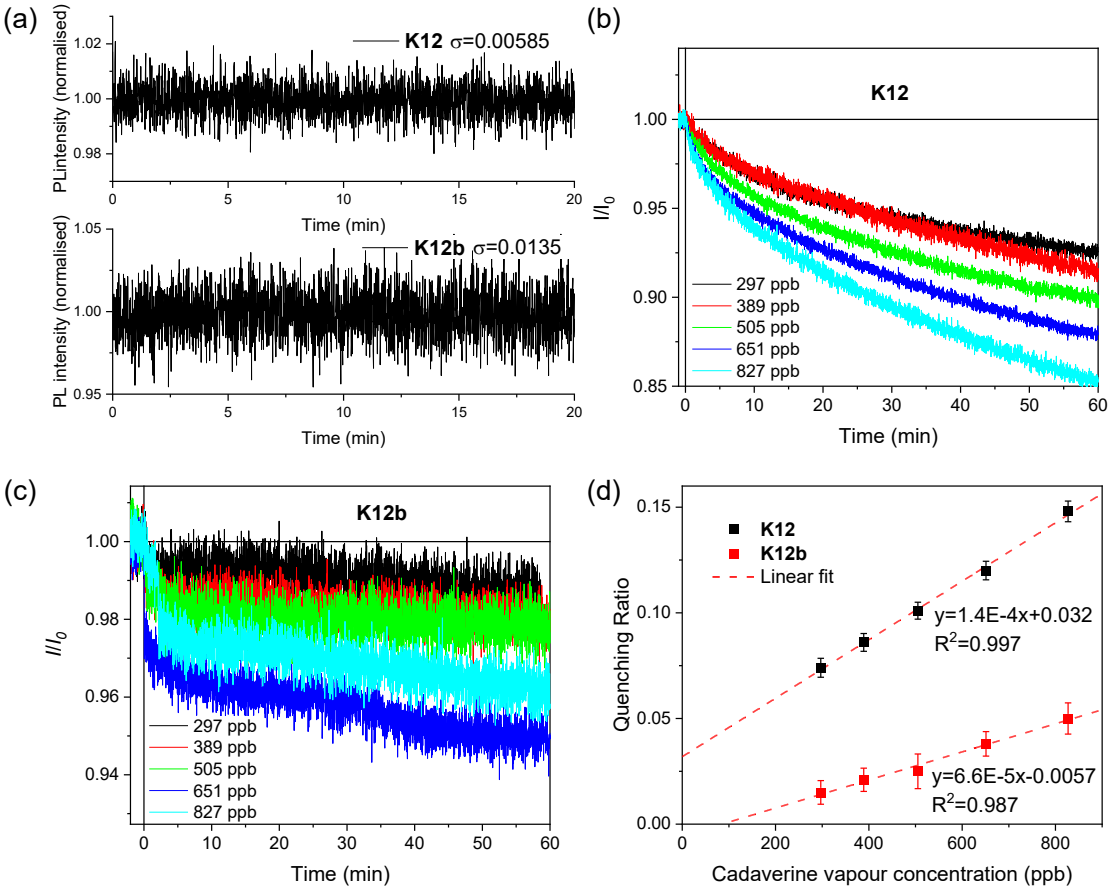


Figure S6 (a) PL intensity recorded for **K12** and **K12b** spin-coated films in the absence of analyte, with the standard deviation listed in figure. PL responses for **K12** (b) and **K12b** (c) films towards cadaverine vapour at different concentrations, and the quenching ratio obtained Figures b and c plotted as a function of cadaverine concentration (d). The linear fits are also given in the Figure.

Table S2 Permeation rate and vapour concentration of cadaverine at different temperatures.

Temperature	**50 ºC**	**80 ºC**	**85 ºC**	**90 ºC**	**95 ºC**	**100 ºC**
Permeation rate (ng/min)	47.7	285	373	485	625	793
Vapour concentration (ppb)	50	297	389	505	651	827

References

1 J. E. Donaghey, A. Armin, P. L. Burn and P. Meredith, *Chem. Commun.*, 2015, **51**, 14115–14118.

2 S. Liu, H. Zhang, Y. Li, J. Liu, L. Du, M. Chen, R. T. K. Kwok, J. W. Y. Lam, D. L. Phillips and B. Z. Tang, *Angew. Chemie Int. Ed.*, 2018, **57**, 15189–15193.

3 K. Gui, K. Mutkins, P. E. Schwenn, K. B. Krueger, A. Pivrikas, P. Wolfer, N. Stingelin Stutzmann, P. L. Burn and P. Meredith, *J. Mater. Chem.*, 2012, **22**, 1800–1806.