

Supporting Information:

Hydroxyquinolines with extended fluorophores: Arrays for turn-on and ratiometric sensing of cations.

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Synthetic experiments:

General: Commercially available solvents and reagents were used as received from the chemical suppliers. Tetrahydrofuran was distilled from K-Na alloy under argon. All reactions were monitored using Whatman K6F Silica Gel 60 Å analytical TLC plates by UV detection (254 and 365 nm). Silica gel (60 Å, 32-63 µm) from EMD Science was used for column chromatography.

Melting points (uncorrected) were measured using Thomas Hoover capillary melting point apparatus. ¹H and ¹³C APT NMR spectra were recorded using either a Varian spectrometer with working frequency 400 MHz or a Bruker instrument (300 MHz). Chemical shifts were referenced to the residual resonance signal of the deuterated solvent. In the NMR data, the asterisk symbol (*) denotes that multiple signals and/or broadened peaks appear due to the diastereoisomerism caused by ethyl-hexyl alkyl chains.

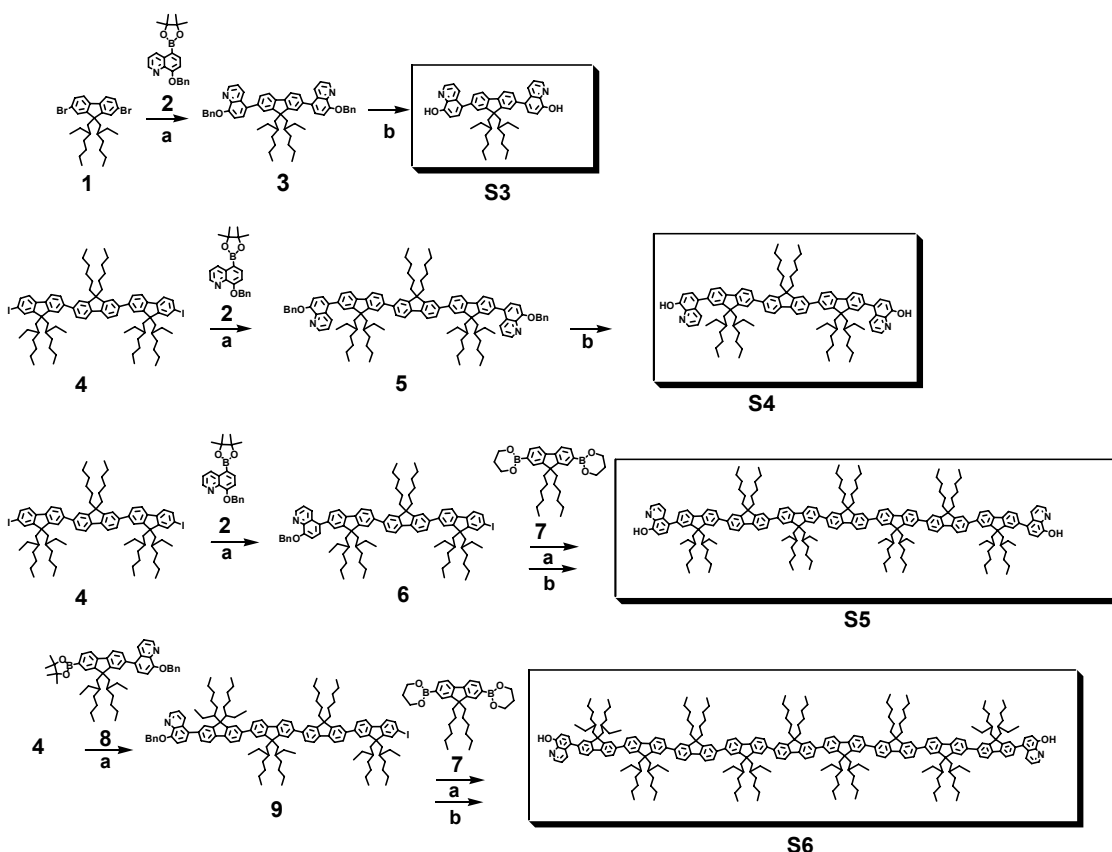
High-resolution mass spectra were measured on a magnetic sector mass spectrometer using electron impact (EI) or electron spray ionization (ESI). MALDI-TOF/MS were recorded using a Bruker Daltonics Omnimflex spectrometer. GC-MS was recorded using Shimadzu GCMS-QP5050.

S1 was commercially available from chemical suppliers. **S2** was synthesized according the published reference.¹ The synthesis of **S3**, **S4**, **S5** and **S6** are described as follow.

Synthetic procedures:

Synthesis of sensors **S3-S6**:

The preparation of sensors **S3**, **S4**, **S5** and **S6** is outlined in **scheme 1**. 2,7-dibromo-9,9-bis(2-ethylhexyl)fluorene (**1**), and 2,7-bis(1,3,2-dioxaborinan-2-yl)-9,9-dihexylfluorene (**7**) were purchased from Aldrich. The building blocks **2**, **4** and **6** were prepared according to the published procedures.^{1b,2}

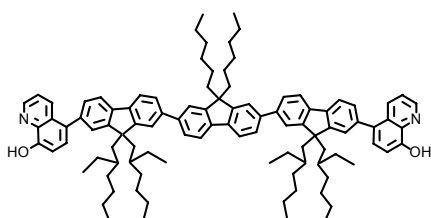


Scheme 1. Synthesis of **S3**, **S4**, **S5** and **S6**. a) Pd(PPh₃)₄, Et₄N⁺OH⁻ in MeOH, toluene, 60 °C; b) 1,4-cyclohexadiene, Pd-C (10%), isopropanol, reflux.

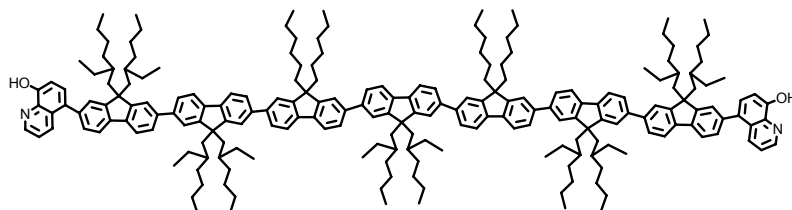
Characterization of sensors **S3-S6**:

(S3): Yield: 123 mg (67%) of white crystals. m.p. 191-192 °C; ¹H NMR (CDCl₃, 300 MHz) δ (ppm): 0.55-0.75 (m, 7H); 0.80-1.00 (m, 8H); 2.05 (m, 2H); 7.29 (d, 1H, *J* = 7.5 Hz); 7.40-7.52 (m, 4H); 7.78 (d, 1H, *J* = 7.7 Hz); 8.31 (m, 1H); 9.02 (dd, 1H, *J* = 1.3, 4.1 Hz); ¹³C APT NMR (CDCl₃, 100 MHz) δ (ppm): 10.4 *CH₃, 14.0 CH₃, 22.8 CH₂, 27.0 *CH₂, 28.5 *CH₂, 34.0 *CH₂, 34.9 CH, 44.7

CH₂, 55.2 C, 109.4 CH, 119.6 CH, 121.6 CH, 125.9 CH, 127.0 C, 128.1 CH, 129.0 CH, 131.5 C, 134.8 CH, 137.8 C, 138.3 C, 140.2 C, 147.7 CH, 151.0 C, 151.5 C; EI/MS: *m/z* 676 (100) [M⁺], 465 (87), 338 (31). Exact mass calculated for C₄₇H₅₂N₂O₂ (M⁺): 676.40. MALDI-TOF/MS: *m/z* 676.43 [M⁺].

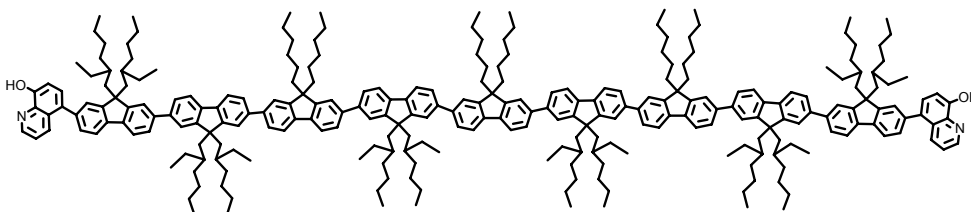


(S4): Yield: 210 mg (79%) of pale yellow crystals. m.p. 81-85 °C; ¹H NMR (CDCl₃, 400 MHz) δ (ppm): 0.50-0.74 (m, 14H); 0.76-1.00 (m, 21H); 1.16 (m, 6H); 2.10 (m, 6H); 7.27 (d, 1H, *J* = 7.8 Hz); 7.38-7.44 (m, 2H); 7.45-7.50 (m, 2H); 7.62-7.72 (m, 4H); 7.83 (m, 3H); 8.32 (m*, 1H); 9.10 (dd, 1H, *J* = 1.1, 4.0 Hz); ¹³C APT NMR (CDCl₃, 100 MHz) δ (ppm): 10.2 *CH₃, 10.3 *CH₃, 10.56 *CH₃, 10.62 *CH₃, 14.0 *CH₃, 22.5 *CH₂, 22.7 *CH₂, 22.9 *CH₂, 23.8 *CH₂, 26.9 *CH₂, 27.5 *CH₂, 28.2 *CH₂, 28.6 *CH₂, 29.7 *CH₂, 31.5 *CH₂, 33.8 *CH₂, 34.3 *CH₂, 34.8 CH, 40.4 *CH₂, 44.5 *CH₂, 55.2 C, 109.45 CH, 119.52 CH, 119.9 CH, 121.6 CH, 122.9 CH, 125.8 CH, 125.9 CH, 126.2 CH, 127.0 C, 128.0 CH, 128.9 CH, 129.0 CH, 131.6 C, 134.8 CH, 137.6 C, 138.3 C, 139.9 C, 140.1 C, 140.2 C, 140.7 C, 147.6 CH, 147.7 CH, 151.1 C, 151.2 C, 151.5 C, 151.7 C; MALDI-TOF/MS: *m/z* 1398.41 [M+H⁺]. HR-MS (ESI/MS): Calculated for C₁₀₁H₁₂₄N₂O₂ (M+H⁺): *m/z* 1397.9741. Found: *m/z* 1397.9755.



(S5): Yield: 109 mg (96%) of off-white solid. m.p. 86-90 °C; ¹H NMR (CDCl₃, 300 MHz) δ (ppm): 0.55-1.10 (m, 75H); 1.15 (m, 18H); 2.20 (m, 14H); 7.28 (d, 1H, obscured by CHCl₃ signal); 7.42-7.58 (m, 4H); 7.65-7.77 (m, 12H); 7.83-7.93 (m, 7H); 8.35 (m*, 1H); 8.86 (br d, 1H); ¹³C APT NMR (CDCl₃, 75.5 MHz) δ (ppm): 10.2 *CH₃, 10.30 *CH₃, 10.49 *CH₃, 10.53 *CH₃, 10.6 *CH₃, 10.7 *CH₃, 14.01 *CH₃, 14.03 *CH₃, 14.1 *CH₃, 22.6 *CH₂, 22.7 *CH₂, 22.78 *CH₂, 22.80 *CH₂, 22.89 *CH₂, 22.91 *CH₂, 23.9 *CH₂, 24.8 *CH₂, 27.0 *CH₂, 27.4 *CH₂, 27.48 *CH₂, 27.51 *CH₂, 28.16 *CH₂, 28.24 *CH₂, 28.3 *CH₂, 28.56 *CH₂, 28.60 *CH₂, 29.1 *CH₂, 29.3 *CH₂, 29.4 *CH₂, 29.5 *CH₂, 29.6 *CH₂, 29.7 *CH₂, 31.47 *CH₂, 31.49 *CH₂, 31.51 *CH₂, 32.0 *CH₂, 33.8 *CH₂, 33.9 *CH₂, 34.0 *CH₂, 34.4 *CH₂, 34.88 CH, 34.92 CH, 40.4 *CH₂, 44.4 *CH₂, 44.5 *CH₂, 44.6 *CH₂, 55.16 C, 55.19 C, 55.21 C, 55.24 C, 55.26 C, 55.28 C, 55.30 C, 109.6 CH, 119.6 CH, 120.0 CH, 121.56 CH, 121.63 CH, 122.8 CH, 122.9 CH, 123.1 CH, 125.3 CH, 125.9 CH, 126.1 CH, 126.2 CH, 126.3 CH, 128.1 CH, 128.15 CH, 128.24 CH, 128.8 CH, 129.0 CH, 129.1 CH, 127.1 C, 131.7 C, 137.6 C, 138.35 C, 138.37 C, 139.9 C, 139.96 C, 140.01 C, 140.1 C, 140.2 C, 140.26 C, 140.30 C, 140.34 C, 140.37 C, 140.40 C, 147.7

CH, 151.0 C, 151.15 C, 151.24 C, 151.3 C, 151.4 C, 151.6 C, 151.70 C, 151.73 C, 151.8 C; Exact mass calculated for $C_{209}H_{268}N_2O_2$ (M^+): 2838.09. MALDI-TOF/MS: m/z 2838.80 [M^+].



(**S6**): Yield: 37 mg (96%) of off-white solid, m.p. 107-110 °C. 1H NMR ($CDCl_3$, 300 MHz) δ (ppm): 0.55-1.10 (m, 105H); 1.15 (m, 18H); 2.20 (m, 18H); 7.31 (d, 1H, $J = 8.1$ Hz); 7.40-7.55 (m, 4H); 7.63-7.78 (m, 16H); 7.81-7.94 (m, 9H); 8.35 (m*, 1H); 8.85 (br d, 1H, $J = 3.3$ Hz). ^{13}C APT NMR ($CDCl_3$, 75.5 MHz) δ (ppm): 10.18 * CH_3 , 10.24 * CH_3 , 10.4 * CH_3 , 10.47 * CH_3 , 10.51 * CH_3 , 14.00 * CH_3 , 14.02 * CH_3 , 22.6 * CH_2 , 22.77 * CH_2 , 22.78 * CH_2 , 22.87 * CH_2 , 22.89 * CH_2 , 23.9 * CH_2 , 26.9 * CH_2 , 27.4 * CH_2 , 28.3 * CH_2 , 28.56 * CH_2 , 28.60 * CH_2 , 29.7 * CH_2 , 31.46 * CH_2 , 31.48 * CH_2 , 31.50 * CH_2 , 34.0 * CH_2 , 34.1 * CH_2 , 34.8 CH, 34.9 CH, 40.5 * CH_2 , 44.4 * CH_2 , 44.6 * CH_2 , 55.12 C, 55.14 C, 55.17 C, 55.24 C, 55.3 C, 109.46 CH, 119.52 CH, 119.9 CH, 121.5 CH, 121.6 CH, 122.9 CH, 123.0 CH, 125.9 CH, 126.1 CH, 126.2 CH, 126.95 C, 127.03 C, 128.1 CH, 129.0 CH, 131.6 C, 131.7 C, 137.6 C, 138.4 C, 139.9 C, 140.1 C, 140.2 C, 140.4 C, 140.6 C, 140.8 C, 140.9 C, 147.7 CH, 151.06 C, 151.12 C, 151.14 C, 151.2 C, 151.26 C, 151.33 C, 151.5 C, 151.73 C, 151.8 C. Exact mass calculated for $C_{267}H_{349}N_2O_2$ ($M+H^+$): 3615.73. MALDI-TOF/MS: m/z 3616.15 [$M+H^+$].

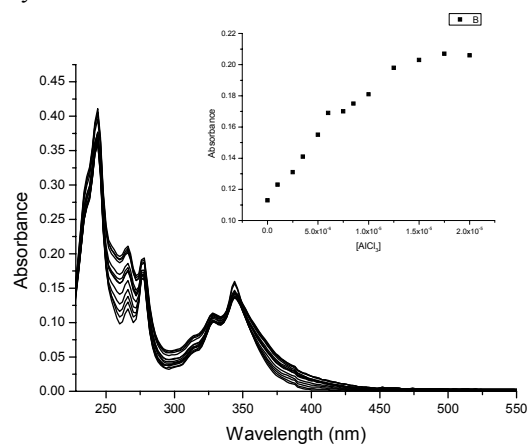
Examples of UV-Visible and fluorescence titration experiments:

General: Absorption spectra were recorded using a Hitachi U-3010 spectrophotometer. Fluorescence measurements were performed on a single photon counting spectrofluorimeter from Edinburgh Analytical Instruments (FL/FS 920). Optically dilute solutions used for all photophysical experiments were prepared using spectroscopic grade solvents unless otherwise stated. For titration experiments the samples were excited at the isosbestic point of the lowest energy.

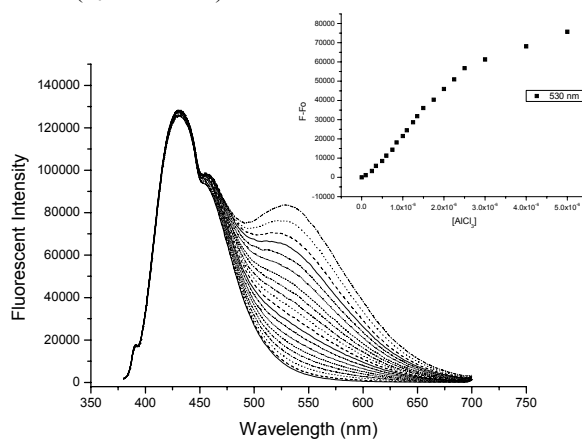
1 UV-vis and fluorescent titration of S2:

1) S2 and aluminum chloride:

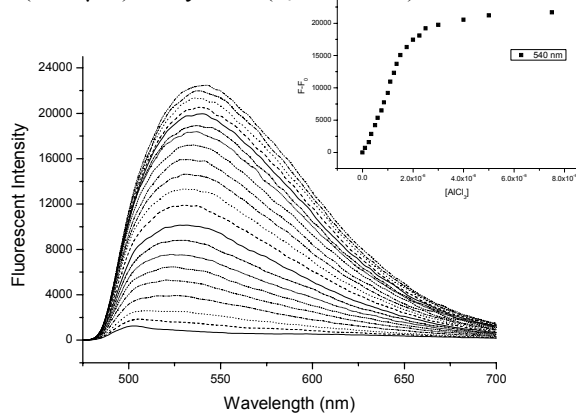
Changes in absorption spectra of S2 (5 μM) upon the addition of aluminum chloride (0-20 μM) in dry THF.



Changes in fluorescent spectra of S2 (0.5 μM) upon the addition of aluminum chloride (0-5 μM) in dry THF. ($\lambda_{\text{ex}} = 350$ nm)

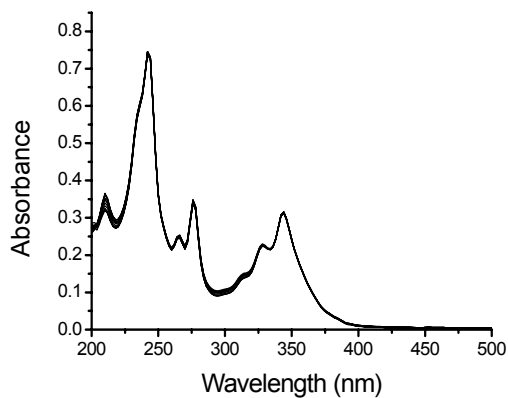


Changes in fluorescent spectra of S2 (0.5 μM) upon the addition of aluminum chloride (0-7.5 μM) in dry THF. ($\lambda_{\text{ex}} = 415$ nm)

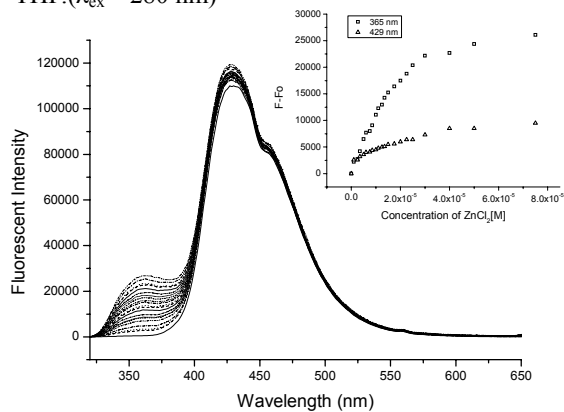


2) S2 and zinc chloride:

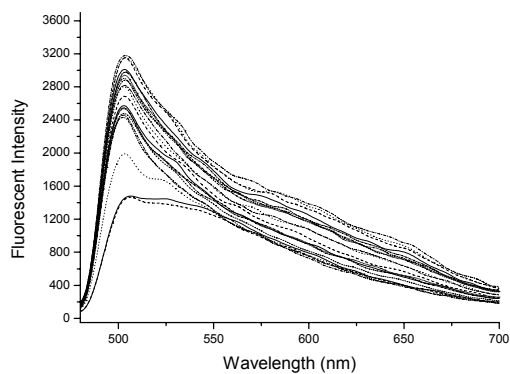
Changes in absorption spectra of S2 (10 μM) upon the addition of zinc chloride (0-40 μM) in dry THF.



Changes in fluorescent spectra of S2 (0.5 μM) upon the addition of zinc chloride (0-75 μM) in dry THF. ($\lambda_{\text{ex}} = 280 \text{ nm}$)

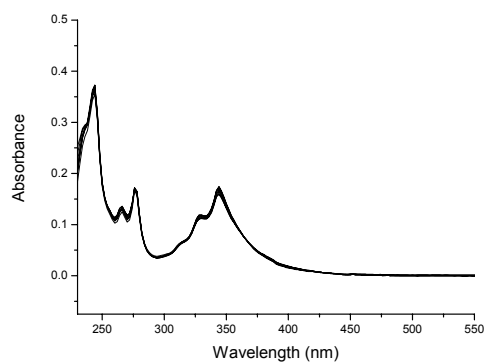


Changes in fluorescent spectra of S2 (0.5 μM) upon the addition of zinc chloride (0-75 μM) in dry THF. ($\lambda_{\text{ex}} = 415 \text{ nm}$)

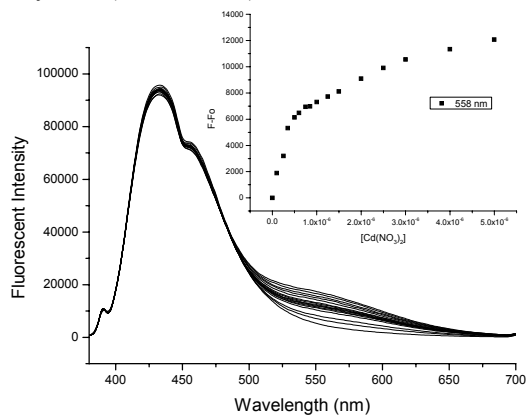


3) S2 and cadmium nitrate:

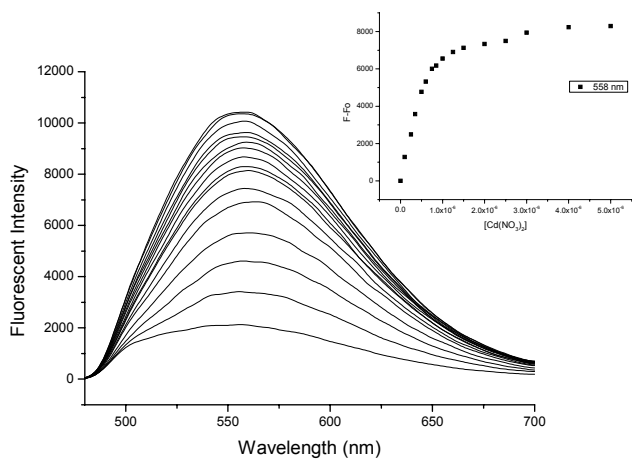
Changes in absorption spectra of S2 (5 μM) upon the addition of cadmium nitrate (0-50 μM) in dry THF.



Changes in fluorescent spectra of S2 (0.5 μM) upon the addition of cadmium nitrate (0-5 μM) in dry THF. ($\lambda_{\text{ex}} = 360 \text{ nm}$)



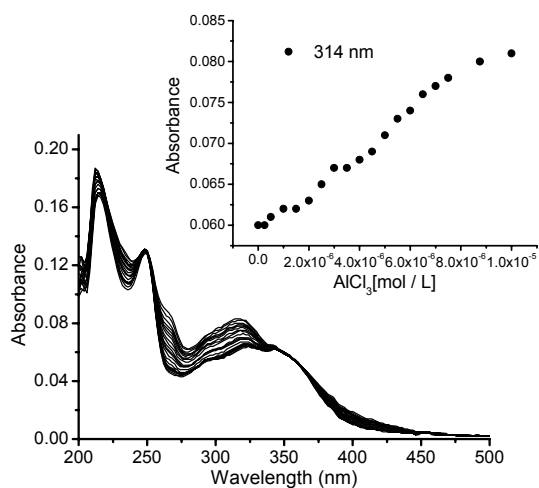
Changes in fluorescent spectra of S2 (0.5 μM) upon the addition of cadmium nitrate (0-5 μM) in dry THF. ($\lambda_{\text{ex}} = 415 \text{ nm}$)



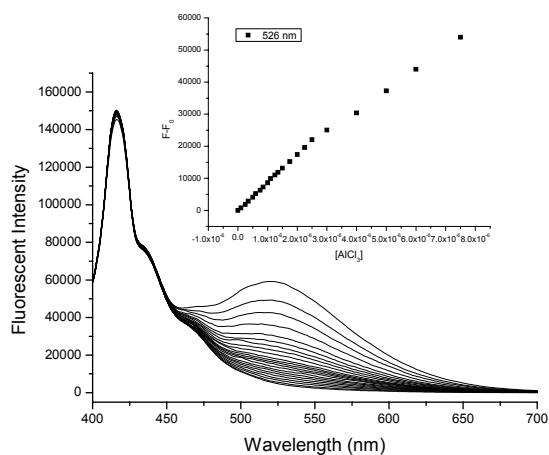
UV-vis and fluorescent titration of **S3**:

1) **S3** and aluminum chloride

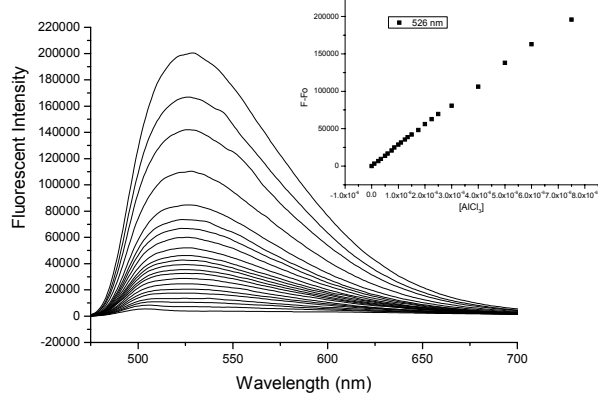
Changes in absorption spectra of **S3** (2.5 μM) upon the addition of aluminum chloride (0-10 μM) in dry THF.



Changes in fluorescent spectra of **S3** (0.5 μM) upon the addition of aluminum chloride (0-7.5 μM) in dry THF. ($\lambda_{\text{ex}} = 372 \text{ nm}$)

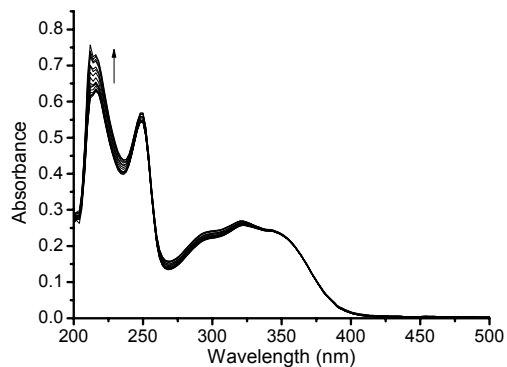


Changes in fluorescent spectra of **S3** (0.5 μM) upon the addition of aluminum chloride (0-7.5 μM) in dry THF. ($\lambda_{\text{ex}} = 415 \text{ nm}$)

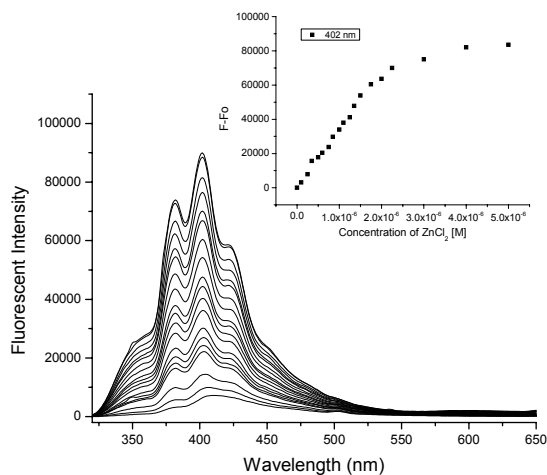


2) S3 and zinc chloride:

Changes in absorption spectra of S3 (10 μM) upon the addition of zinc chloride (0-40 μM) in dry THF.

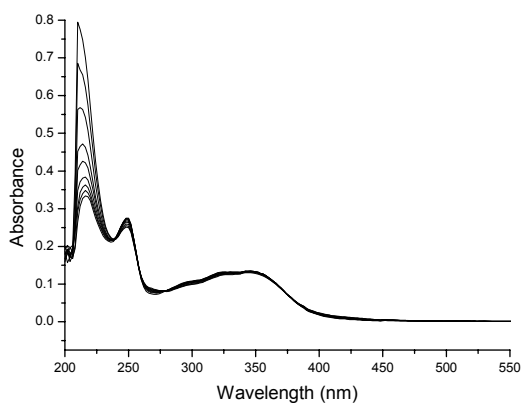


Changes in fluorescent spectra of S3 (0.5 μM) upon the addition of zinc chloride (0-5 μM) in dry THF. ($\lambda_{\text{ex}} = 252 \text{ nm}$)

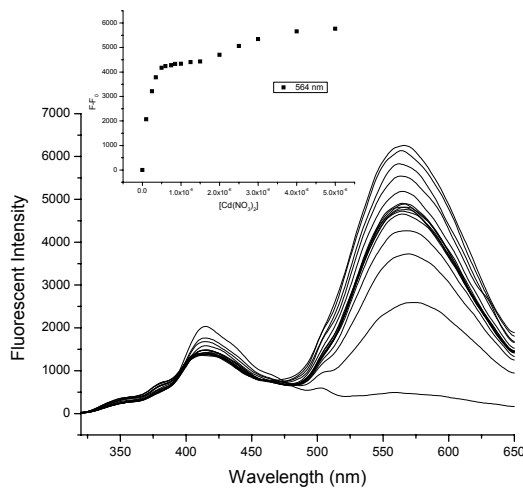


3) S3 and cadmium nitrate:

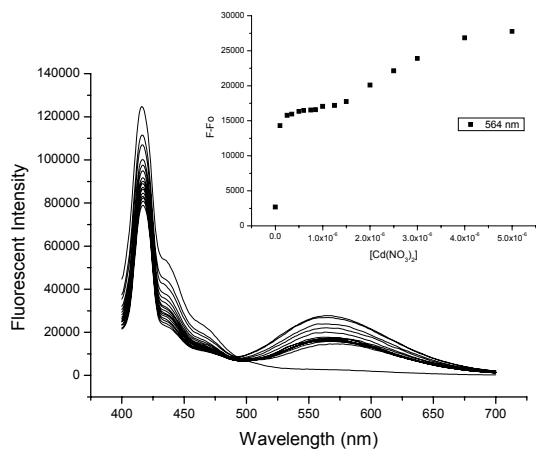
Changes in absorption spectra of S3 (5 μM) upon the addition of cadmium nitrate (0-50 μM) in dry THF.



Changes in fluorescent spectra of S3 (0.5 μM) upon the addition of cadmium nitrate (0-5 μM) in dry THF. ($\lambda_{\text{ex}} = 256 \text{ nm}$)



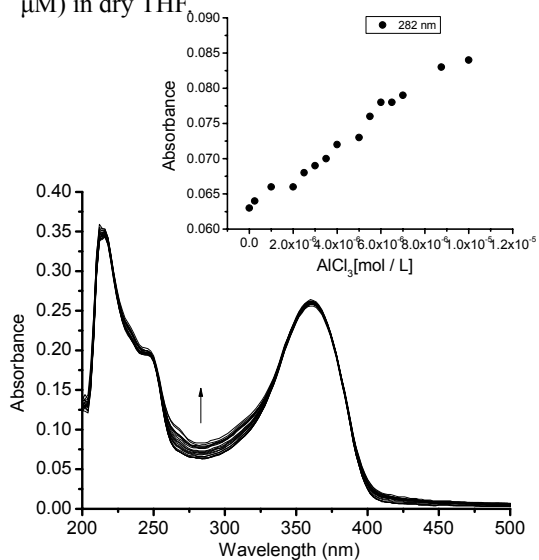
Changes in fluorescent spectra of **S3** (0.5 μM) upon the addition of cadmium nitrate (0-5 μM) in dry THF. ($\lambda_{\text{ex}} = 372 \text{ nm}$)



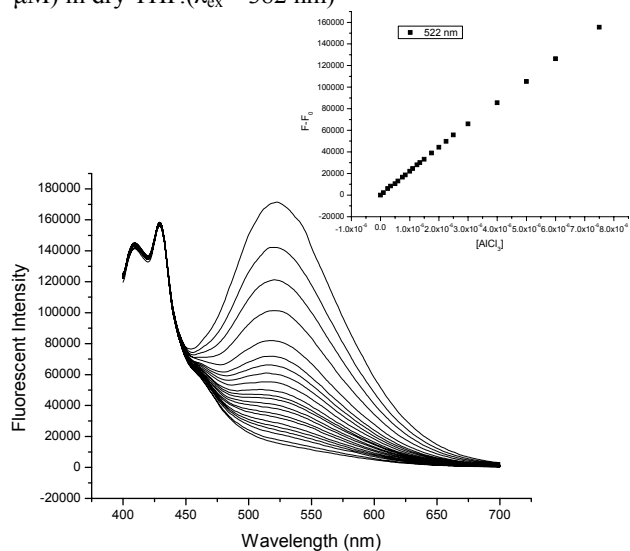
UV-vis and fluorescent titration of **S4**:

1) **S4** and aluminum chloride

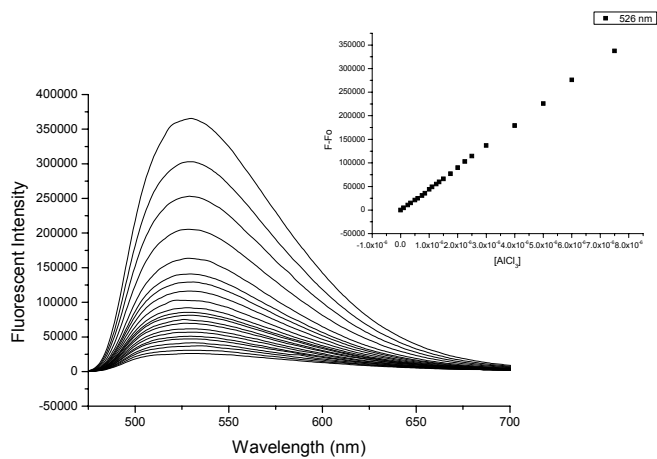
Changes in absorption spectra of **S4** (2.5 μM) upon the addition of aluminum chloride (0-10 μM) in dry THF



Changes in fluorescent spectra of **S4** (0.5 μM) upon the addition of aluminum chloride (0-7.5 μM) in dry THF. ($\lambda_{\text{ex}} = 382 \text{ nm}$)

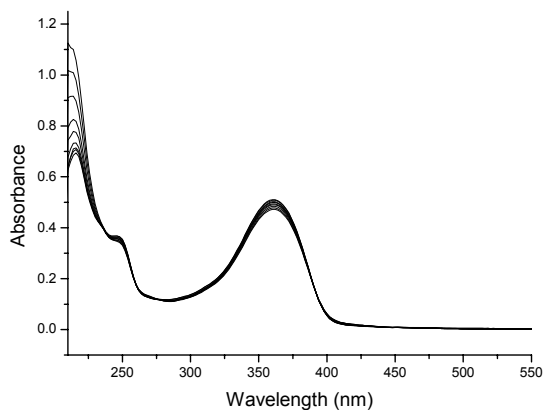


Changes in fluorescent spectra of **S4** (0.5 μM) upon the addition of aluminum chloride (0-7.5 μM) in dry THF. (λ_{ex} = 415 nm)

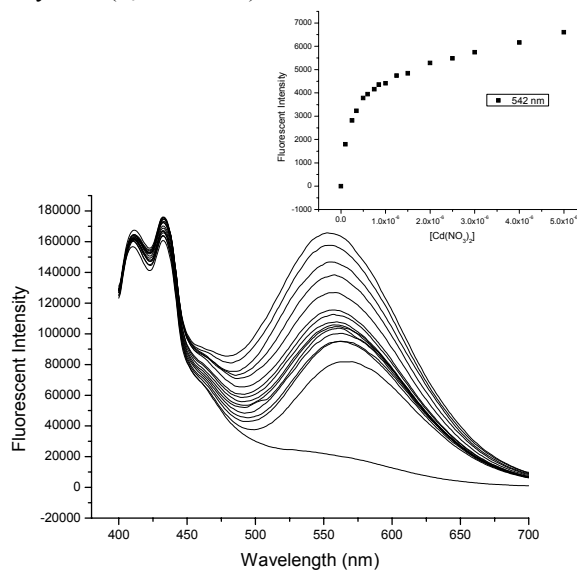


2) **S4** and cadmium nitrate:

Changes in absorption spectra of **S4** (5 μM) upon the addition of cadmium nitrate (0-50 μM) in dry THF.

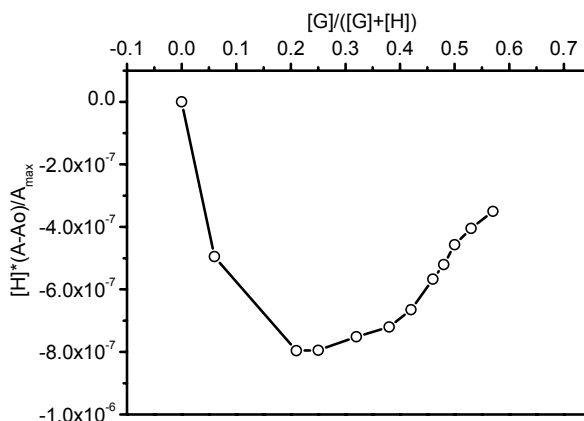


Changes in fluorescent spectra of **S4** (0.5 μM) upon the addition of cadmium nitrate (0-5 μM) in dry THF. (λ_{ex} = 386 nm)



Example of Job Plot

The following graph shows a Job plot for **S2** titrated with aluminum chloride. The experiment indicates 3:1 binding stoichiometry between **S2** and aluminum cation. [G] is the concentration of aluminum cation. [H] is the concentration of **S2**.



Preparation of sub-microliter sensor arrays for cation sensing

The sensor materials were prepared by incorporating sensors **S1-S6** into polyurethane matrices, which were prepared by casting solutions containing the sensors (approx. 0.07% sensor in polyurethane, w/w) in a TecophilicTM THF solution (6 % w/w) onto a multi-well 10x8 (sub-microliter) size plate made by ultrasonic drilling. The chloride salts of the cations were administered as aqueous solutions (400nL, 1mM). pH controlled experiments were carried out in the presence of HEPES (10mM) pH 7.4.

Supporting Information References:

1. a) Montes, V. A.; Pohl, R.; Shinar, J.; Anzenbacher, P., Jr. *J. Org. Chem.* 2004, **69**, 1723-1725. b) Montes, V. A.; Pohl, R.; Shinar, J.; Anzenbacher, P., Jr. *Chem.-Eur. J.* 2006, **12**, 4523-4535.
2. Montes, V. A.; Pérez-Bolívar, C.; Agarwal, N.; Shinar, J.; Anzenbacher, P. Jr. *J. Am. Chem. Soc.* 2006, **128**, 12436-12438.