Colorimetric response to anions by a "robust" copper(II) complex of a [9]aneN$_3$ pendant arm derivative: CN$^-$ and I$^-$ selective sensing

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Electronic Supplementary Information

Experimental details

All melting points are uncorrected. Microanalytical data were obtained using a Fisons EA CHNS-O instrument (T = 1000°C). UV-Vis spectra were recorded on a Thermo Nicolet Evolution 300 spectrophotometer. Spectrophotometric titrations in MeCN and H_2O of the complex [Cu**L**](BF$_4$)$_2$·MeCN **(1)** with anions were performed by adding to a solution of **1** (2.5 mL) increasing volumes (μL) of a solution the anion (0.14 M) in the same solvent as a ^{n}Bu$_4$N$^+$ salt (F$^-$, Cl$^-$, Br$^-$, I$^-$, MeCO$_2^-$, PhCO$_2^-$, H$_2$PO$_4^-$, HSO$_4^-$, NO$_3^-$, N$_3^-$, CN$^-$ and SCN$^-$) or a Et$_4$N$^+$ salt (HCO$_3^-$). All solvents and starting materials were purchased from commercial sources where available. 1-(2-quinolinylmethyl)-1,4,7-triazacyclononane (**L**) was prepared following a literature procedure[1]. Solvents and starting materials where purchased from commercial sources where available.

[1] M. Mameli, M. C. Aragoni, M. Arca, M. Atzori, A. Bencini, C. Bazzicalupi, A. J. Blake, C. Caltagirone, F. A. Devillanova, A. Garau, M. B. Hursthouse, F. Isaia, V. Lippolis and B. Valtancoli, *Inorg. Chem.*, 2009, **48**, 9236

Synthesis of [CuL](BF$_4$)$_2$·MeCN (1)

A solution of Cu(BF$_4$)$_2$·xH$_2$O (3.40 mg, 0.014 mmol) in MeCN (5 mL) was added to a solution of 1-(2-quinolinylmethyl)-1,4,7-triazacyclononane (**L**) (3.87 mg, 0.014 mmol) in MeCN (5 mL). The resulting blue solution was stirred at room temperature for one hour. The solvent volume was then reduced to 3 mL under reduced pressure. The product was isolated as a blue powder after Et$_2$O vapours diffusion into the concentrated MeCN solution (5 mg, 9.11×10^{-3} mmol, 35% yield). Mp. 155°C (decomp.). Elemental analysis: found (calculated for $C_{18}H_{25}B_2CuF_8N_5$): C 39.37 (39.41); H 4.63 (4.59); N 12.78 (12.77). UV-Vis: λ/nm (ε/M^{-1}cm^{-1}): 600 (106) in MeCN; 634 (78) in H$_2$O.

Synthesis of [Cu(L)CN]BF$_4$·½H$_2$O

To a solution of [CuL](BF$_4$)$_2$·MeCN (**1**) (5.00 mg, 9.11×10^{-3} mmol) in MeCN (5mL) ^{n}Bu$_4$NCN was added (2.44 mg ,9.11×10^{-3} mmol) as a solid. The solution turned dark blue immediately after the addition. Dark blue crystals were obtained by slow evaporation of the solution (1.87 mg, $4.10 \times$

10^{-3} mmol, 54% yield). Mp. 187°C (decomp.). Elemental analysis found (calculated for $C_{17}H_{23}BCuF_4N_5O_{0.5}$): C 44.86 (44.80); H 5.13 (5.09); N 15.39 (15.37). UV-Vis: λ/nm (ε/$M^{-1}cm^{-1}$): 585 (144) in MeCN; 595 (97) in H_2O.

Synthesis of [Cu(L)I]I

To a solution of [Cu**L**]$(BF_4)_2$·MeCN (1) (5.00 mg, 9.11×10^{-3} mmol) in MeCN (5mL) $^nBu_4NI$ was added (6.74 mg ,0.019 mmol) as a solid. The solution turned green immediately after the addition. Green crystals were obtained by diffusion of Et_2O vapours in the solution (3.10 mg, 5.28×10^{-3} mmol, 58% yield) Mp. 178 (decomp.). Elemental analysis found (calculated for $C_{16}H_{22}CuI_2N_4$): C 32.74 (32.70); H 3.79 (3.77); N 9.51 (9.53). UV-Vis: λ/nm (ε/$M^{-1}cm^{-1}$): 630 (330), 420 (1330) in MeCN; 627 (85), 390 (156) in H_2O.

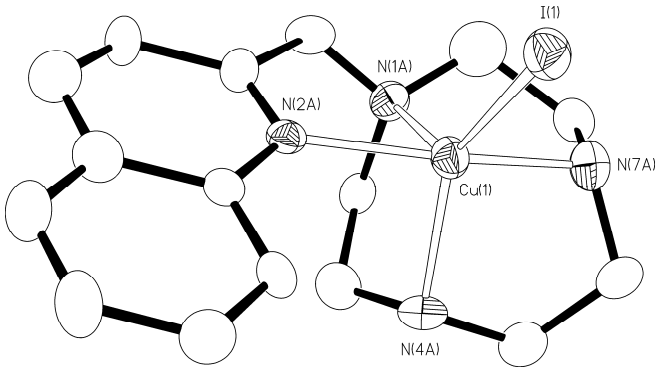

Figure S1. ORTEP view of the complex cation $[Cu\mathbf{L}(I)]^+$ in [Cu(**L**)I]I. Hydrogen atoms have been omitted for clarity. Displacement ellipsoids are draw at a 30% probability level. Cu(1)-I(1) 2.583(2), Cu(1)-N(2A) 2.008(14), Cu(1)-N(7A) 2.013(15), Cu(1)-N(1A) 2.120(13), Cu(1)-N(4A) 2.156(13) Å, N(2A)-Cu(1)-N(7A) 164.6(6), N(2A)-Cu(1)-N(1A) 79.6(6), N(7A)-Cu(1)-N(1A) 85.0(6), N(2A)-Cu(1)-N(4A) 93.6(6), N(7A)-Cu(1)-N(4A) 83.7(6), N(1A)-Cu(1)-N(4A) 84.7(6), N(2A)-Cu(1)-I(1) 97.8(4), N(7A)-Cu(1)-I(1) 93.6(4), N(1A)-Cu(1)-I(1) 133.4(5), N(4A)-Cu(1)-I(1) 141.6(4)°.

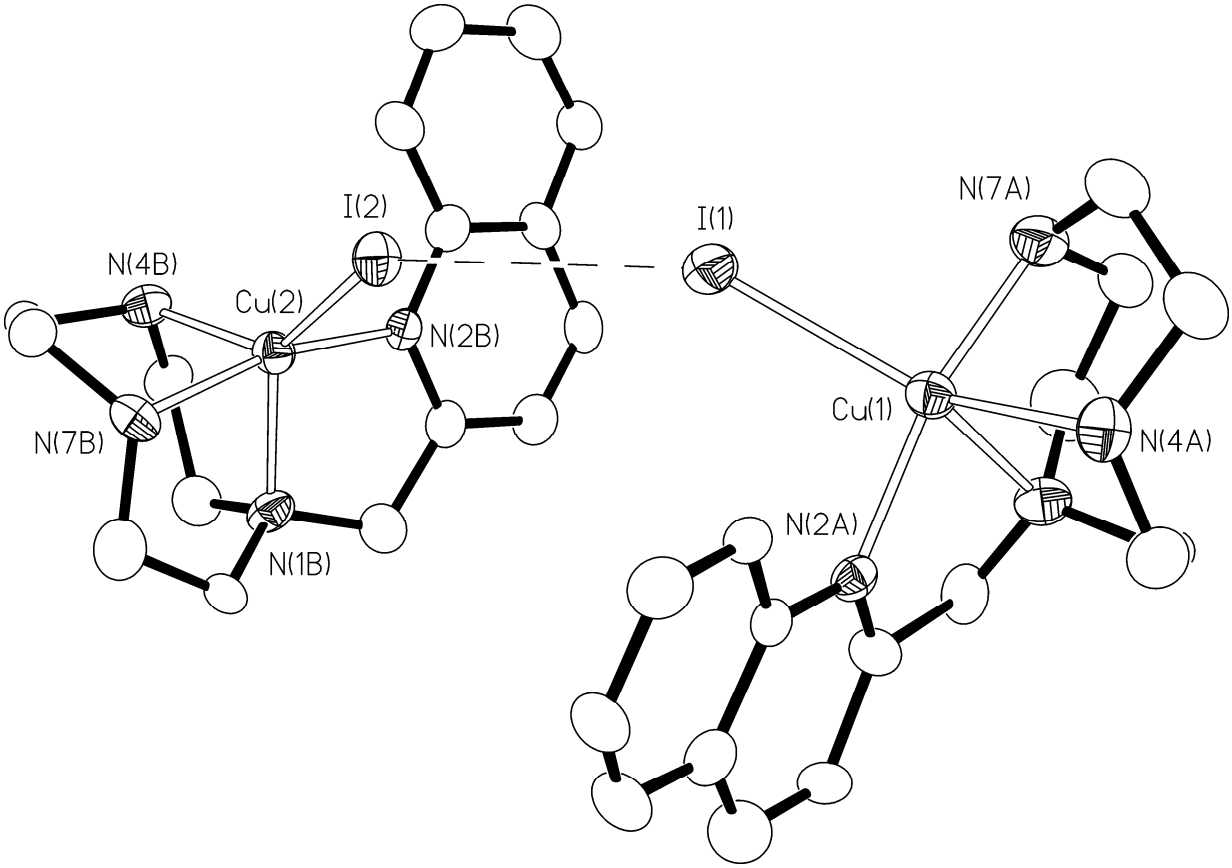

Figure S2. ORTEP view of two independent $[Cu(\mathbf{L})I]^+$ cations interacting *via* a soft-soft I···I contact Hydrogen atoms are omitted for clarity. Displacement ellipsoids are draw at a 30% probability level. I(1)-(I2), 4.140(2), Cu(2)-I(2) 2.584(2), Cu(2)-N(7B) 1.974(14), Cu(2)-N(2B) 1.999(14), Cu(2)-N(1B) 2.095(14), Cu(2)-N(4B) 2.118(14) Å, N(7B)-Cu(2)-N(2B) 165.3(6), N(7B)-Cu(2)-N(1B) 84.1(6), N(2B)-Cu(2)-N(1B) 81.2(6), N(7B)-Cu(2)-N(4B) 83.7(6), N(2B)-Cu(2)-N(4B) 95.2(6), N(1B)-Cu(2)-N(4B) 85.2(6), N(7B)-Cu(2)-I(2) 93.5(4), N(2B)-Cu(2)-I(2) 97.1(4), N(1B)-Cu(2)-I(2) 136.8(4), N(4B)-Cu(2)-I(2) 137.5(4)°. I(2)-I(1)-Cu(1) 146.25, I(1)-I(2)-Cu(2) 144.66.

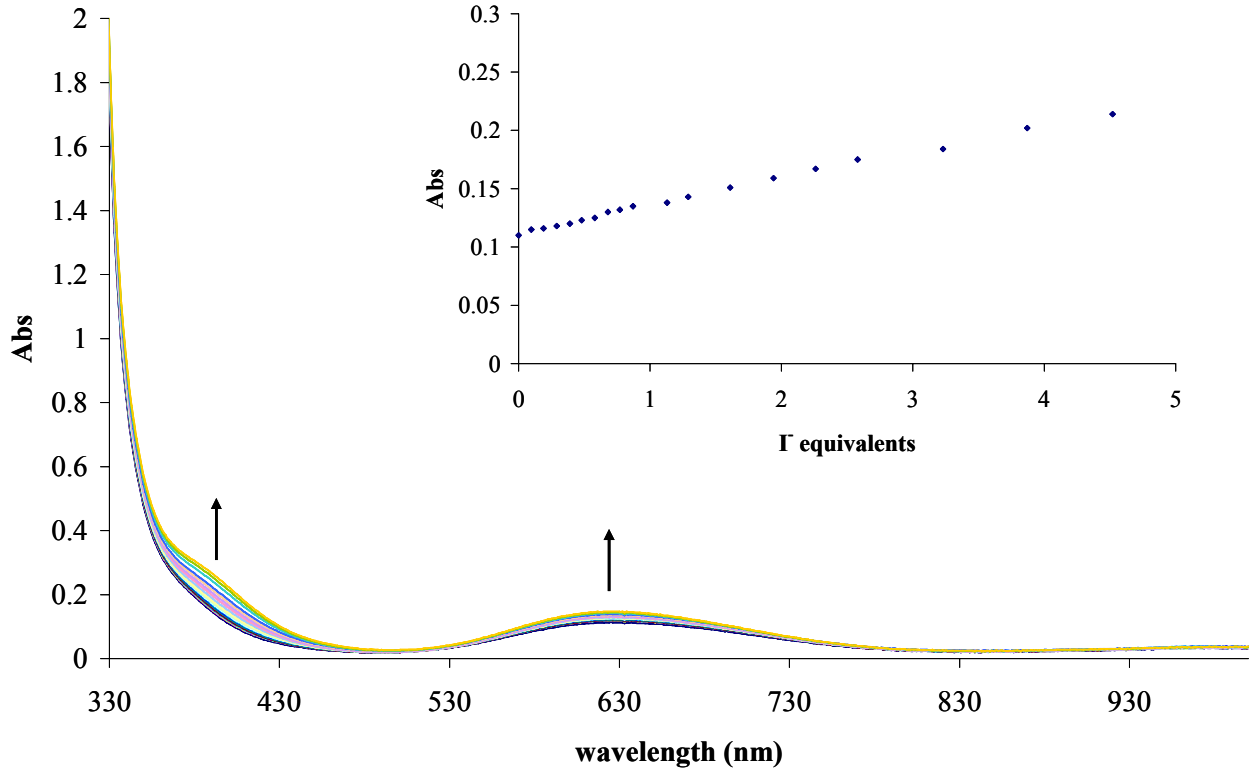

Figure S3. Absorption changes of **1** (1.72×10^{-3} M) in H_2O upon addition of increasing amounts of $^{n}Bu_4NI$ (0.14 M). Inset: titration curve at 390 nm.

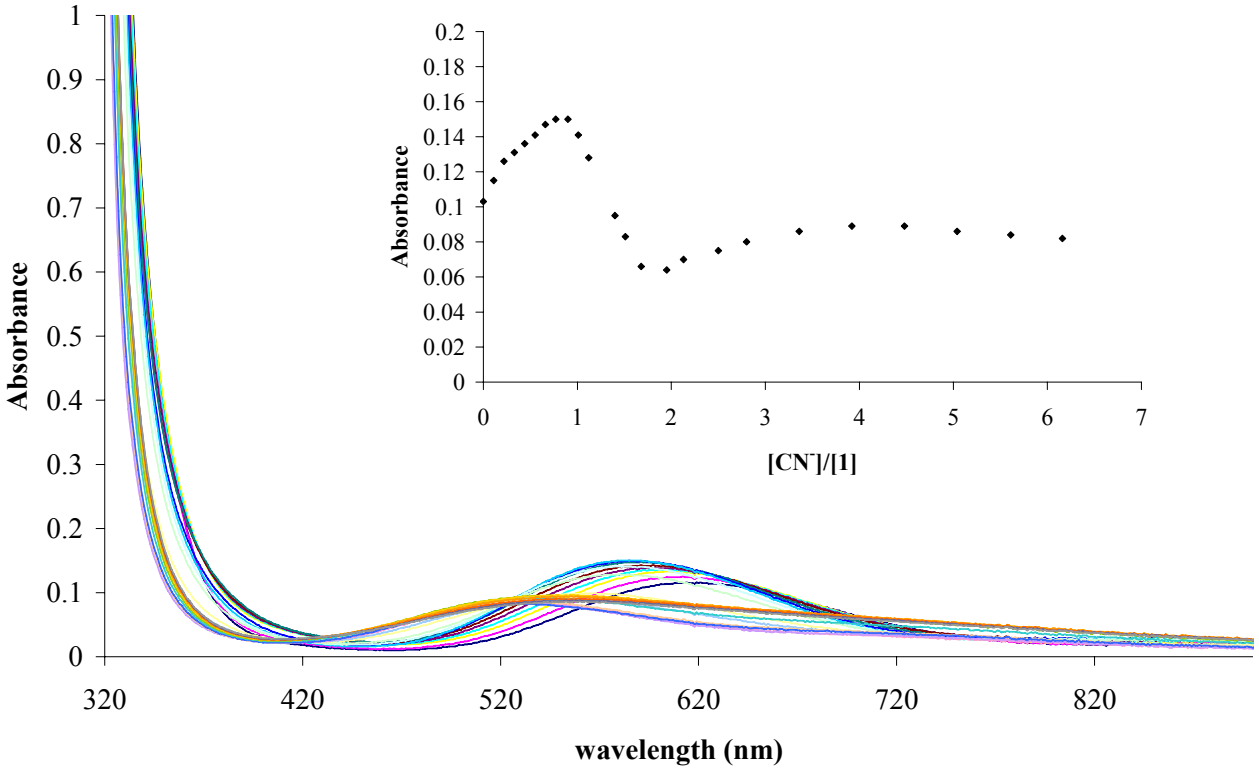

Figure S4. Absorption changes of **1** (1.00×10^{-3} M) in MeCN upon addition of increasing amounts of $^{n}Bu_4NCN$ (0.14 M). Inset: titration curve at 585 nm.

Figure S5. Colour change of **1** (1.00×10^{-3} M) after addition of different anions in MeCN. From left to right: **1**, **1** + 1 eq. of F^-, **1** + 1 eq. of Cl^-, **1** + 1 eq. of Br^-, **1** + 1 eq. of $MeCO_2^-$, **1** + 1 eq. of $PhCO_2^-$, **1** + 1 eq. of $H_2PO_4^-$, **1** + 1 eq. of HSO_4^-, **1** + 1 eq. of HCO_3^-, **1** + 1 eq. of NO_3^-, **1** + 1 eq. of N_3^-, **1** + 1 eq. of SCN^-, **1** + 1 eq. of CN^-, **1** + 2 eqs. of CN^-, **1** + 1 eq. of I^-.

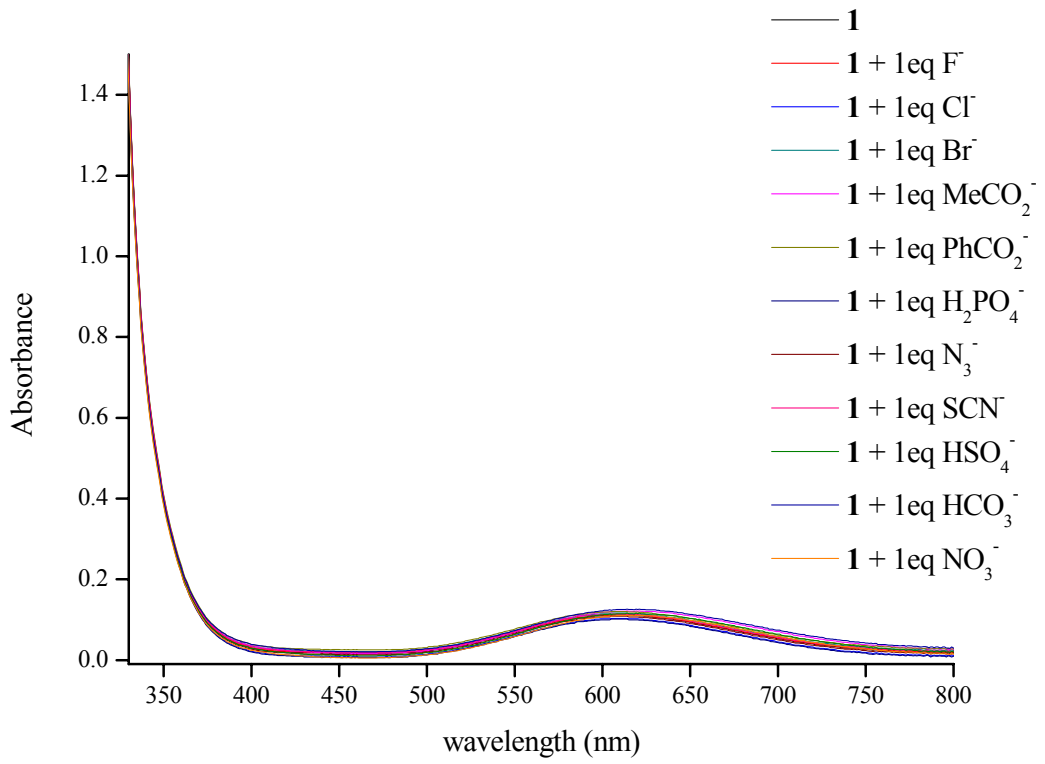

Figure S6. Absorption changes of **1** (1.00×10^{-3} M) in MeCN upon addition 1 equiv. of all ions considered except I^- and CN^-.

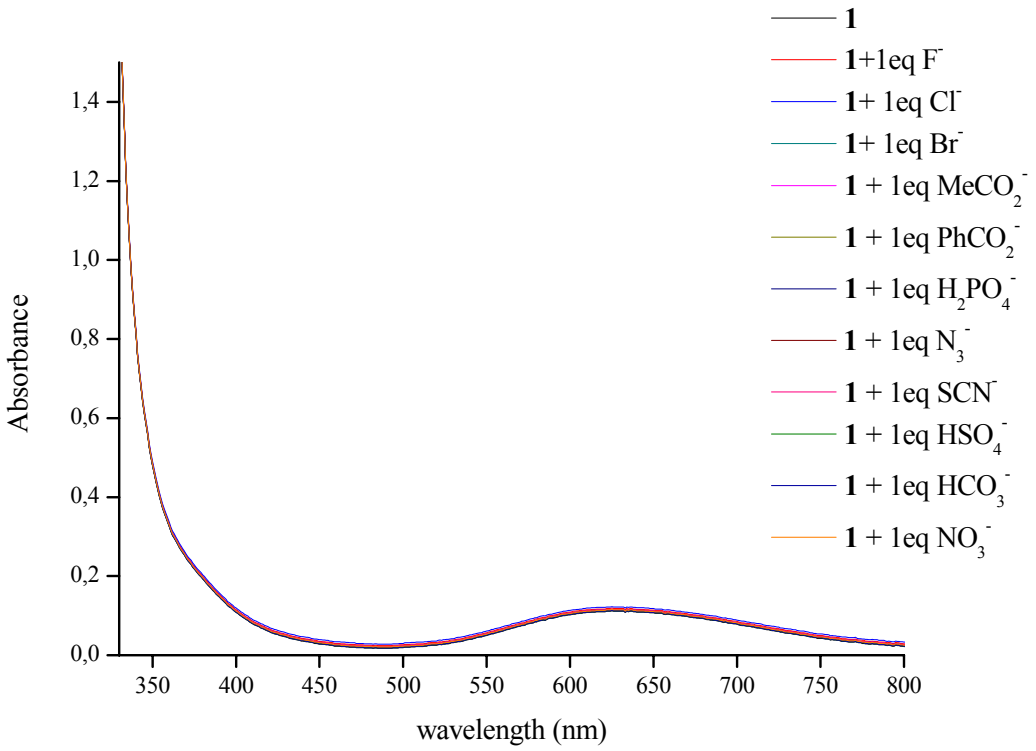

Figure S7. Absorption changes of **1** (1.00×10^{-3} M) in H_2O upon addition of 1 equiv. of all ions considered except I^- and CN^-.

A Dual sensor is normally defined as a supramolecular system which uses two different transducer approaches for identifying the targeted species. Borrowing from this, we have defined **1** as a "solvent-based dual sensor" because it can identify the target species in two different solvents. Alternatively, adopting the Boolean logic language, we can say that **1** performs the logical OR operation if the nature of the sensed anions (I^-, CN^-) and the solvents (MeCN, H_2O) are considered as inputs and what ever colour change as output (see truth below).

Truth table of the OR operation performed by **1** on solvents (H_2O, MeCN) and anions (I^-; CN^-) inputs

Outputs	Inputs	
	Solvent[a]	anion[b]
0 (no colour change of **1**)	0	0
1 (colour change to green of **1**)	1	0
1 (colour change to blue of **1**)	0	1
1 (colour change to blue or pink of **1**)	1	1

[a] H_2O (0); MeCN (1)

[b] I^- (0); CN^- (1)