# Supporting Information

## A rationally designed, spiropyran-based chemosensor for magnesium

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**Characterisation Spectra**

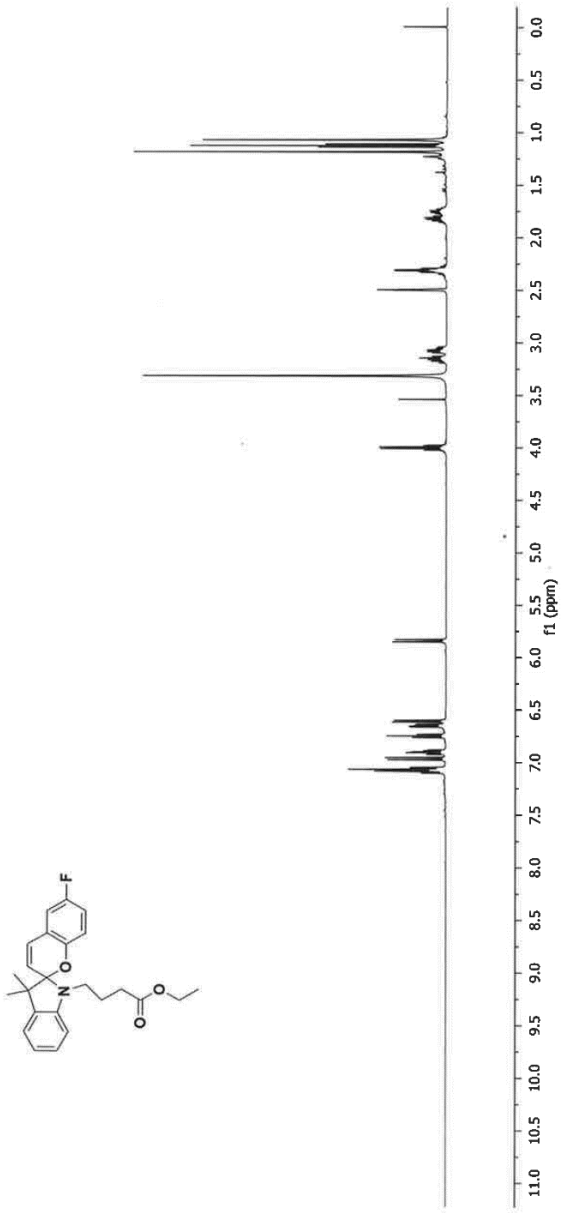



**Figure S1.** $^{1}H$ NMR spectrum of chemosensor **4** recorded in DMSO-$D_6$ at 500 MHz.

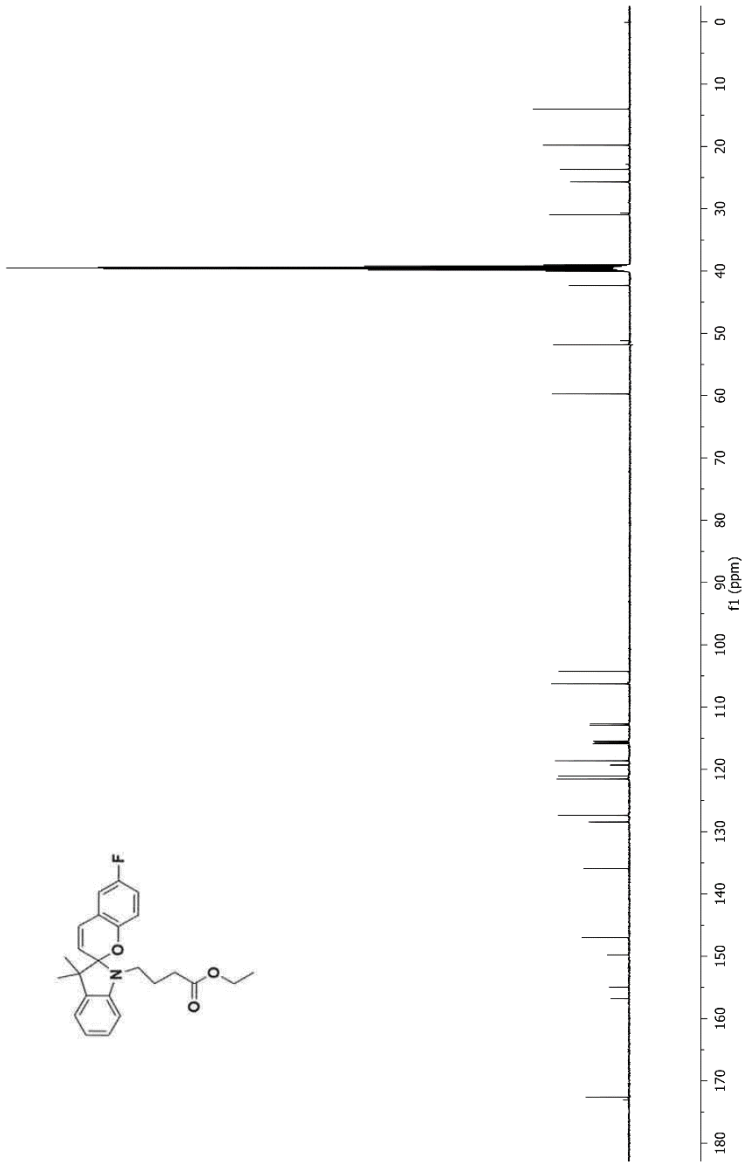



**Figure S2.** $^{13}C$ NMR spectrum of chemosensor **4** recorded in DMSO-$D_6$ at 500 MHz.

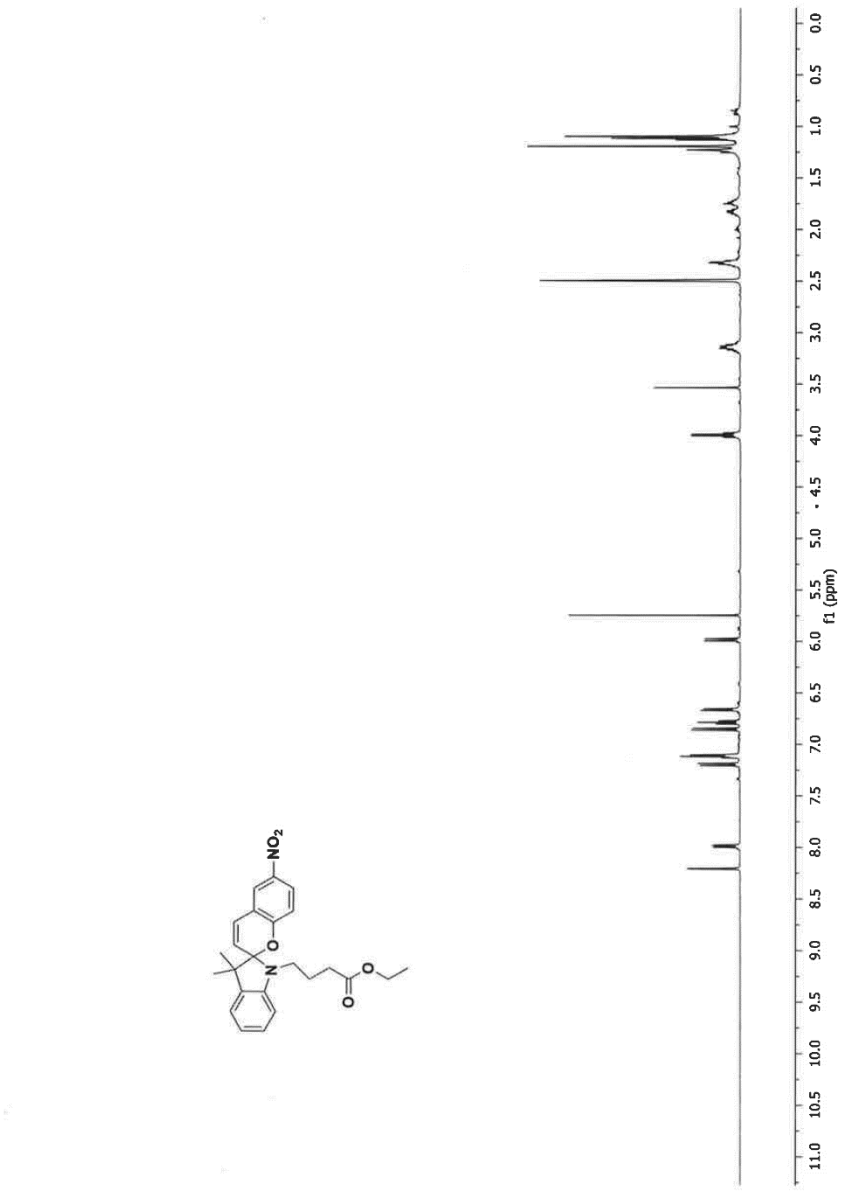



**Figure S3.** $^{1}$H NMR spectrum of chemosensor **3** recorded in DMSO-$D_6$ at 500 MHz.

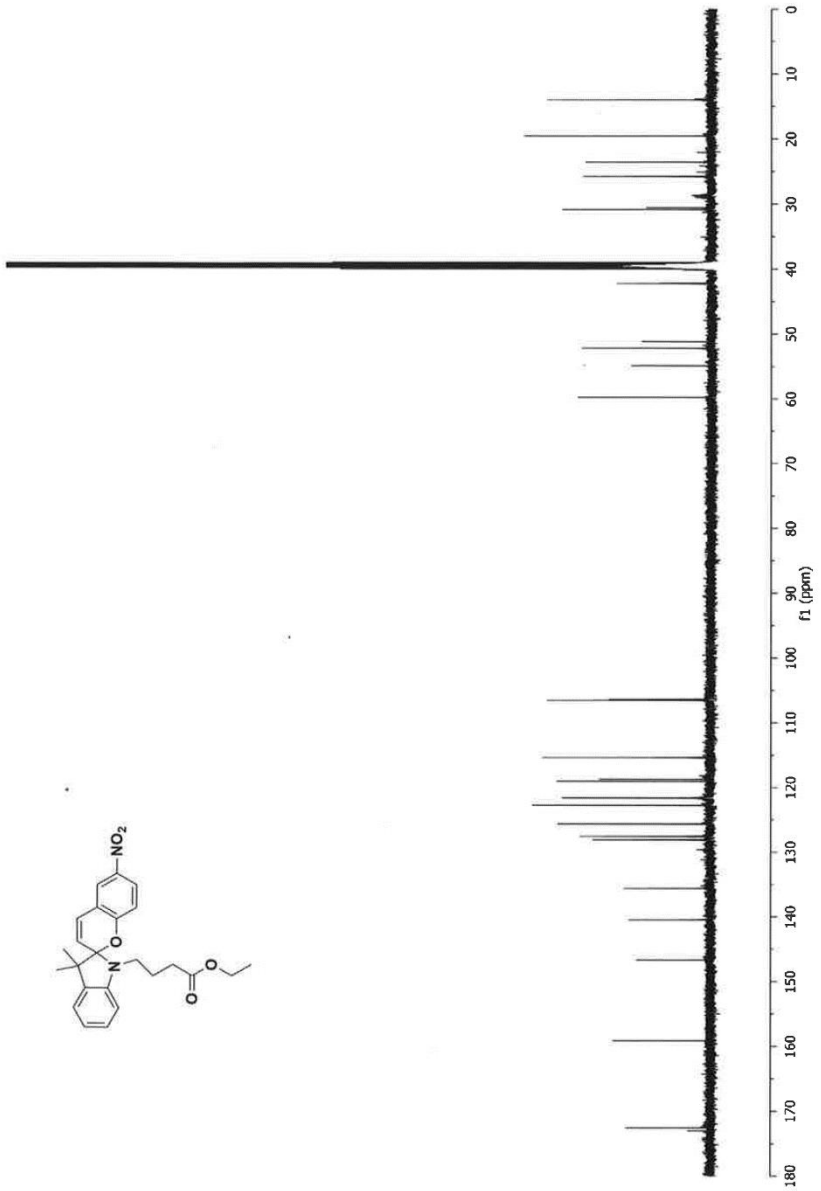



**Figure S4.** $^{13}C$ NMR spectrum of chemosensor **3** recorded in DMSO-$D_6$ at 500 MHz.

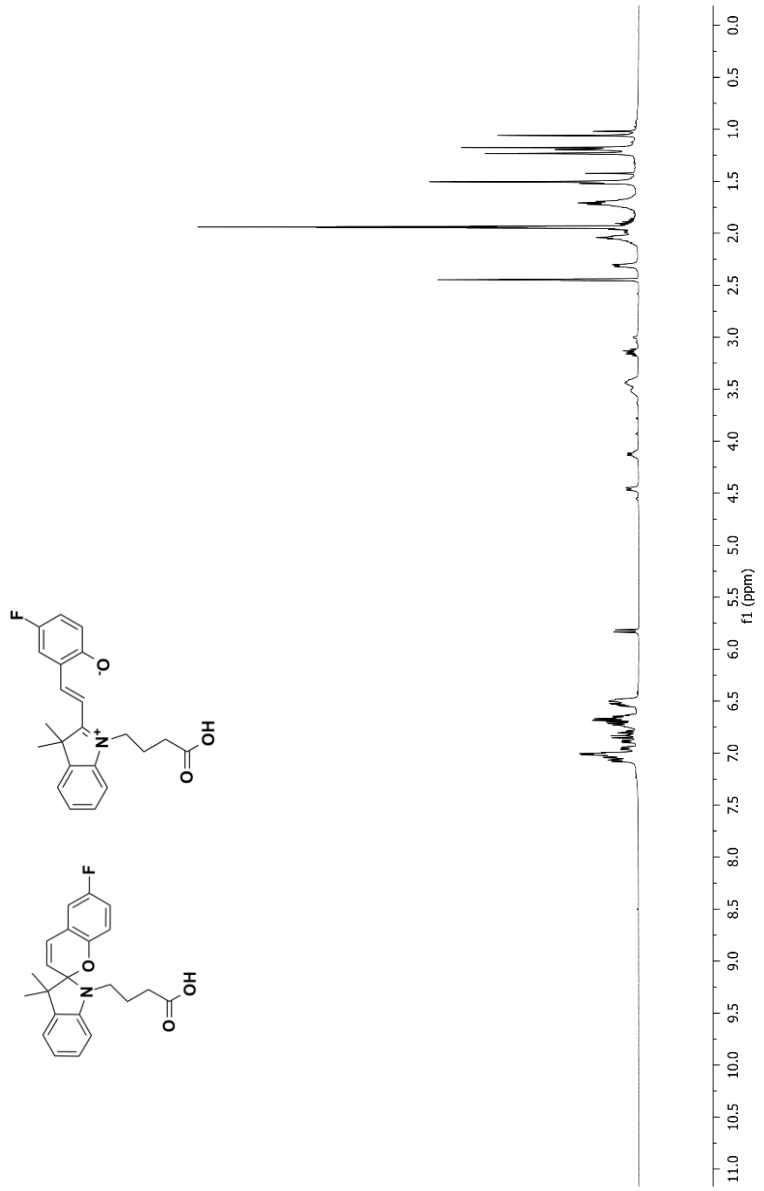



**Figure S5.** $^{1}H$ NMR spectrum of chemosensor **2** recorded in $CD_3CN$ and $d_6$-DMSO at 500 MHz. The sensor is present in both the merocyanine and spiropyran forms in the spectrum. $H_2O$ signal at δ 3.1 ppm supressed.

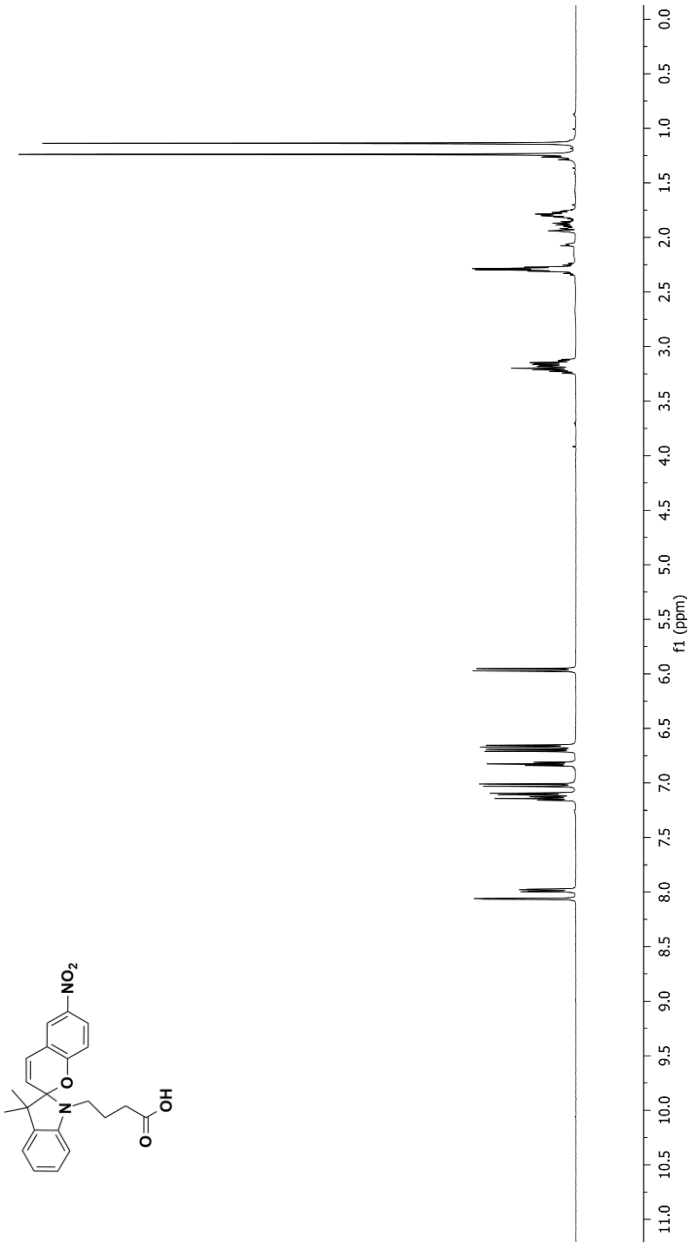



**Figure S6.** $^{1}H$ NMR spectrum of chemosensor **1** recorded in $CD_3CN$ at 500 MHz.

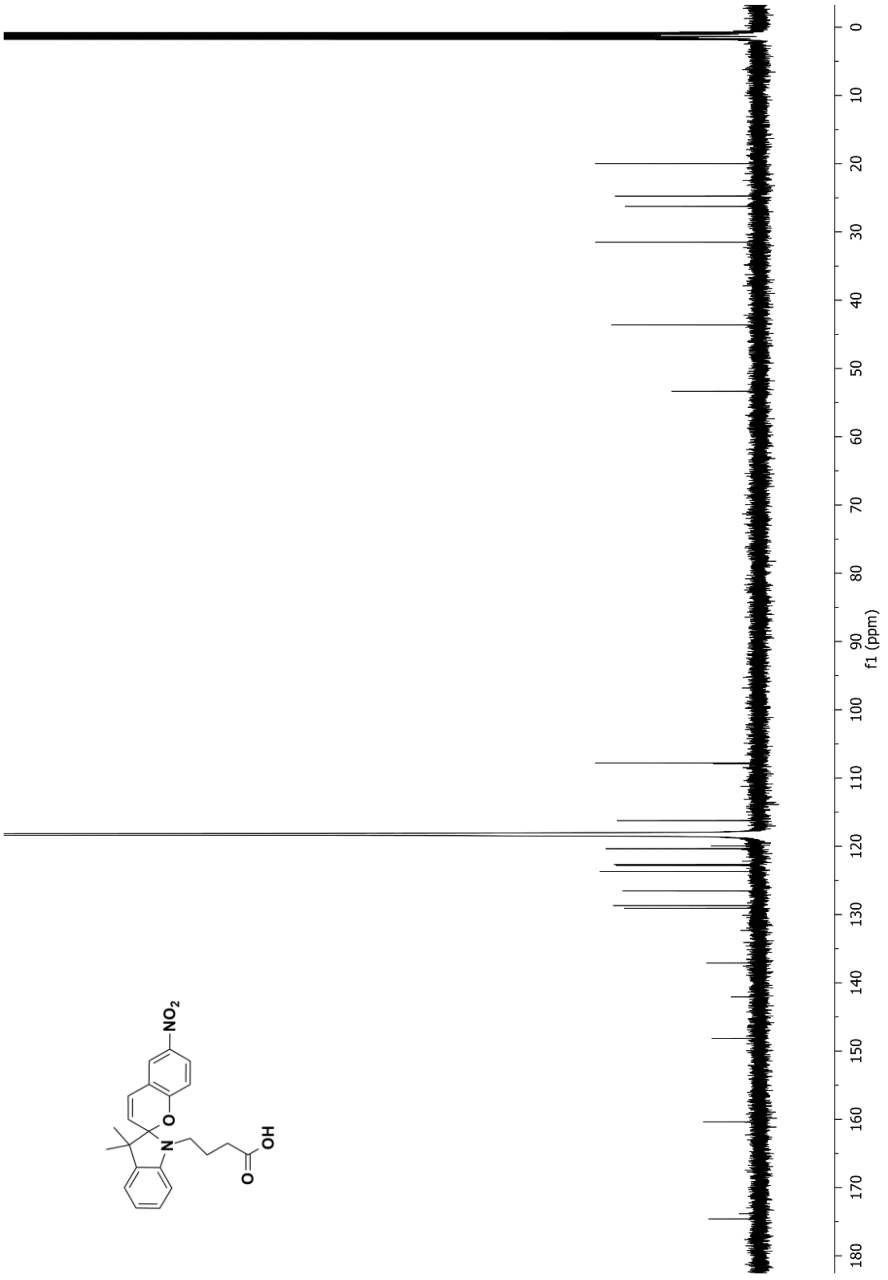
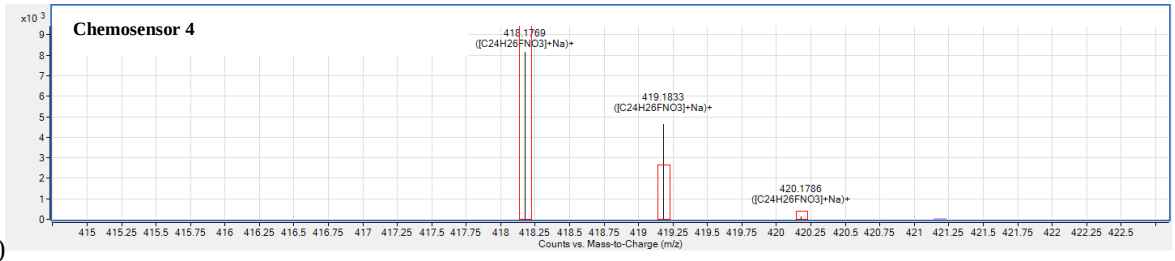
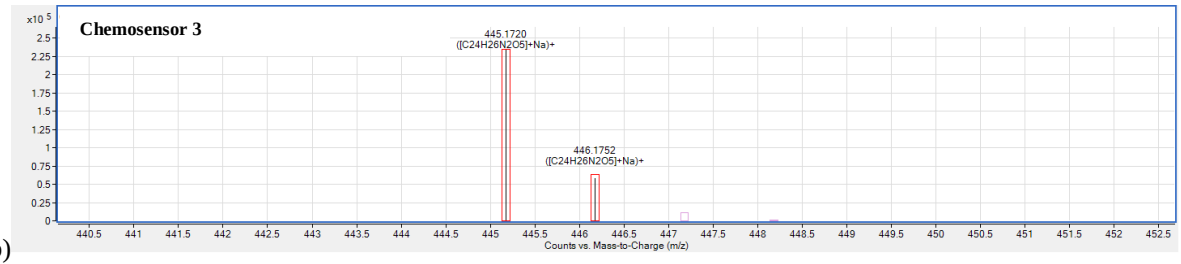


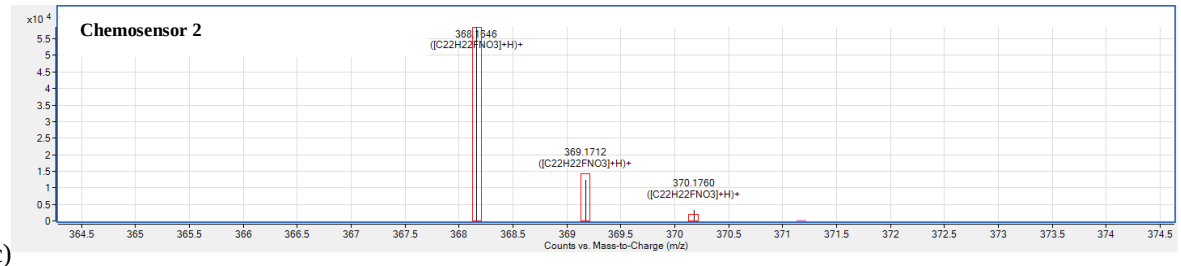

**Figure S7.** $^{13}C$ NMR spectrum of chemosensor **1** recorded in $CD_3CN$ at 500 MHz.



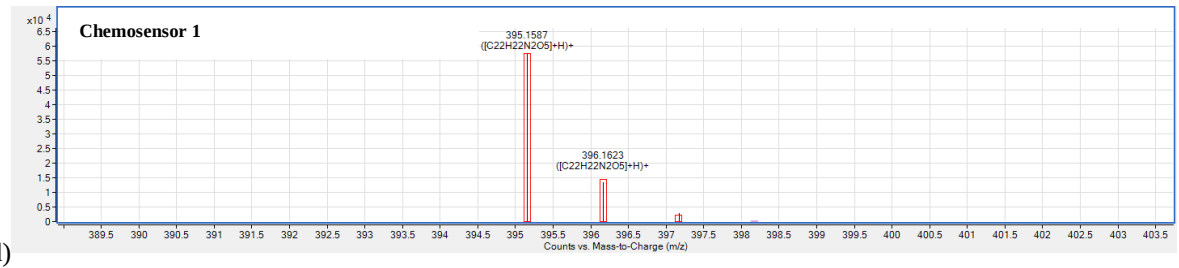

(a)




(b)




(c)



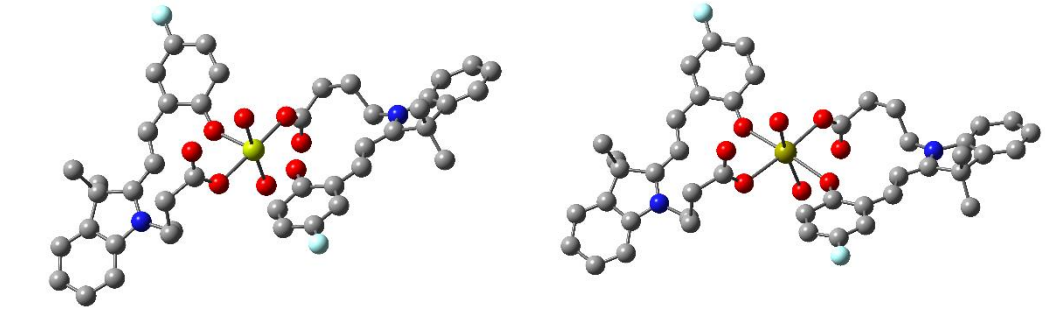

(d)

**Figure S8.** ESI-HRMS spectra of chemosensors (a) **4**, (b) **3**, (c) **2** and (d) **1**.

**DFT Calculations**

Reaction energies were calculated based on the following equation, where 'M' denotes $Mg^{2+}$ or $Ca^{2+}$, and 'MC' denotes the merocyanine form of chemosensor **1** or **2**.

$$2(MC^{-}) + M\,[(H_2O)_6]^{2+} \rightarrow M\,[MC_2(H_2O)_2] + 4(H_2O)$$



(a) (b)

**Figure S9.** B3LYP/6-311G** optimized structure of chemosensor **2** bound to (A) $Mg^{2+}$ (yellow) and (B) $Ca^{2+}$ (gold), respectively, in a 2:1 ratio, showing oxygen atoms (red) chelating to the metal ion. Hydrogen atoms are omitted for clarity. The $Mg^{2+}\cdots O$ distances are between 2.08 and 2.12 Å, and $Ca^{2+}\cdots O$ distances are between 2.36 and 2.45 Å. Reaction energies for the formation of the M[**2**$(MC)_2(H_2O)_2$] species were calculated to be -315.7 kJ/mol and -151.2 kJ/mol for $Mg^{2+}$ and $Ca^{2+}$, respectively.

$Mg[(\mathbf{1}MC)_2(OH_2)_2]^{2+}$ structural coordinates

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -9.7382 | -2.39273 | -0.54798 | C | -2.66296 | -3.36218 | -1.43183 |
| C | -8.87202 | -3.2718 | -1.20323 | C | -1.66747 | -2.19761 | -1.52686 |
| C | -7.52126 | -2.95646 | -1.38327 | O | -1.34872 | -1.66068 | -0.41583 |
| C | -7.08145 | -1.73431 | -0.88255 | O | -1.28239 | -1.83632 | -2.66599 |
| C | -7.93223 | -0.84443 | -0.22548 | C | 9.18571 | 2.88535 | -1.41215 |
| C | -9.27104 | -1.16691 | -0.0557 | C | 8.14126 | 3.7884 | -1.62533 |
| N | -5.78434 | -1.17661 | -0.93401 | C | 6.80687 | 3.40416 | -1.45829 |
| C | -5.73025 | 0.02647 | -0.31428 | C | 6.56533 | 2.08803 | -1.07215 |
| C | -7.14816 | 0.39615 | 0.16917 | C | 7.59713 | 1.17238 | -0.85884 |
| O | -1.66707 | 1.19762 | 0.03309 | C | 8.91722 | 1.56536 | -1.02702 |
| C | -1.93797 | 2.42205 | 0.21574 | N | 5.32412 | 1.44881 | -0.84912 |
| C | -3.31945 | 2.87881 | 0.42033 | C | 5.49117 | 0.1486 | -0.49843 |
| C | -4.45858 | 2.0476 | 0.29223 | C | 6.99965 | -0.16796 | -0.46795 |
| C | -4.52934 | 0.73487 | -0.15626 | O | 1.668 | -1.45168 | -0.06084 |
| C | -0.90636 | 3.43212 | 0.24791 | C | 2.04201 | -2.5826 | 0.36824 |
| C | -1.18322 | 4.74063 | 0.52665 | C | 3.46534 | -2.93974 | 0.43283 |
| C | -2.52098 | 5.14616 | 0.78367 | C | 4.51382 | -2.0384 | 0.12753 |
| C | -3.55454 | 4.24287 | 0.73063 | C | 4.40953 | -0.69916 | -0.23026 |
| C | -7.19331 | 0.61189 | 1.69913 | C | 1.09185 | -3.5766 | 0.80721 |
| C | -7.71777 | 1.6217 | -0.59249 | C | 1.48887 | -4.81801 | 1.21652 |
| C | -4.67018 | -1.84589 | -1.61489 | C | 2.87038 | -5.15644 | 1.22841 |
| Mg | -0.00768 | -0.13283 | -0.00115 | C | 3.82739 | -4.24498 | 0.85261 |
| C | -3.95854 | -2.89702 | -0.75039 | C | 7.38235 | -1.24429 | -1.51364 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 7.47021 | -0.56908 | 0.95209 | H | -3.96826 | -1.07835 | -1.94341 |
| C | 4.049 | 2.16693 | -1.01577 | H | -3.7004 | -2.45748 | 0.21735 |
| C | 3.69056 | 3.08214 | 0.1667 | H | -4.62917 | -3.74349 | -0.56478 |
| C | 3.36822 | 2.36982 | 1.48434 | H | -2.2121 | -4.16048 | -0.83273 |
| C | 2.0898 | 1.51788 | 1.51054 | H | -2.85514 | -3.75541 | -2.43453 |
| O | 1.48707 | 1.31391 | 0.40186 | H | 10.21294 | 3.20848 | -1.54642 |
| O | 1.7455 | 1.07584 | 2.63151 | H | 8.36413 | 4.80774 | -1.92435 |
| O | -0.25121 | -0.43107 | 2.05714 | H | 6.00277 | 4.11153 | -1.62327 |
| O | 0.38039 | 0.06833 | -2.07103 | H | 9.73269 | 0.86611 | -0.86603 |
| N | -2.80268 | 6.53712 | 1.09163 | H | 5.50574 | -2.4728 | 0.2134 |
| O | -3.97486 | 6.86179 | 1.31297 | H | 3.40959 | -0.29102 | -0.27361 |
| O | -1.85117 | 7.32484 | 1.11584 | H | 0.04723 | -3.28823 | 0.78121 |
| N | 3.27817 | -6.48402 | 1.65388 | H | 0.77391 | -5.56636 | 1.53669 |
| O | 4.48501 | -6.75262 | 1.65833 | H | 4.87089 | -4.53752 | 0.89295 |
| O | 2.39298 | -7.27843 | 1.98845 | H | 8.47102 | -1.34598 | -1.54852 |
| H | -10.7815 | -2.6619 | -0.4184 | H | 6.95961 | -2.22076 | -1.26935 |
| H | -9.24854 | -4.2183 | -1.57794 | H | 7.03676 | -0.96245 | -2.51177 |
| H | -6.85268 | -3.64574 | -1.88619 | H | 7.19826 | 0.19427 | 1.6858 |
| H | -9.94991 | -0.48622 | 0.44998 | H | 7.03738 | -1.5186 | 1.27269 |
| H | -5.39081 | 2.55043 | 0.53222 | H | 8.55925 | -0.67261 | 0.95833 |
| H | -3.59577 | 0.25168 | -0.41625 | H | 3.24799 | 1.44841 | -1.17057 |
| H | 0.10517 | 3.09023 | 0.06301 | H | 4.14659 | 2.75791 | -1.93191 |
| H | -0.40251 | 5.49099 | 0.56291 | H | 2.82243 | 3.66794 | -0.154 |
| H | -4.56365 | 4.59575 | 0.91291 | H | 4.50609 | 3.79565 | 0.3349 |
| H | -8.22856 | 0.76645 | 2.01721 | H | 3.27753 | 3.1074 | 2.28874 |
| H | -6.61073 | 1.48444 | 2.00218 | H | 4.19427 | 1.71531 | 1.7903 |
| H | -6.80215 | -0.26012 | 2.2298 | H | -1.07838 | -0.03345 | 2.35485 |
| H | -7.65258 | 1.47701 | -1.67406 | H | 0.50159 | 0.14396 | 2.42784 |
| H | -8.77235 | 1.74866 | -0.33133 | H | -0.26919 | -0.61842 | -2.43856 |
| H | -7.19645 | 2.54631 | -0.33883 | H | 1.24239 | -0.36552 | -2.13824 |
| H | -5.07873 | -2.30317 | -2.5216 | | | | |

$Mg[(\mathbf{2}MC)_2(OH_2)_2]^{2+}$ structural coordinates

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -9.77165 | -1.76887 | -0.99545 | C | -0.73946 | 3.5606 | 0.65698 |
| C | -8.90115 | -2.73158 | -1.51186 | C | -0.98841 | 4.85751 | 1.01967 |
| C | -7.51948 | -2.51549 | -1.54449 | C | -2.32198 | 5.30478 | 1.1868 |
| C | -7.05048 | -1.30377 | -1.04304 | C | -3.38027 | 4.47459 | 0.9806 |
| C | -7.90645 | -0.332 | -0.52084 | C | -7.29231 | 1.12271 | 1.44017 |
| C | -9.27506 | -0.55709 | -0.49608 | C | -7.48013 | 2.10511 | -0.91417 |
| N | -5.72242 | -0.83857 | -0.96665 | C | -4.5887 | -1.61738 | -1.47021 |
| C | -5.6494 | 0.38907 | -0.3825 | F | -2.52111 | 6.59387 | 1.5517 |
| C | -7.0855 | 0.86601 | -0.07059 | Mg | 0.07669 | -0.05726 | 0.3008 |
| O | -1.55253 | 1.39633 | 0.14366 | C | -4.03918 | -2.62708 | -0.45173 |
| C | -1.8045 | 2.60961 | 0.44184 | C | -2.72079 | -3.23894 | -0.95203 |
| C | -3.17562 | 3.10914 | 0.58729 | C | -1.66679 | -2.13397 | -1.09937 |
| C | -4.32794 | 2.33839 | 0.34198 | O | -1.3448 | -1.53856 | -0.02139 |
| C | -4.43349 | 1.02766 | -0.12845 | O | -1.25855 | -1.85761 | -2.256 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 9.29145 | 2.00875 | -1.88277 | H | -8.34656 | 1.34278 | 1.63386 |
| C | 8.31061 | 2.97953 | -2.09674 | H | -6.69865 | 1.96751 | 1.79548 |
| C | 6.96531 | 2.72776 | -1.80653 | H | -7.01662 | 0.24257 | 2.02696 |
| C | 6.64215 | 1.47162 | -1.29642 | H | -7.31185 | 1.92311 | -1.97894 |
| C | 7.61248 | 0.48929 | -1.08011 | H | -8.54408 | 2.31647 | -0.77143 |
| C | 8.94294 | 0.75104 | -1.3714 | H | -6.91809 | 2.99598 | -0.6274 |
| N | 5.37725 | 0.96602 | -0.93767 | H | -4.92444 | -2.12719 | -2.37866 |
| C | 5.4636 | -0.32182 | -0.48874 | H | -3.80878 | -0.92023 | -1.7792 |
| C | 6.94132 | -0.7607 | -0.53662 | H | -3.84619 | -2.11469 | 0.49553 |
| O | 1.60205 | -1.46091 | 0.42988 | H | -4.78636 | -3.40654 | -0.26241 |
| C | 1.8897 | -2.61714 | 0.86245 | H | -2.36784 | -3.97494 | -0.22251 |
| C | 3.26723 | -3.12268 | 0.84155 | H | -2.85511 | -3.74166 | -1.91449 |
| C | 4.36075 | -2.35962 | 0.39457 | H | 10.32874 | 2.22859 | -2.11433 |
| C | 4.34791 | -1.04285 | -0.07738 | H | 8.59212 | 3.94988 | -2.49419 |
| C | 0.87311 | -3.49347 | 1.39664 | H | 6.21231 | 3.48895 | -1.9743 |
| C | 1.17549 | -4.75032 | 1.84539 | H | 9.70716 | -0.00421 | -1.21001 |
| C | 2.51248 | -5.22192 | 1.79668 | H | 5.31523 | -2.87716 | 0.44552 |
| C | 3.52618 | -4.45072 | 1.31814 | H | 3.38087 | -0.5615 | -0.10373 |
| C | 7.15553 | -1.9448 | -1.51002 | H | -0.13909 | -3.10613 | 1.41161 |
| C | 7.48653 | -1.0865 | 0.87509 | H | 0.40959 | -5.40843 | 2.24534 |
| C | 4.15539 | 1.77355 | -1.06934 | H | 4.53865 | -4.8431 | 1.30446 |
| F | 2.75838 | -6.47618 | 2.24921 | H | 8.22579 | -2.15205 | -1.60565 |
| C | 3.97062 | 2.80576 | 0.05653 | H | 6.66275 | -2.85376 | -1.15948 |
| C | 3.67318 | 2.22683 | 1.44437 | H | 6.76569 | -1.7088 | -2.5037 |
| C | 2.30599 | 1.54628 | 1.61274 | H | 7.32999 | -0.24663 | 1.55719 |
| O | 1.60007 | 1.37732 | 0.56131 | H | 7.00422 | -1.9666 | 1.30517 |
| O | 1.98954 | 1.20199 | 2.77612 | H | 8.56206 | -1.28076 | 0.81747 |
| O | -0.22028 | -0.06698 | 2.38103 | H | 3.28891 | 1.11713 | -1.1124 |
| O | 0.26235 | 0.19099 | -1.79301 | H | 4.22522 | 2.28524 | -2.03509 |
| H | -10.8396 | -1.96105 | -0.97885 | H | 3.14188 | 3.45238 | -0.25143 |
| H | -9.29879 | -3.66708 | -1.89285 | H | 4.86316 | 3.44054 | 0.115 |
| H | -6.8494 | -3.27097 | -1.93869 | H | 3.73575 | 3.01827 | 2.19948 |
| H | -9.95623 | 0.18882 | -0.09624 | H | 4.43413 | 1.49214 | 1.73573 |
| H | -5.25399 | 2.87685 | 0.52023 | H | -0.96962 | 0.49362 | 2.61589 |
| H | -3.50819 | 0.49576 | -0.31002 | H | 0.61715 | 0.42847 | 2.67914 |
| H | 0.2707 | 3.18939 | 0.52707 | H | -0.28036 | -0.60563 | -2.10915 |
| H | -0.17934 | 5.56237 | 1.18721 | H | -0.2928 | 0.96139 | -1.97346 |
| H | -4.38976 | 4.85496 | 1.10446 | | | | |

$Ca[(\mathbf{1}MC)_2(OH_2)_2]^{2+}$ structural coordinates

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 9.92152 | 2.45964 | -1.42888 | C | 5.96159 | 0.12296 | -0.51419 |
| C | 8.97202 | 3.43805 | -1.73433 | C | 7.43346 | -0.33259 | -0.4231 |
| C | 7.60272 | 3.18143 | -1.61054 | O | 1.96521 | -1.08881 | 0.33915 |
| C | 7.22961 | 1.91356 | -1.17272 | C | 2.29089 | -2.29233 | 0.56391 |
| C | 8.16453 | 0.9258 | -0.86016 | C | 3.68806 | -2.74676 | 0.52855 |
| C | 9.52036 | 1.19149 | -0.98861 | C | 4.78881 | -1.9205 | 0.20014 |
| N | 5.92993 | 1.39687 | -0.97254 | C | 4.79688 | -0.58612 | -0.18568 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 1.29094 | -3.29022 | 0.87452 | H | 10.97825 | 2.68411 | -1.53174 |
| C | 1.61776 | -4.58796 | 1.14674 | H | 9.29782 | 4.41685 | -2.07183 |
| C | 2.979 | -4.99667 | 1.12548 | H | 6.87252 | 3.94792 | -1.84359 |
| C | 3.97837 | -4.10358 | 0.82639 | H | 10.26273 | 0.43447 | -0.75247 |
| C | 7.83296 | -0.70947 | 1.02356 | H | 5.74334 | -2.43575 | 0.24571 |
| C | 7.74206 | -1.48296 | -1.41518 | H | 3.83935 | -0.08508 | -0.23591 |
| C | 4.72374 | 2.19153 | -1.23277 | H | 0.25725 | -2.9586 | 0.88501 |
| Ca | 0.01642 | 0.30535 | 0.53418 | H | 0.86112 | -5.32616 | 1.38412 |
| C | 4.30175 | 3.04453 | -0.02647 | H | 5.00352 | -4.45716 | 0.81428 |
| C | 2.99343 | 3.80858 | -0.30424 | H | 8.90811 | -0.90699 | 1.06429 |
| C | 1.86777 | 2.805 | -0.58261 | H | 7.311 | -1.60259 | 1.37235 |
| O | 1.30667 | 2.28677 | 0.43396 | H | 7.61209 | 0.10665 | 1.71648 |
| O | 1.65155 | 2.51031 | -1.78819 | H | 7.4411 | -1.21531 | -2.43147 |
| C | -8.71098 | -3.58511 | -2.27919 | H | 8.81879 | -1.67588 | -1.42083 |
| C | -7.55369 | -4.36578 | -2.3392 | H | 7.23501 | -2.41033 | -1.14247 |
| C | -6.31191 | -3.84992 | -1.95505 | H | 4.93543 | 2.82532 | -2.09842 |
| C | -6.27904 | -2.52962 | -1.51269 | H | 3.92144 | 1.52073 | -1.53855 |
| C | -7.42424 | -1.73511 | -1.45264 | H | 4.15756 | 2.39418 | 0.8433 |
| C | -8.65158 | -2.25819 | -1.83448 | H | 5.10542 | 3.74702 | 0.22351 |
| N | -5.16413 | -1.76993 | -1.08589 | H | 2.74284 | 4.4123 | 0.57232 |
| C | -5.52145 | -0.50482 | -0.75837 | H | 3.11407 | 4.46863 | -1.16913 |
| C | -7.04393 | -0.35211 | -0.95513 | H | -9.66303 | -4.00948 | -2.58107 |
| O | -2.00353 | 1.58809 | 0.18238 | H | -7.61444 | -5.39178 | -2.688 |
| C | -2.58925 | 2.67125 | 0.48257 | H | -5.41979 | -4.46295 | -2.00311 |
| C | -4.04691 | 2.8135 | 0.3962 | H | -9.55301 | -1.65346 | -1.79481 |
| C | -4.91733 | 1.7677 | -0.00274 | H | -5.96261 | 2.06028 | -0.03583 |
| C | -4.59344 | 0.45932 | -0.33636 | H | -3.55193 | 0.18171 | -0.25354 |
| C | -1.83971 | 3.82539 | 0.91992 | H | -0.76099 | 3.7115 | 0.9726 |
| C | -2.45074 | 5.00731 | 1.23377 | H | -1.88412 | 5.87242 | 1.55686 |
| C | -3.86346 | 5.12271 | 1.13309 | H | -5.70992 | 4.19164 | 0.66531 |
| C | -4.63511 | 4.06006 | 0.72589 | H | -8.46008 | 0.68954 | -2.23097 |
| C | -7.3843 | 0.70608 | -2.03338 | H | -7.11389 | 1.71553 | -1.7186 |
| C | -7.76403 | -0.05205 | 0.38309 | H | -6.86514 | 0.49086 | -2.97108 |
| C | -3.8142 | -2.35841 | -1.04147 | H | -7.51698 | -0.80366 | 1.13742 |
| C | -3.5894 | -3.2925 | 0.15943 | H | -7.49853 | 0.92924 | 0.78058 |
| C | -3.55913 | -2.60273 | 1.52623 | H | -8.84628 | -0.07311 | 0.2254 |
| C | -2.3574 | -1.67688 | 1.77617 | H | -3.0726 | -1.5639 | -1.02442 |
| O | -1.55241 | -1.47828 | 0.80471 | H | -3.68793 | -2.90932 | -1.97888 |
| O | -2.26621 | -1.1823 | 2.92458 | H | -2.62791 | -3.78559 | -0.01589 |
| O | -0.14661 | 0.30877 | 2.92943 | H | -4.35583 | -4.07611 | 0.16221 |
| O | -0.18056 | 0.61432 | -1.89582 | H | -3.55525 | -3.35661 | 2.32098 |
| N | 3.31827 | -6.37836 | 1.41537 | H | -4.46846 | -2.01292 | 1.69684 |
| O | 4.51052 | -6.70533 | 1.39554 | H | -0.2327 | 1.06973 | 3.51344 |
| O | 2.39255 | -7.1574 | 1.66596 | H | -0.97142 | -0.26779 | 3.05865 |
| N | -4.50408 | 6.38376 | 1.46465 | H | 0.52633 | 1.32741 | -1.97795 |
| O | -5.73376 | 6.45944 | 1.36302 | H | -1.01214 | 1.11012 | -1.8976 |
| O | -3.78219 | 7.31665 | 1.83143 | | | | |

$Ca[(\mathbf{2}MC)_2(OH_2)_2]^{2+}$ structural coordinates

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 10.12629 | 1.6176 | -1.01688 | C | -4.1411 | 4.48082 | 1.19941 |
| C | 9.2791 | 2.63956 | -1.45173 | C | -7.54859 | 1.70212 | -1.45465 |
| C | 7.88933 | 2.48087 | -1.44437 | C | -7.77761 | 0.76179 | 0.91309 |
| C | 7.38749 | 1.26461 | -0.98748 | C | -4.29757 | -1.81862 | -1.1652 |
| C | 8.22019 | 0.23466 | -0.54556 | F | -3.56664 | 6.62941 | 1.98073 |
| C | 9.59712 | 0.40303 | -0.55982 | C | -4.06518 | -2.91886 | -0.11629 |
| N | 6.04418 | 0.84824 | -0.88829 | C | -3.82533 | -2.41748 | 1.31061 |
| C | 5.94186 | -0.40576 | -0.36995 | C | -2.48827 | -1.69691 | 1.54602 |
| C | 7.36644 | -0.94832 | -0.1184 | O | -2.22314 | -1.39588 | 2.73529 |
| O | 1.81452 | -1.32633 | 0.11034 | O | -1.75682 | -1.45677 | 0.52804 |
| C | 2.04551 | -2.53149 | 0.45677 | O | -0.031 | -0.01684 | 2.73986 |
| C | 3.40199 | -3.06876 | 0.59455 | O | 0.30953 | 0.02931 | -2.07947 |
| C | 4.57339 | -2.33292 | 0.33203 | H | 11.2013 | 1.76544 | -1.0313 |
| C | 4.71167 | -1.0211 | -0.12575 | H | 9.70186 | 3.57649 | -1.80077 |
| C | 0.95483 | -3.43568 | 0.73882 | H | 7.2389 | 3.28123 | -1.77792 |
| C | 1.16908 | -4.72943 | 1.13398 | H | 10.25985 | -0.3892 | -0.22298 |
| C | 2.49117 | -5.21828 | 1.27316 | H | 5.48532 | -2.89643 | 0.50471 |
| C | 3.57081 | -4.43051 | 1.01636 | H | 3.79851 | -0.46708 | -0.29873 |
| C | 7.6075 | -1.26372 | 1.37702 | H | -0.05081 | -3.04203 | 0.62487 |
| C | 7.68693 | -2.17085 | -1.01429 | H | 0.34133 | -5.39921 | 1.34745 |
| C | 4.92703 | 1.70789 | -1.29048 | H | 4.56988 | -4.84106 | 1.12802 |
| F | 2.65729 | -6.50326 | 1.66778 | H | 8.65866 | -1.52586 | 1.53079 |
| Ca | -0.06606 | 0.23258 | 0.33666 | H | 6.99582 | -2.09914 | 1.72328 |
| C | 4.46677 | 2.65655 | -0.17213 | H | 7.38112 | -0.39486 | 2.00067 |
| C | 3.21928 | 3.45847 | -0.58812 | H | 7.50352 | -1.94251 | -2.06755 |
| C | 2.06603 | 2.48615 | -0.86634 | H | 8.74317 | -2.43441 | -0.90448 |
| O | 1.43771 | 2.05215 | 0.14852 | H | 7.09121 | -3.04558 | -0.74664 |
| O | 1.89719 | 2.12814 | -2.06298 | H | 5.25362 | 2.27527 | -2.16697 |
| C | -9.41212 | -2.35984 | -1.92603 | H | 4.10442 | 1.07856 | -1.62897 |
| C | -8.37112 | -3.25087 | -2.19575 | H | 4.22935 | 2.0701 | 0.72217 |
| C | -7.04168 | -2.91953 | -1.91309 | H | 5.28631 | 3.33515 | 0.09252 |
| C | -6.79695 | -1.66695 | -1.35269 | H | 2.94475 | 4.1346 | 0.22628 |
| C | -7.82695 | -0.7621 | -1.08604 | H | 3.42554 | 4.04802 | -1.48713 |
| C | -9.14147 | -1.10265 | -1.36885 | H | -10.4358 | -2.6409 | -2.15155 |
| N | -5.56287 | -1.09148 | -0.98836 | H | -8.59228 | -4.22041 | -2.63136 |
| C | -5.72592 | 0.17428 | -0.50037 | H | -6.24123 | -3.61823 | -2.12574 |
| C | -7.2325 | 0.51333 | -0.51415 | H | -9.95254 | -0.40843 | -1.16742 |
| O | -1.91833 | 1.69596 | 0.31979 | H | -5.77661 | 2.69963 | 0.46846 |
| C | -2.32902 | 2.8365 | 0.69344 | H | -3.6555 | 0.57098 | -0.14199 |
| C | -3.75509 | 3.17305 | 0.75162 | H | -0.33794 | 3.61634 | 1.01586 |
| C | -4.7774 | 2.28311 | 0.37721 | H | -1.10625 | 5.87076 | 1.79147 |
| C | -4.65871 | 0.97074 | -0.09314 | H | -5.19279 | 4.74598 | 1.25293 |
| C | -1.39234 | 3.86725 | 1.08005 | H | -8.63285 | 1.82988 | -1.52962 |
| C | -1.81316 | 5.09981 | 1.49937 | H | -7.12111 | 2.63804 | -1.09049 |
| C | -3.19937 | 5.3951 | 1.55771 | H | -7.15914 | 1.51878 | -2.45954 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | -7.55701 | -0.085 | 1.56843 | H | -3.86905 | -3.25597 | 2.01442 |
| H | -7.35034 | 1.65952 | 1.36414 | H | -4.62234 | -1.73396 | 1.62883 |
| H | -8.86427 | 0.88512 | 0.87309 | H | 0.66061 | -0.48721 | 3.21814 |
| H | -3.46971 | -1.11439 | -1.14072 | H | -0.87994 | -0.56414 | 2.85308 |
| H | -4.32641 | -2.25646 | -2.16897 | H | 0.86595 | 0.86191 | -2.19686 |
| H | -3.18888 | -3.48377 | -0.45122 | H | 0.96159 | -0.68592 | -2.07069 |
| H | -4.91492 | -3.61158 | -0.12036 | | | | |

Sensor **1**(MC) structural coordinates

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 5.27391 | -2.4027 | -0.46016 | O | 1.61985 | 1.21483 | 2.80677 |
| C | 5.62874 | -1.16485 | -1.00067 | N | -6.0465 | -1.04299 | 0.64108 |
| C | 4.6906 | -0.13544 | -1.13021 | O | -5.72276 | -1.97821 | 1.39201 |
| C | 3.39042 | -0.38943 | -0.69761 | O | -7.23036 | -0.73717 | 0.41515 |
| C | 3.01521 | -1.63123 | -0.17694 | H | 6.02032 | -3.18583 | -0.36529 |
| C | 3.95628 | -2.64122 | -0.04575 | H | 6.65036 | -0.99267 | -1.3274 |
| N | 2.26593 | 0.45748 | -0.73396 | H | 4.9708 | 0.82138 | -1.55261 |
| C | 1.13931 | -0.20969 | -0.367 | H | 3.67806 | -3.60745 | 0.36632 |
| C | 1.52982 | -1.61182 | 0.13587 | H | -1.23349 | -1.12223 | 0.5672 |
| O | -2.11432 | 1.85488 | -1.98539 | H | -0.2555 | 1.23287 | -1.12414 |
| C | -2.97096 | 1.2165 | -1.34748 | H | -4.64149 | 2.30743 | -2.19444 |
| C | -2.64148 | 0.12406 | -0.39614 | H | -6.42254 | 0.99849 | -1.0296 |
| C | -1.31277 | -0.2709 | -0.10378 | H | -3.45801 | -1.39872 | 0.91313 |
| C | -0.14187 | 0.31889 | -0.55687 | H | 1.19902 | -3.71178 | -0.30702 |
| C | -4.39699 | 1.49527 | -1.51684 | H | -0.261 | -2.72671 | -0.47401 |
| C | -5.37014 | 0.78461 | -0.88485 | H | 0.99622 | -2.65822 | -1.71749 |
| C | -5.01359 | -0.28076 | -0.00376 | H | 1.64567 | -0.83115 | 2.19359 |
| C | -3.68676 | -0.5886 | 0.22862 | H | 0.22865 | -1.84521 | 1.88829 |
| C | 0.81752 | -2.74146 | -0.64113 | H | 1.81298 | -2.61912 | 2.03952 |
| C | 1.29337 | -1.72867 | 1.66815 | H | 1.36671 | 2.31867 | -0.7776 |
| C | 2.34917 | 1.90772 | -0.9962 | H | 2.59137 | 2.05823 | -2.05583 |
| C | 3.33904 | 2.6548 | -0.07371 | H | 3.02408 | 3.70182 | -0.12396 |
| C | 3.28493 | 2.19672 | 1.38841 | H | 4.36348 | 2.60168 | -0.46456 |
| C | 1.8216 | 2.11555 | 1.95165 | H | 3.84863 | 2.91685 | 1.99734 |
| O | 1.02096 | 2.95906 | 1.4759 | H | 3.78048 | 1.22911 | 1.52155 |

Sensor **2**(MC) structural coordinates

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 4.89339 | -2.27376 | -0.35189 | C | 0.63545 | -0.32058 | -0.29162 |
| C | 5.13107 | -1.11982 | -1.10065 | C | 1.15613 | -1.58877 | 0.41121 |
| C | 4.12441 | -0.17131 | -1.3121 | O | -2.82145 | 1.19375 | -2.0613 |
| C | 2.87322 | -0.41403 | -0.74556 | C | -3.59625 | 0.62389 | -1.26534 |
| C | 2.61478 | -1.58035 | -0.01515 | C | -3.14832 | -0.24615 | -0.15231 |
| C | 3.62313 | -2.50762 | 0.19501 | C | -1.79527 | -0.49089 | 0.12708 |
| N | 1.70321 | 0.3573 | -0.82063 | C | -0.67795 | 0.08343 | -0.49027 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -5.04467 | 0.77387 | -1.40679 | H | -1.61787 | -1.1913 | 0.93982 |
| C | -5.93547 | 0.1381 | -0.5908 | H | -0.88199 | 0.88327 | -1.19026 |
| C | -5.45984 | -0.70325 | 0.45015 | H | -5.37728 | 1.42265 | -2.21123 |
| C | -4.13077 | -0.89345 | 0.66859 | H | -7.00925 | 0.25627 | -0.71212 |
| C | 0.47081 | -2.87833 | -0.08915 | H | -3.80999 | -1.53651 | 1.4838 |
| C | 1.03932 | -1.43586 | 1.95366 | H | 0.93843 | -3.75054 | 0.38029 |
| C | 1.66465 | 1.76589 | -1.25466 | H | -0.59247 | -2.8912 | 0.15761 |
| F | -6.38742 | -1.32282 | 1.23642 | H | 0.56767 | -2.98317 | -1.17409 |
| C | 2.70648 | 2.67248 | -0.56393 | H | 1.37895 | -0.44479 | 2.28465 |
| C | 2.83047 | 2.43316 | 0.94458 | H | 0.0001 | -1.55271 | 2.27523 |
| C | 1.44537 | 2.46059 | 1.68491 | H | 1.63222 | -2.22117 | 2.43708 |
| O | 0.60741 | 3.26861 | 1.21247 | H | 0.69014 | 2.14977 | -0.95852 |
| O | 1.33825 | 1.67678 | 2.66428 | H | 1.75804 | 1.80842 | -2.3479 |
| H | 5.69118 | -2.99431 | -0.19664 | H | 2.33173 | 3.68943 | -0.71833 |
| H | 6.11465 | -0.94948 | -1.53008 | H | 3.6848 | 2.60351 | -1.05756 |
| H | 4.31605 | 0.71854 | -1.89858 | H | 3.4582 | 3.23017 | 1.36779 |
| H | 3.43317 | -3.40955 | 0.77116 | H | 3.34337 | 1.49036 | 1.16104 |

**Fluorescence Experiments**

Job's Plots

Stock solutions of spiropyran chemosensor (SP, 100 µM) and metal ion salts (M, 100 µM) were prepared separately in HPLC-grade acetonitrile. Solutions were prepared (in triplicate) in the same clear-bottom microplate tray from varying volumes of the spiropyran stock solution and of the ion stock solutions, respectively, until the total volume of each replicate was 200 µL. The concentration ratios of ([SP], [M]) in µM were (100, 0), (95, 5), (80, 20), (70, 30), (50, 50), (40, 60), (30, 70), (20, 80), (5, 95) and (0, 100). As such, each solution contained a constant total combined concentration of spiropyran and metal ion ([SP]+ [M] = 100 µM). Fluorescence emission spectra were recorded between 555 and 800 nm, respectively, at 25 °C using a BioTek Synergy H4 Hybrid Multi-Mode Microplate Reader. Fluorescence excitation was at 532 nm, with 100 gain setting and scanning resolution was 5nm, with band pass of 9 nm. Job's plots were derived by plotting the mean fluorescence at the maximum emission wavelength for each concentration ratio of (SP], [M]).

Dissociation Constants ($K_d$)

Stock solutions of metal ion salts (0.02-2 mM) were prepared separately in HPLC-grade acetonitrile. Replicate solutions were prepared (in triplicate) in the same clear-bottom microplate tray from 2 µL of spiropyran stock (5 mM) and 10 µL of the respective ion stock solutions. 188 µL of HPLC grade acetonitrile was then added to dilute each replicate, such that the final concentrations of spiropyran and metal ions in each solution were 50 µM and 1-100 µM, respectively. Fluorescence emission spectra were recorded between 555 and 800 nm, at 25 °C using a BioTek Synergy H4 Hybrid Multi-Mode Microplate Reader. Fluorescence excitation was at 532 nm, with 100 gain setting and scanning resolution was 5nm, with band pass of 9 nm. Concentration curves were prepared from the fluorescence emission maxima for each ion concentration. The apparent dissociation constants ($K_d$) of spiropyrans for metal ions were then calculated by fitting an appropriate non-linear regression in GraphPad Prism version 7.02. The 'Hill Plot with Specific Binding' model was selected, as it represents a saturation binding experiment, where concentration of 'radioligand' (i.e. metal ion) is varied and binding to the 'recepter' (i.e. merocyanine isomer) is measured, in this case as a fluorescence emission. The model uses the following equation,

$$Y = Bmax*X^h/(K_d^h + X^h)$$

Where Y is the relative fluorescence intensity at any given concentration of metal ion, Bmax is the maximum specific binding in the same units as Y (i.e. in this case the fluorescence at sensor saturation), X is the concentration of metal ion and $K_d$ is the metal ion concentration needed to achieve the half-maximum binding at equilibrium, expressed in the same units as X. The parameter h is the Hill slope, and h = 1.0 when a monomer binds with no cooperativity to one site. If h > 0, i.e. the 'receptor' (merocyanine) or 'radioligand' (metal ion) has multiple binding sites with positive cooperativity, and the graph will have a sigmoidal appearance [1].

Quantum Yield (Φ)

A stock solution containing spiropyran chemosensor (SP, 50 µM) and metal ion salt (M, 100 µM) was prepared in HPLC-grade acetonitrile. Solutions were prepared (in triplicate) on the same clear-bottom microplate tray from varying volumes of the combined spiropyran/metal ion stock solution and HPLC-grade acetonitrile, until the volume of each replicate was 200 µL. The concentration ratios of ([SP], [M]) in µM were (10, 20), (20, 40), (30, 60), (40, 80), (50, 100), (60, 120), (80, 160) and (100, 200). Absorbance (400-600 nm, 2nm band pass) and

fluorescence emission spectra (535-800 nm, 5nm band pass, excitation 514 nm, 80 gain) were recorded at 25 °C using a BioTek Synergy H4 Plate Reader. These absorbance and fluorescence measurements was repeated for Rhodamine B (0, 1, 2, 3, 4, 5 µM), and a graph of integrated fluorescence *vs* absorbance at 514 nm (up to an approximate absorbance value of 0.1) was obtained. Quantum yield was calculated using the following equation:

$$\Phi_x = \Phi_{ST} (Grad_x/Grad_{ST})(\eta^2_x/\eta^2_{ST})$$

Where subscripts ST and X denote standard (Rhodamine B) and the unknown (spiropyran), respectively. Φ is fluorescence quantum yield, Grad is the gradient from the plot of integrated fluorescence intensity vs absorbance and η is the refractive index of the solvent ($\eta_{(water)}$ = 1.330, $\eta_{(acetonitrile)}$ = 1.344). The fluorescence quantum yield of Rhodamine B in water at $\lambda_{ex}$ = 514 nm is 0.31, as reported in the literature [2].

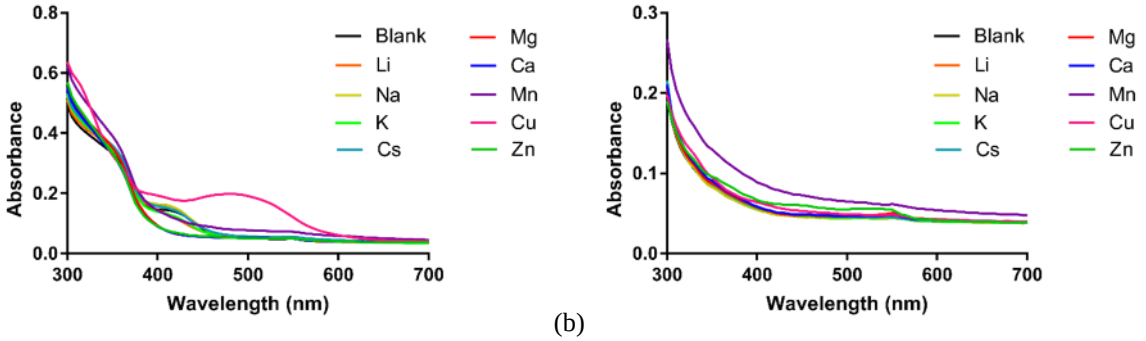



**Figure S10.** Absorbance spectra of (a) chemosensor **1** (50 µM) and (b) chemosensor **2** (50 µM) in the presence of an excess of biologically relevant metal ions (100 µM). Experiments were performed under ambient light conditions in acetonitrile solvent.

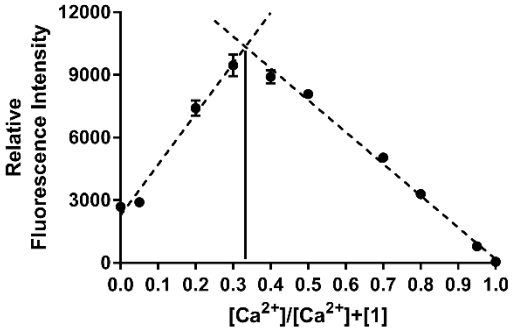
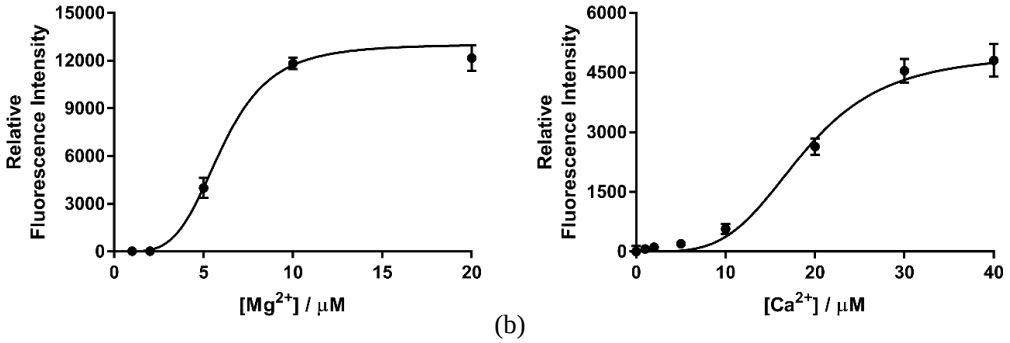
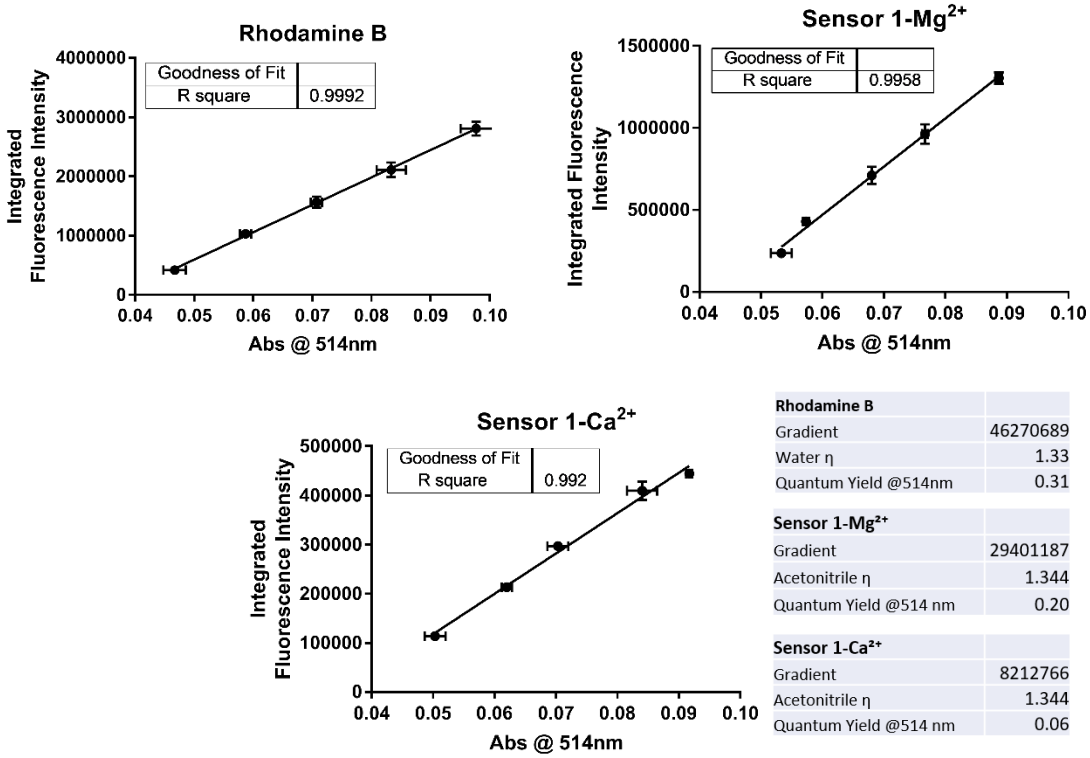



**Figure S11.** Job's plot of chemosensor **1** (50 µM) in the presence of $Ca^{2+}$ ions (100 µM). Fluorescence excitation was at 532 nm, with experiments performed under ambient light conditions in acetonitrile solvent.




(a) (b)

**Figure S12.** Metal ion titration curves of chemosensor **1** (50 μM) with (a) $Mg^{2+}$ (Kd ($Mg^{2+}$) = 6.0 ± 0.3 μM, h = 4.3 ± 0.9) and (b) $Ca^{2+}$ (Kd ($Ca^{2+}$) = 18.7 ± 0.6 μM, h = 4.0 ± 0.5) measured from their respective maximum emissions. Experiments were recorded in HPLC-grade acetonitrile, with excitation at 532 nm under ambient light conditions.




| Rhodamine B | |
|---|---|
| Gradient | 46270689 |
| Water η | 1.33 |
| Quantum Yield @514nm | 0.31 |
| **Sensor 1-Mg²⁺** | |
| Gradient | 29401187 |
| Acetonitrile η | 1.344 |
| Quantum Yield @514 nm | 0.20 |
| **Sensor 1-Ca²⁺** | |
| Gradient | 8212766 |
| Acetonitrile η | 1.344 |
| Quantum Yield @514 nm | 0.06 |

**Figure S13.** Integrated fluorescence spectra after excitation at 514 nm versus the absorbance at 514 nm for Rhodamine B (0 – 5 μM, water); (**1**)MC-$Mg^{2+}$ (0-100 μM, acetonitrile) in the presence of a 2-fold excess of $Mg^{2+}$; and (**1**)MC-$Ca^{2+}$ (0-100 μM, acetonitrile) in the presence of a 2-fold excess of $Ca^{2+}$. Spectra were recorded under ambient light conditions, in acetonitrile solvent. The quantum yield of (**1**)MC-$Mg^{2+}$ was calculated to be Φ = 0.20, and the quantum yield of (**1**)MC-$Ca^{2+}$ was calculated to be Φ = 0.06.

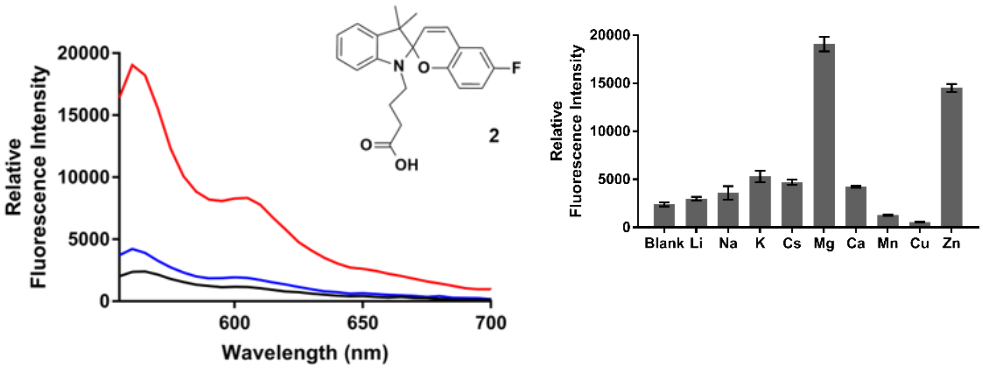



**Figure S14.** Fluorescence emission spectra of chemosensor **2** (50 µM) in the absence (black) and presence of excess $Mg^{2+}$ (red, 100 µM) and $Ca^{2+}$ (blue, 100 µM), respectively. Inset: Selectivity profile of chemosensor **2** in the presence of various biologically relevant metal ions (100 µM), with $\lambda_{max}$ at 560 nm. Excitation was at 532 nm, and all experiments were performed under ambient light conditions, in HPLC-grade acetonitrile solvent.

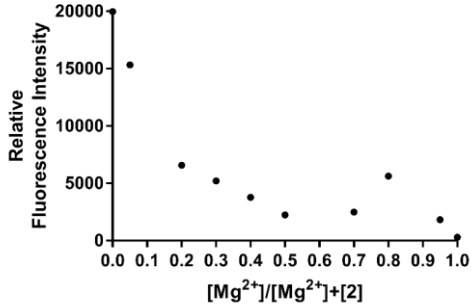



**Figure S15.** Job's plot of chemosensor **2** (50 µM) in the presence of $Mg^{2+}$ ions (100 µM), with $\lambda_{max}$ at 560 nm. Fluorescence excitation was at 532 nm, with experiments performed under ambient light conditions in acetonitrile solvent. The plot suggests a more complex binding stoichiometry for chemosensor **2**.

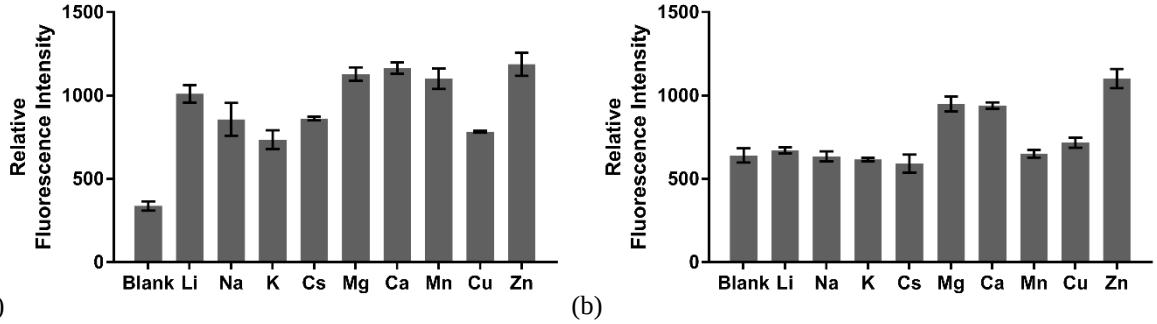



**Figure S16.** Selectivity profiles of (a) compound **3** (50 µM) and (b) compound **4** (50 µM) in the presence of an excess of biologically relevant metal ions (100 µM) in HPLC-grade acetonitrile. Fluorescence excitation was at 532 nm.

**References**


1. "Equation: Specific binding with Hill slope", GraphPad Curve Fitting Guide. Accessed 10 April 2018. https://www.graphpad.com/guides/prism/7/curve-fitting/index.htm?reg_specific_hill.htm.
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